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A. F. WELLS

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PREFACE

As a practical science crystallography was for many years restricted to the measurement and description of the geometrical forms and physical properties of crystals, though quite naturally the study of crystals led to much speculation concerning the fine structure of matter. With the discovery of the diffraction of X-rays by crystals, however, the status of crystallography in relation to the other physical sciences was changed. It gave rise to a method of studying atomic arrangement not only in the well-developed single crystals studied by the classical crystallographer but also in powders, in quasi-crystalline materials such as fibres, and even in glasses and liquids; for vapours the electron diffraction method has proved more useful. The results of X-ray crystallographic studies therefore form a considerable part of structural chemistry. To ensure that these results are incorporated into chemistry as quickly as possible it is necessary that the chemist should be able to appreciate the geometry of the 3-dimensional arrays of atoms which constitute solids, thereby extending the scope of his subject beyond the finite groups of atoms to which he has hitherto confined his attention. Also, it would seem that the crystallographer has an obligation towards the chemist, not only to co-operate in solving structural problems but also to make available, in a form intelligible to chemists, the results of X-ray work. Real dangers can arise from the increasing specialization which is inevitable in modern science. The new specialized knowledge tends to remain separated from the main body of the subject, and this reacts unfavourably not only on the other branches of the subject but ultimately on the work of the specialist himself. In the preface to *The Study of Crystals*, T. V. Barker wrote (in 1930): 'I suppose every author is necessarily an optimist, so I may be allowed to hope that this book will awaken interest in a branch of study which has been too long divorced from the routine teaching of chemistry and physics.' Now, after fifteen years in which the study of atomic arrangement has been actively pursued, it is more than ever necessary that the chemist should understand and make use of the results obtained by the new structural methods.

Although much material for this book has been derived from original papers, full use has been made of monographs and reviews (see p. 571). Since Pauling and his school have contributed so largely in recent years to the literature of structural chemistry, any writer in this field must be indebted to him to a considerable degree. His treatments of certain topics have been adopted because they appear to be best suited, at the present time, to the scheme of this book.

March 1945. A. F. W.

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INTRODUCTION

THE intensive study of chemistry has now proceeded for about a century and a half. Chemistry as a science began with the quantitative investigation into the weights or volumes of substances which take part in chemical reactions. Until nearly the end of the nineteenth century it was concerned with establishing the correct empirical formulae of compounds and the laws of chemical combination in terms of atoms, the precise nature of which was not known. Modern chemistry begins with the discovery of the electron and the subsequent development of the first clear ideas of the structure of the atom. It then became possible to account for the empirical formulae of many compounds in terms of the electronic structures of the constituent atoms, making certain assumptions about the part played by electrons in forming bonds between the atoms. Owing firstly to the importance of the study of reactions between gases in establishing the laws of chemical combination and in indicating the correct relation between atoms and molecules—so making possible the determination of atomic weights—and secondly to the rapid progress made in organic chemistry, there developed the idea that the molecule was the ultimate unit of structure of a compound corresponding to the atom in the case of an element. While it is true that the molecule is the smallest portion of a compound which retains the same composition and characteristic properties as the compound in bulk, it was not realized that discrete molecules do not necessarily exist in the solid state.

The study of the solid state has become possible only during the past thirty years. Previous to this the chemist's knowledge of the structure of a solid compound was confined to a knowledge of its empirical formula—which simply gives the ratios of the numbers of atoms of different kinds in the solid. This fact has had a profound effect on the development of inorganic chemistry, but very little in the case of organic chemistry, for the following reason. Very many elements and compounds are solid at ordinary temperatures, and in order to study the chemical properties of a compound the procedure is usually to dissolve the solid in a suitable solvent or, less frequently, to vaporize it. Now in the case of most organic compounds the process of dissolution merely separates the molecules forming the crystal. The molecules in solution are just the same tightly bound groups of atoms as were present in the crystal, in which they were held together by quite weak forces which in general do not appreciably affect the internal structure of the molecule. When an inorganic salt is dissolved in water, however, much more drastic changes may take place, often involving the separation of positively and negatively charged ions. By analogy with organic compounds it was at first thought that a solid like NaCl consisted of molecules which became ionized in solution. There was clearly no chemical means of discovering the atomic structure of the

crystal since chemical reactions necessarily involved the breaking up of the crystal. In the case of organic compounds, however, the molecules could be studied in solution or in the vapour state and it was possible to find out something about their structure by various indirect methods.

The study of the spatial arrangement of atoms in molecules (and complex ions) is termed stereochemistry. Since so few purely inorganic substances were amenable to treatment by the methods of classical stereochemistry it is not surprising that stereochemistry has become regarded almost as a branch of *organic* chemistry. Before the modern methods of studying structure became available, stereochemistry was confined to the study of finite groups of atoms in solution or in the liquid or vapour states. Classical stereochemistry was largely limited to the investigation of stereoisomerism and optical activity and could seldom provide much information about molecules or complex ions which do not exhibit one or other of these properties. The information obtained was, moreover, qualitative and referred only to the general shape of the molecule, e.g. the planar or tetrahedral bonds in a molecule Ma_4. It was not possible to determine interbond angles or the distances between atoms. With the introduction of the newer methods of studying structure, however, not only has it become possible to obtain more precise information about the structures of finite groups of atoms but also we can investigate the infinite arrays of atoms in solids. In addition therefore to enlarging the scope of stereochemistry by providing more accurate data on interatomic distances and interbond angles, the study of the solid state has greatly increased our knowledge of the different types of chemical bonds. Moreover, by indicating the relation between the constitution of substances in the solid and in other states of aggregation it now makes clear the limitations of empirical formulae as a means of representing the *structures* of solids and indicates to what extent such fundamental concepts as the Law of Constant Composition are applicable to solids.

The fact that it has only been possible to study the structure of the solid state comparatively late in the development of inorganic chemistry as we know it has had important effects on the development of the subject. In the first place, the idea of a finite molecule as the unit of structure was applied to inorganic compounds, including those which exist only in the solid state. We shall have to consider the relation between the structure of a substance in the solid and in other states of aggregation. On the one hand, deductions from the solid state may be very misleading unless this relationship is taken into account. As an example, we may quote the postulation of series of fictitious silicic acids with formulae based on those of complex silicates, before the structures of these compounds—which exist only in the crystalline state—were known. On the other hand, the chemist may well inquire what is the use of knowing the structure of a solid if he uses compounds in solution, and a radical change in structure has taken place during the process of dissolution. Secondly, X-ray crystallographic research began to develop for the most part in minera-

logical and physical rather than chemical laboratories. This has had a number of results. Much more attention has been devoted to minerals as compared with ' synthetic ' compounds than their importance in structural chemistry would justify. Also, since the crystallographer is more interested in a crystal *per se* than in the importance of its structure to the chemist, he has tended to study any easily accessible compounds, preferably those which are stable and solid at ordinary temperatures, in which he has happened to be interested. When one makes a general survey such as that attempted in the latter part of the present book, the lack of systematic studies of important groups of compounds becomes evident. Indeed it may be hoped that one of the results of such a survey may be to direct attention to some of the gaps in our knowledge. A more important result of this lack of contact between the X-ray crystallographer and the chemist is that there has been comparatively little assimilation into chemistry of the results of structural studies of crystals. Apart from the fact that the results of much crystallographic research are not easily accessible to the chemist, there is the difficulty that it is not easy to understand and assess the value of such research without a somewhat specialized knowledge of the methods of X-ray crystallography. As a result, much of what we shall include under the name of structural inorganic chemistry has become segregated into yet another subdivision called crystal chemistry.

The reasons for writing this book were, firstly, the conviction that the structural side of inorganic chemistry cannot be put on a sound basis until this knowledge gained from the study of the solid state has been incorporated into chemistry as an integral part of that subject, and secondly, the equally strong conviction that it is unsatisfactory merely to add information about the structures of solids to the descriptions of the elements and compounds as usually presented in a systematic treatment of inorganic chemistry. This brings us to the more general question of the presentation of inorganic chemistry.

A sound general knowledge of the preparative methods and of the properties of the more important elements and compounds is essential to the inorganic chemist. This enables him to answer the questions, How is a substance made, and how is it converted into other substances? If, however, too much emphasis is placed on this side of the subject, systematic inorganic chemistry tends to resemble a collection of recipes, and there is not the feeling of unity and logical development which makes organic chemistry such a fascinating study. For many purposes it would appear unnecessary to relate, for element after element, the preparation and properties of its various compounds. In any case, many of the properties attributed to compounds are not so much those of the compound itself as those of the ions into which it dissociates in solution. More general sections on such topics as the preparation of halides, oxides, and so on could replace for many purposes the more detailed information usually given. The next set of questions one might reasonably ask about a

compound are: What is it made of, what holds the constituent parts together, and how are they arranged? These are the questions we set out to answer in this book. We shall not generally describe the preparation or properties of compounds, so that in this sense the present volume is complementary to the usual text-book of inorganic chemistry. We shall also not be directly concerned with questions of a third type such as, Why does a compound AB exist but not AB_2, and why do two particular substances react with one another, and what is the mechanism of the process?

We have said that modern chemistry began when our ideas on the structure of the atom became clarified and it became possible to account for the empirical formulae of compounds in terms of the arrangement of electrons in the constituent atoms. The application of the early electronic theory of valency, notably by Sidgwick, to a wide variety of compounds showed that systematic inorganic chemistry could be something far more than a collection of recipes. This early theory was, however, limited to showing that reasonable electronic structures could be assigned to many compounds and in this sense accounting for their empirical formulae. Many questions remained unanswered. For example, it was not possible to account for the stability of particular groups of valency electrons or for the spatial arrangement of the bonds they formed. Secondly, electronic structural formulae cannot be assigned to substances in the solid state unless we know the spatial arrangement of the atoms, and empirical formulae do not necessarily give any indication of the atomic structure of the solid. Thus the compounds $CaCO_3$, $CaSiO_3$, and $CaTiO_3$, for example, can all be given structural formulae of the type $Ca^{2+}(MO_3)^{2-}$, with discrete Ca^{2+} and MO_3^{2-} ions. These actually are the structural units in crystalline $CaCO_3$, but no such complex ions containing Si or Ti linked to three oxygen atoms occur in crystalline $CaSiO_3$ or $CaTiO_3$, which have quite different structures (see p. 338). This question is linked up with the third point we wish to emphasize. The number and arrangement of the outer orbital electrons of an atom are not the only factors determining its chemical properties and the structures of its compounds. Not only may series of compounds with exactly similar empirical formulae have quite different atomic structures but the stabilities of such compounds may vary greatly and some may not exist at all (compare, for example, the ions FO_3^-, ClO_3^-, BrO_3^-, and IO_3^-). We must therefore take into account not only the outer electronic structure of atoms but also other factors such as their relative sizes and electronegativities.

The general plan of this book is therefore as follows. In Part I we first consider the structure of the atom and the kinds of forces acting between them in substances of different types. This is followed by a discussion of the sizes of atoms and the spatial arrangement of the various types of bonds. Some account is then given of the characteristics of the states of aggregation and of the relation between the structures of a substance in these different states. One chapter is devoted to a more detailed treat-

ment of the crystalline state. In the last chapter of Part I we mention some of the more important experimental methods of structural chemistry. In Part II we attempt a systematic description of the structures of some of the more important classes of inorganic substances. The intention has been to write this in a reasonably readable form rather than attempt anything in the nature of a compendious book of reference.

The following notes may be helpful to the reader.

Diagrams of Crystal Structures. Owing to the three-dimensional nature of crystals, diagrams of their structures are at best a poor substitute for models. The diagrams in this book have, with very few exceptions, been drawn or redrawn by the author with the object of showing as clearly as possible the features they are intended to illustrate. The following conventions have been adopted. Atoms are represented by circles of arbitrary sizes, thickness of line decreasing with increasing distance from the observer. Unbroken straight lines represent chemical bonds, thickness of line again being graded. The edges of unit cells, or other lines which do not represent bonds, are drawn as broken lines.

References to the Literature. Papers recording the results of X-ray and electron diffraction studies are scattered throughout many journals. Early X-ray crystallographic work was summarized by Wyckoff in *The Structure of Crystals* (Chemical Catalog Co., New York, 1931) and the Supplement for the years 1930–4 (Reinhold Publishing Corporation, New York, 1935). A much more comprehensive, but less critical, compilation is the *Strukturbericht* (Akademische Verlagsgesellschaft, Leipzig). The first four volumes of this work were available to the author at the time of writing this book; they include references to all X-ray and electron diffraction work up to the end of 1936. References to the literature are collected together into two short sections at the end of the present volume. The 'References to Special Topics' are largely confined to review articles and books, and they are given in the order in which the subjects are discussed in the book. They are followed by references to a number of original papers, mostly published since 1936.

Indexes. There are two indexes. If a group of compounds is discussed as a group (e.g. the heteropolyacids) it will be found listed in the Subject Index, which also includes the names of a number of alloys, minerals, and organic compounds. The names of many complex inorganic compounds are cumbersome, for example, octammino-μ-dihydroxy-dicobaltictetrabromide for $[(NH_3)_4Co(OH)_2Co(NH_3)_4]Br_4$ and tetrakis (monoiodotriethylarsinecopper) for $Cu_4I_4[As(C_2H_5)_3]_4$. Some are unsound and a systematic nomenclature is not generally adopted. A second index, of Chemical Formulae, is therefore given. In the case of compounds containing a complex ion we have departed from the usual convention by placing first in the formula the central atom of the complex ion (e.g. $[Fe(CN)_6]K_4$ and $(CuCl_4)K_2$ instead of $K_4Fe(CN)_6$ and K_2CuCl_4). The

justification for thus rearranging the chemical formulae is that these compounds are of interest in this book chiefly in connexion with the stereochemistry of iron and copper respectively, and unless the reader knows which particular salt was studied it would otherwise be necessary to look through all the compounds of caesium, lithium, potassium, sodium, and rubidium, to mention only the alkali metals. References to structural studies are included in the formula index.

PART I

CHAPTER I

THE STRUCTURE OF THE ATOM

FROM time to time, since the days of the Greek philosophers, the opinion has been expressed that there is a limit to the extent to which matter may be subdivided. This idea, that matter is made up of discrete atoms and is not a continuum, was put into a more precise form by Dalton in 1802. He suggested that the ultimate particles or atoms of any pure substance are of the same size and weight, that they cannot be further subdivided, created, or destroyed (Law of Conservation of Matter), and that these elementary atoms combine together in simple integral ratios to form 'compound atoms' or molecules. The latter postulate is consistent with the laws of fixed, multiple, and reciprocal proportions which are fundamental to chemistry. Later work has, however, altered our views on the properties of atoms. We now know, for example, that all the atoms of a particular element have not in general the same mass, though they all exhibit the same chemical behaviour and are not separable by chemical methods. We also know that an atom is not only divisible into simpler components but may even be converted into an atom of another element, either spontaneously (in radioactive changes) or artificially.

Another early conception of the structure of matter was that all elements were derived from one basic element, an idea revived in Prout's hypothesis (1816) that the masses of all atoms were integral multiples of that of the hydrogen atom. We shall see later that the approximation of many atomic weights determined by chemical methods to whole numbers is not of any fundamental importance since the chemical atomic weight of an element is the average mass of the atoms and is therefore a function of the masses and proportions of the various isotopes. The relative masses of these isotopes are, however, of the greatest importance and will be discussed later in connexion with the equivalence of mass and energy. Our immediate problem is to set out in the limited space available some of the more important evidence for the present view of the structure of the atom. Modern physics begins with the detailed study of the passage of electrical discharges through gases, a study which soon led to the discovery of three types of radiation, cathode rays, positive rays, and X-rays. We shall consider these briefly in turn.

ELECTRONS AS CONSTITUENTS OF ATOMS

Cathode Rays

If a high voltage, of several thousands of volts, is applied between two plates enclosed in a glass tube and the pressure of gas inside the tube is reduced until it is of the order of 0·01 mm., all coloured discharge ceases

and the glass itself begins to show a faint greenish fluorescence. This is due to electrons, drawn from the cathode by the applied field, impingeing on the glass. These particles were shown to have the following properties:

1. They travel in straight lines.
2. They possess momentum and energy, and therefore mass.
3. They are negatively charged. A stream of charged particles behaves like an electric current and is deflected by a magnetic field. From the direction of deviation the sign of the charge can be deduced.
4. They possess considerable penetrating power, passing, for example, through a thin aluminium foil and still producing fluorescence.
5. Their velocity may be varied by altering the applied voltage and may be determined by acting on them simultaneously with electric and magnetic fields. The force exerted by an electric field of strength E is Ee if the charge on the electron is e. If this be counterbalanced by the force Hev due to a magnetic field of strength H, then we have $v = E/H$. The velocity of the cathode rays produced in the way described above is of the order of one-fifth of the velocity of light.

The ratio of the charge to the mass of the electron (e/m) was determined by measuring the deflexion produced by the magnetic field alone. This causes the beam of electrons to move along the arc of a circle as if acted upon by a centripetal force mv^2/r which must equal Hev. Hence $e/m = v/Hr$, where r is the radius of the circular arc and v is determined as above. In this way the ratio e/m was found to be $5{\cdot}27 \times 10^{17}$ e.s.u./gram. To find the mass of the electron we still need to determine the charge e. The charge on the electron was measured by observing the motion, between charged plates, of minute droplets of oil carrying one or more electronic charges. The charges on the oil drops were produced by ionizing the air between the plates by means of X-rays. One oil drop which has passed through a small hole in the upper plate is observed through a microscope. When there is no difference of potential between the plates the drop soon reaches an equilibrium velocity from which its mass may be calculated. Before the drop reaches the lower plate the potential of the upper plate is made positive with respect to that of the lower. Since the drop carries a negative electric charge the upward electric force acting on it opposes gravity. By measuring the constant upward velocity of the drop with known difference of potential across the plates the charge on the drop can be determined. It is found to be always either equal to or an integral multiple of $-4{\cdot}802 \times 10^{-10}$ e.s.u. (The drop may carry several electrons.) From the values of e/m and e the mass of the electron is found to be $9{\cdot}11 \times 10^{-28}$ gram, or 1/1850 of the mass of a hydrogen atom. An alternative method of evaluating the electronic charge e is based on the measurement of the angle of diffraction of X-rays by a crystal of known structure. The expression for e involves the glancing angle for a particular reflection (see p. 195), the molecular weight of the substance, the density of the crystal, the value of the Faraday, and the wavelength of the X-rays.

The latter is determined from diffraction experiments with ruled gratings of known spacing.

Positive Rays

Cathode rays streaming from the cathode to the anode in a discharge tube occasionally collide with atoms of gas and knock one or more electrons from them, leaving positively charged ions. Owing to their charge these proceed towards the cathode. They constitute a stream of positive rays moving in the opposite direction to the cathode rays. Like the latter they travel in straight lines, but whereas the mass and charge of every electron is the same, the particles constituting the positive rays are found to have different charges and masses. They are in fact charged atoms or molecules of the various gases present in the discharge tube, as is proved by their behaviour in electric and magnetic fields. Their velocities depend on their positions in the tube at the moment of ionization. The earliest study of these positive rays was made by J. J. Thomson in his mass spectrograph. The ions were deflected by means of electric and magnetic fields to form parabolic traces on a photographic plate or fluorescent screen. The ions produced near the anode are deflected much less than those formed near the cathode, so that the trace is spread out according to the velocity of the ions. Each kind of ion gives a separate parabola, the heaviest ions being the least deflected and so forming the near-in parabolas. By reversing the polarity of the magnet a symmetrical photograph is obtained. Later forms of mass spectrograph have been developed by Aston, Dempster, and Bainbridge, employing different methods of focusing the ions.

When examining neon in 1912 Thomson found two parabolas corresponding to atoms of masses 20 and 22 (relative to oxygen = 16), and subsequently it has been found that most elements are mixtures of from two to ten atoms of different mass. These atoms having the same outer electronic structure but different masses are called *isotopes*. (*Isobars* are atoms of different elements having the same mass, e.g. the principal isotopes of argon and calcium both have mass 40.) The atomic weights of the elements are referred to that of oxygen as standard. Until 1927 only one isotope of oxygen with mass 16 was known, but then it was found that there are also isotopes O_{17} and O_{18}, though these are few in number compared with O_{16}. (In every 10,000 atoms of oxygen there are 16 O_{18} and 3 O_{17}.) The arbitrary choice of unit atomic mass is taken as 1/16 the mass of the O_{16} isotope. On this basis the mass of the H_1 isotope is 1·008. We shall discuss the masses of atoms later.

X-rays

When studying the green fluorescence in a discharge tube Röntgen, in 1895, found that invisible rays of considerable penetrating power were emitted from the fluorescent glass. These he called X-rays. They result from the impact of electrons on the glass. By designing the tube so that

the electron beam impinges on a target of metal a powerful beam of X-rays may be obtained and studied. Modern tubes are highly evacuated and employ a tungsten filament as the source of electrons, and it is necessary to cool the target effectively, usually by making it hollow and passing a stream of water through it.

X-rays are absorbed by matter in any state of aggregation, the absorption being in general greater for heavy than for light atoms. In the process, atoms of the absorbing medium are ionized. Like visible light they behave as waves, but their wavelength is much shorter. The diffraction of X-rays was first demonstrated by Laue, Friedrich, and Knipping in 1912, the grating employed being a crystal of zinc-blende. This experiment marked the beginning of the science of X-ray crystallography. The X-rays from a metal target do not consist simply of a continuous spectrum but of a few discrete wavelengths, known as the characteristic radiation of the element, accompanied by a weaker continuous spectrum. Just as visible light may be analysed by means of an optical diffraction grating, so an X-ray emission spectrum may be analysed by using a crystal face as a grating. The distances between the rows and planes of atoms in a crystal are of the same order of magnitude as the wavelengths of X-rays. The X-ray emission spectrum of a particular element consists of a number of rays of different wavelengths, the *K*, *L*, etc. series, the origin of which can be better understood after we have described the Bohr model of the atom. The relation between the wavelengths of the lines of a particular series (e.g. the *K* series) emitted by different elements and the atomic numbers of the elements is mentioned later.

We have remarked that atoms of certain elements change spontaneously into atoms of other elements. The study of these *radioactive* processes was of the greatest importance in the development of atomic theory.

Radioactivity

The study of radioactivity began with the discovery by Becquerel in 1896 that uranium emits some form of rays which will penetrate several layers of thick black paper and still affect a photographic plate. The isolation of radium and other radioactive elements from the mineral pitchblende by the Curies in 1898 made possible the detailed study of this new radiation. It was established, particularly by the experiments of Rutherford, that there are three kinds of rays emitted by radioactive materials, α, β, and γ rays. The latter are unaffected by magnetic or electric fields, whereas in either type of field the α and β rays are deflected in opposite directions. In an electric field the α rays are deflected towards the negative plate, showing that they are positively charged. They were later shown to be doubly ionized helium atoms. The β rays were found to be ordinary electrons. The γ rays are light waves with wavelengths of the same order as those of X-rays and travelling with the velocity of light. The α rays travel with only 1/10 to 1/100 of the velocity of light, whereas β rays have anything up to 99 per cent. of the velocity of light. When

α, β, or γ rays penetrate matter they cause ionization, and in thus losing energy they are absorbed. As might be expected, the relative penetrating powers of the rays are roughly inversely proportional to their ionizing powers. The α ray is finally brought to rest by taking up permanently two electrons and becoming a normal (uncharged) helium atom.

The phenomena arising from the passage of an electrical discharge through a gas (the formation of electrons and positively charged ions), those of radioactivity and of the photoelectric effect to be described shortly, all show that atoms contain electrons. Since atoms are normally electrically neutral, there must also be a positive charge located somewhere within the atom. Before we describe the photoelectric effect or proceed any further with the problem of the structure of the atom we must note a development in theoretical physics of the greatest importance.

THE QUANTUM THEORY

A heated solid emits radiation of a whole range of wavelengths—the continuous emission spectrum—and if the energy emitted is plotted against the wavelength the curve shows a maximum. Such curves may be plotted for a series of temperatures, and it is found that the maximum moves towards shorter wavelengths as the temperature rises. Actually the wavelength corresponding to maximum energy is inversely proportional to the absolute temperature, as expressed in Wien's displacement law: $\lambda_{max}\,\theta$ = constant. According to classical physics the energy emitted by unit area of a black body (i.e. a body which neither reflects nor transmits light) in unit time is proportional to λ^{-4} (Rayleigh–Jeans radiation law). The energy/wavelength curves follow this law at long wavelengths, but the law obviously breaks down for shorter wavelengths, for it predicts that more and more energy should be radiated as λ decreases. Moreover, according to classical theory the light emitted by a body should remain of the same colour, only its intensity altering with temperature. It is well known that the colour of a heated body changes through red and yellow to white as its temperature increases. Classical theory also failed to account for the values of the specific heats of solids. It predicted that the atomic heats (see p. 31) of all solids should be the same (5·96), and independent of temperature. Although the atomic heats of many elements have values around 6 at ordinary temperatures, those of certain light elements (e.g. B, C) are much less. Moreover, in all cases the atomic heat tends to zero at the absolute zero of temperature. To overcome these difficulties Planck (1901) introduced his quantum hypothesis. According to this hypothesis an atom must be in one of a finite number of discrete energy states in any one of which it possesses an integral number of quanta of energy. The quantum of energy is expressed in the form $h\nu$ where h is a universal constant for all atoms and ν is a frequency, of which more will be said later. If the atom changes from one state, in which it possesses the energy $n_1 h\nu$, to another of lower energy $n_2 h\nu$, then the

difference in energy $(n_1-n_2)h\nu$ is emitted as radiation. The quantum hypothesis was soon incorporated in the theory of the photoelectric effect and in Bohr's theory of the nuclear atom.

We may mention here in addition to the continuous emission spectrum of a hot solid the line emission spectrum of a hot gas. When an element is vaporized and raised to a high temperature it emits light of definite discrete wavelengths which are characteristic of the element and constitute its line emission spectrum. The term 'line spectrum' arises from the fact that a slit is used to limit the light entering the spectroscope, each line of the spectrum being the image of the slit for a particular wavelength. Simple relations are found between the wavelengths of certain groups of lines in these spectra. For example the lines of the Balmer series in the hydrogen spectrum obey the relation

$$\frac{1}{\lambda} = \text{constant}\left(\frac{1}{4}-\frac{1}{n^2}\right), \quad \text{where} \quad n = 3, 4, \text{etc.}$$

This equation was derived from the measured wavelengths of the spectral lines, and it must therefore be explained by any atomic model. Molecules also give spectra consisting of lines, but these are grouped closely together, giving the appearance of continuous bands which higher resolution shows to consist of sets of regularly spaced lines. Corresponding to continuous and line emission spectra there are also continuous and line absorption spectra. Spectra cannot be considered in any detail in this book, but they are of considerable importance in chemistry. In the first place the emission of energy from an atom is due to changes within the atom which must be accounted for by any theory of the structure of the atom. Secondly, after the development of a satisfactory atomic model the analysis of spectra can yield much information about the structure of molecules, a topic which is considered briefly in Chapter VI.

The Photoelectric Effect

When light falls on a metal electrons may be emitted if the energy of the photons (light) is great enough. For the alkali metals the energy of visible light is sufficient; in other cases ultra-violet light, the quantum of which is greater, must be used. The velocity of the photoelectrons is (1) independent of the intensity of the light, increase in intensity merely increasing the number of photoelectrons, and (2) dependent on the wavelength of the light, increasing as the wavelength decreases. In 1905 Einstein derived his photoelectric equation based on Planck's quantum hypothesis:

$$h\nu = W+\tfrac{1}{2}mv^2,$$

where $h\nu$ is the energy of a single quantum of light falling on the metal. This energy is imparted to a single electron and is used up (*a*) in removing the electron from the metal, a process which requires the expenditure of an amount of energy W (the work function), (*b*) in giving the electron

kinetic energy $\frac{1}{2}mv^2$. An important method of determining the value of Planck's constant h is based on this equation. The kinetic energy of photoelectrons is determined for different light frequencies ν and the values are plotted against ν. By extrapolation the threshold frequency ν_0 is obtained for which each incident photon has just enough energy $h\nu_0$ to free an electron from the metal surface without imparting to it any kinetic energy. Therefore $h\nu_0 = W$, so that in the equation $h\nu = h\nu_0 + \frac{1}{2}mv^2$ everything except h is known. Light of frequency less than ν_0 does not eject photoelectrons. It may be noted that the photoelectric effect is the reverse of the production of X-rays. In the former process a photon incident on the surface of the metal ejects an electron, while in the production of X-rays an electron impingeing on the metal gives rise to an X-ray photon.

Before leaving the electron we may mention two other points. Soon after the discovery of the electron in 1898 Lorentz found it necessary to assume in his electron theory of matter that the mass of an electron increases as its velocity increases according to the following relation:

$$m = \frac{m_0}{\sqrt{\{1-(v/c)^2\}}},$$

where v is the velocity of the electron and c that of light. This equation was derived later by Einstein and has been tested most thoroughly for high-speed electrons, though it should apply to all bodies. Some high-speed β rays from radioactive elements have velocities up to 99 per cent. that of light, and for these the ratio $m/m_0 = 7{\cdot}1$.

We have seen that positive rays consist of ions. These are atoms which have lost electrons and so acquired one or more unit positive charges depending on the number of electrons lost. Certain atoms, for reasons which we shall discover later, prefer to take up one or more electrons, thereby becoming negative ions. Many inorganic compounds dissolve in water and other solvents with high dielectric constants to form solutions which conduct electricity. We now know that the conducting power of such solutions is due to the presence of ions which were separated from one another in the process of dissolution. When a current is passed through the solution the ions travel towards the electrodes, at which they are discharged. (Further processes may then take place at the electrodes, e.g. the combination of atoms to form molecules or interaction of the atoms with the solvent, but these do not concern us here.) The process of decomposing a compound by the passage of an electric current is termed *electrolysis*. If we denote by x the charge carried by an ion we may call $1/x$th of the atomic weight the equivalent of the element, for the following reason. Faraday showed that the quantity of electricity required to liberate one gram equivalent of any ion is constant. This amount is termed one Faraday (F). It is found that the charges on ions are all integral multiples of the electronic charge e (with opposite sign in the case of positive ions). The identity of the elementary charges separated during

the ionization of a gas and those found on ions in solution was demonstrated by Townsend in 1900. For an ion such as Cl^- which carries a single charge e,

$$F = Ne = 30{\cdot}5 \times 10^{13} \text{ e.s.u. (or 96,500 coulombs)},$$

where N, the Avogadro number, is the number of atoms (molecules) in one gram atomic (molecular) weight of the element.

THE SIZE OF ATOMS

So far we have said nothing about the size of atoms. Long before we had any precise idea of the dimensions of atoms or molecules an upper limit could be set to molecular size. Careful study of soap films, for example, showed that they could be made as thin as $4{\cdot}5 \times 10^{-7}$ cm., and films of oil on water were obtained only $1{\cdot}1 \times 10^{-7}$ cm. thick. Gold leaf can be prepared of thickness 10^{-5} cm., which is therefore an upper limit for the diameter of the gold atom. We have already mentioned Avogadro's number, N, the number of atoms in the gram atomic weight of an element. If we know N and the density of the element, and hence the volume occupied by N atoms, we can calculate the effective mean volume of an atom (or molecule). The value of N may be determined in various ways, for example by studies of the Brownian movement, from the values of F and e (see above), and from data on radioactive materials. If we measure the volume of helium produced in a given time by, say, the radioactive element polonium and also count the number of α particles ejected by means of an automatic recording device, we may determine N directly. Viscosity measurements give the product $N\sigma^2$, σ being the molecular radius, and compressibility data for gases (the value of b in van der Waals' equation) give $N\sigma^3$. From these quantities both N and σ may be obtained. Direct measurement of the dielectric constant or refractive index of gases affords alternative methods of calculating molecular radii. From experiments such as these we know that the radii of atoms are of the order of 10^{-8} cm. The most precise values of atomic and ionic radii now come from X-ray studies of crystals. These atomic radii and their physical significance will be discussed in later chapters.

THE NUCLEAR ATOM

We have now reviewed some of the evidence for the existence of electrons in atoms. Since these electrons are negatively charged, there must be a positive charge or positive charges somewhere within the atom. Also, since the mass of the electrons is negligible compared with the total mass of an atom, there must be heavy particles in atoms. From the results of experiments on the absorption of cathode rays in thin films of metals Lenard (1903) concluded that the mass of the solid metal is not uniformly distributed but is concentrated in isolated centres. During the next ten years Rutherford and others studied the scattering of α particles by solids and deduced that the positive charge and mass of an

atom are restricted to a particle less than 10^{-12} cm. in diameter. The radioactive element radon was used as a source of high-speed α particles, a fine beam of which impinged on a thin metal foil. The numbers of particles scattered at various angles were measured. Most of the α particles go straight through the film, suffering little or no deflexion. Some, however, are scattered at larger angles and a few are deflected back almost along the line of incidence. Experiments showed that the proportion of α particles deflected through large angles increases with the atomic weight of the scattering element. These and other facts could be explained only by assuming that (*a*) all the positive charge of an atom is confined to a particle less than 10^{-12} cm. in diameter, (*b*) practically all the mass of the atom lies within the same volume, and (*c*) the amount of positive charge is approximately one-half of the atomic weight.

The Atomic Model of Bohr

This atomic model, incorporating the idea of a central heavy nucleus and based on the quantum hypothesis of Planck, successfully accounted for the known spectral series of hydrogen. The main characteristics of the Bohr atom may be summarized as follows:

(1) The central nucleus of the atom carries a positive charge equal to the atomic number Z. The atomic numbers of atoms are, with three exceptions noted later, the ordinal numbers of the atoms when they are arranged in order of their atomic weights. The chemical atomic weights are those determined by chemical methods and are the weighted means of the masses of the isotopes.

(2) To maintain electrical neutrality the number of orbital electrons in the atom also equals Z. We shall see shortly that there are direct methods of determining the total numbers of orbital electrons in atoms.

(3) It is assumed that the single electron in the hydrogen atom (for which alone calculations were at first possible) revolves around the nucleus in a circular orbit, of radius r. The attractive force e^2/r^2 must be balanced by an equal centrifugal force mv^2/r to keep the electron at a constant distance r from the nucleus.

(4) It is further assumed that the electron is limited to a number of discrete orbits the radii of which are determined by the relation $mv^2/r = e^2/r^2$ and the quantum restriction that 2π times the angular momentum of the electron, mvr, equals nh ($2\pi mvr = nh$). From these two equations we find

$$r^2 = \frac{n^2h^2}{4\pi^2me^2}, \quad \text{whence} \quad r = 0{\cdot}5 \text{ A}.$$

n is termed the principal quantum number, and since it can have only integral values the radii of the permissible orbits are fixed as r, $4r$, $9r$, etc.

(5) Finally it was postulated that light is not emitted when the electron is moving in a given orbit but only when it jumps from one orbit to another. The frequency of the light emitted depends on the difference in

energy of the two orbits: $E_1 - E_2 = h\nu$. The energy ($\frac{1}{2}mv^2$) of the electron is given by

$$-\frac{2\pi me^4}{n^2h^2},$$

the minus sign arising because the energy is greater in the larger orbit. Hence the frequency

$$\nu = \frac{2\pi^2me^4}{h^3}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right),$$

where n_1 and n_2 are the quantum numbers of the initial and final orbits. Since $c = \nu\lambda$ we have

$$\frac{1}{\lambda} = \frac{2\pi^2me^4}{ch^3}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right),$$

giving Balmer's series for $n_2 = 2$, $n_1 = 3, 4, 5$, etc.

In the atom in its normal state the electron is in the most stable orbit. It is removed to an outer orbit when the atom is excited and is completely removed in the process of ionization. The return from an outer orbit to the inner may take place in one jump or in a series of successive jumps. Spectral lines arising from an ionized atom appear only under the most vigorous treatment, e.g. in the arc or spark spectrum. In addition to accounting for the wavelengths of the lines in Balmer's series which were already known the Bohr atom predicted other spectral series which have since been discovered, e.g. the Lyman series in the extreme ultra-violet ($n_2 = 1$), the Paschen series in the infra-red ($n_2 = 3$), and the Brackett series in the far infra-red ($n_2 = 4$).

The Bohr model for the hydrogen atom was extended to heavier atoms in which it was assumed that the orbital electrons, equal in number to the Atomic Number, were arranged in orbits of increasing size, the maximum number of electrons which could be accommodated in successive orbits being $2n^2$. Thus the K, L, M, N, etc. shells would contain respectively 2, 8, 18, 32, etc. electrons. In a later section we shall see that there are departures from this simple rule and we shall consider in more detail the arrangement of the electrons in the various shells.

We have now a picture of the atom consisting of a central nucleus responsible for the mass of the atom and carrying a positive charge Z. This nucleus is surrounded by Z electrons occupying various orbits. We have seen that this atomic model accounts satisfactorily for the simple series of hydrogen spectral lines, and we must now briefly reconsider the production of X-rays and the photoelectric effect in terms of this Bohr atom.

The Origin of X-rays

High-speed electrons striking the metal target ionize atoms in the surface layer. When an electron is removed from an inner shell (e.g. K shell) an electron from the next shell takes its place in the K shell,

emitting in the process a photon of energy $h\nu$ called the K radiation. The electron jumping from the L to the K shell leaves a vacant place in the L shell which is immediately filled by an electron from the M shell, the L radiation being emitted. This process continues until the outer shell is reached, when the vacant place in the latter is filled with the emission of visible light. In this way an atom can emit a whole series of X-rays of different wavelengths simultaneously. The continuous X-ray spectrum is due to another process. Some electrons incident on the target do not cause ionization but are merely deflected on passing close to the nucleus, and in this process the electron is slowed down from its initial velocity v to v_1. The energy lost by the electron is emitted as a photon of energy $h\nu = \frac{1}{2}mv^2 - \frac{1}{2}mv_1^2$. The closer the approach of the electron to the nucleus the greater is the frequency and energy of the radiated photon, and the maximum value of $h\nu$ corresponds to complete stopping of the electron. This radiation is therefore continuous but has a definite maximum ($h\nu_{max} = \frac{1}{2}mv^2$) determined by the energy of the incident electrons.

The Photoelectric Effect with X-rays

This constitutes one of the best proofs that the electrons surrounding the nucleus of an atom are arranged in successive shells. When monochromatic X-rays are incident on a suitable metal surface photoelectrons with different velocities are ejected in well-defined groups. The different velocity groups are associated with the different shells in the atoms of the metal. The energy W to remove an electron is greater for the inner shells, and since $h\nu$, the energy of the incident photons, is constant, the electrons from different shells are ejected with different velocities, for $h\nu = W + \frac{1}{2}mv^2$. The electrons ejected are subsequently replaced with emission of X-rays as in the normal production of X-rays. In the photoelectric effect all the energy of the original X-ray photon is used up in ejecting the photoelectron which may come from one of the inner shells of the atom. There is a related phenomenon, the Compton effect, in which only part of the energy of the X-ray photon is transferred to the electron. In contrast to the photoelectric effect the Compton effect occurs only with free or loosely bound electrons. It is found that some of the monochromatic X-rays scattered by carbon have wavelengths different from that of the original X-rays and that as the angle of scattering increases the change in wavelength increases. (The wavelengths of the scattered X-rays are determined by reflecting them from a crystal face and observing the spectrum.) The obvious interpretation of this effect is that a single X-ray photon, behaving like a material particle, collides with an electron which in recoiling takes up some of the energy of the photon. The X-ray photon therefore loses this amount of energy ($\frac{1}{2}mv^2$) and its frequency falls to a new value ν_1 given by $h\nu = h\nu_1 + \frac{1}{2}mv^2$. Confirmation of the production of recoil electrons was obtained later by C. T. R. Wilson and by Bothe and Becker.

THE WAVE NATURE OF THE ELECTRON

All the processes involving electrons which we have so far considered are consistent with the view that the electron behaves as a charged particle. In the case of light the corpuscular theory accounted for many of the observed phenomena and was modified only when diffraction was

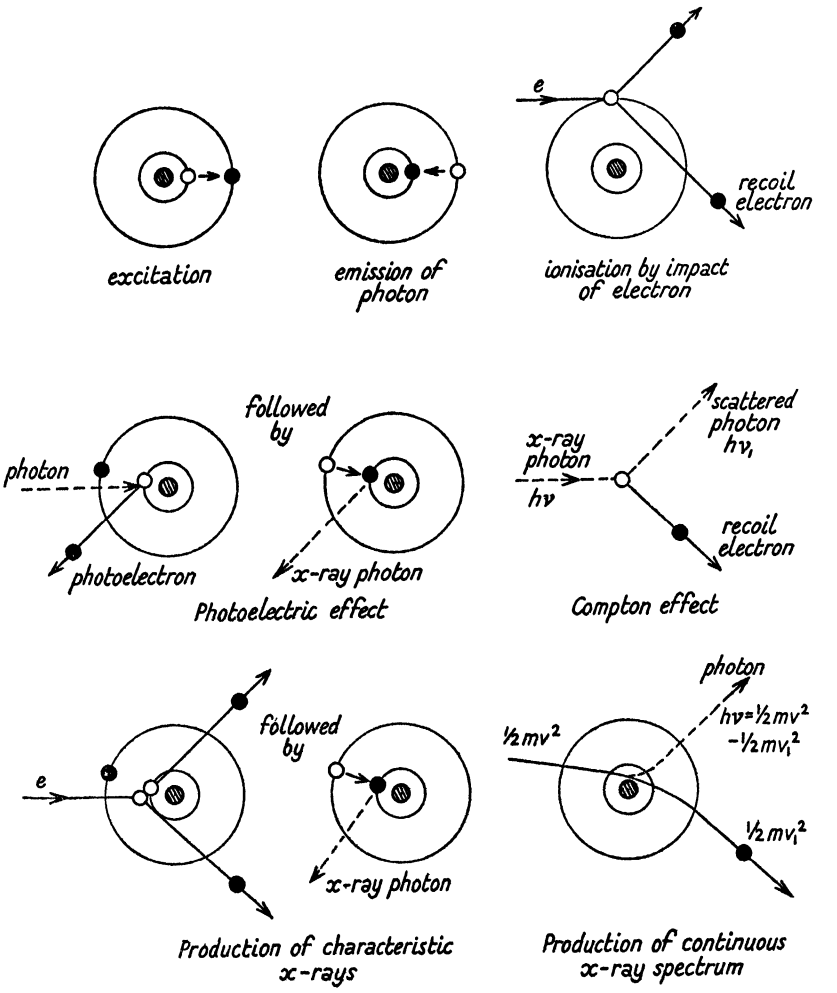


FIG. 1. Some electronic processes in atoms.

demonstrated. Moreover, the conception of the dual behaviour of photons as particles and as waves is still of value. For example the photoelectric effect is quite reasonably regarded as due to the impact on the atom of an X-ray photon, with energy $h\nu$, which leads to the ejection of an electron (see Fig. 1).

On the other hand, the diffraction of X-rays by crystals is best treated from the wave standpoint. In 1924 de Broglie put forward the suggestion

that all atomic particles have associated with them waves of definite wavelength. A beam of atoms or other particles should therefore behave like a train of waves or a beam of photons with wavelength given by $\lambda = h/mv$ so that the greater the velocity of the particles the shorter the wavelength. The wave nature of the electron was demonstrated experimentally by Davisson and Germer in 1927. A narrow beam of electrons from a heated filament was directed on to the polished face of a crystal of nickel. Electrons were diffracted in certain directions only, determined for a given crystal only by the voltage applied to the filament. This determines the velocity and therefore the wavelength of the electrons. The nickel crystal behaves as a simple diffraction grating, and from the known spacing of the atoms in the plane of the surface the wavelength of the electrons can be determined from measurements of the angles of diffraction. The value of λ so obtained agrees with that calculated from de Broglie's equation using the value of v from $Ve = \frac{1}{2}mv^2$, where V is the potential on the filament. It has since been shown that after transmission through thin metal films electrons produce diffraction effects similar to those produced by X-rays.

This new conception of the nature of the electron naturally modifies our views on the atom, the modern picture of which is due to Schrödinger, Heisenberg, Dirac, and others. Instead of the electron being a particle moving in well-defined orbits we may now regard it as a wave packet rather analogous to 'standing' sound waves. For such a standing wave to be set up the length of the path of the electron around the nucleus in a hydrogen atom must be a whole number of wavelengths, and since the circumference of a circle is $2\pi r$ and $\lambda = h/mv$ we have

$$\frac{nh}{mv} = 2\pi r, \quad \text{where} \quad n = 1, 2, 3, \text{ etc.}$$

This is exactly the same equation as that derived by Bohr, so that the new theory gives the same equations for the frequencies of the hydrogen spectral lines as did the Bohr atom. The behaviour of an electron is now defined by an equation, due to Schrödinger, of the form

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(W - V)\psi = 0$$

$\left(\nabla^2\psi \text{ is merely an abbreviation for } \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right)$, which is easily derived from the equation for a 3-dimensional wave of a quantity ψ propagated with velocity u:

$$\nabla^2\psi - \frac{1}{u^2}\frac{\partial^2\psi}{\partial t^2} = 0.$$

This is the de Broglie wave associated with the electron of which W and V are the total and potential energies. For our purposes we may say that the wave function ψ is such that its square (ψ^2) represents the probability of finding the electron at a certain point. We cannot usefully amplify this

rather inexact statement without a much more detailed treatment of Schrödinger's equation than is possible here. The wave function associated with the orbital motion of the electron is now often referred to simply as its orbital. Since this new atomic model regards the mass and charge of the electrons as distributed around the nucleus in three dimensions and not confined to plane orbits as in the Bohr atom, it is interesting to note here an important experimental method of determining the radial electron distribution in an atom. If this distribution could be calculated from the new atomic model it would provide valuable confirmation of the wave-mechanical theory. Also it will be remembered that Bohr made the obvious and reasonable assumption that the number of orbital electrons is equal to the atomic number Z. This also can be demonstrated experimentally.

THE NUMBER OF ORBITAL ELECTRONS IN AN ATOM

An early formula, due to J. J. Thomson, gave the fraction ϕ of the incident X-rays scattered by a cubic centimetre of material containing n electrons per c.c. as

$$\phi = \frac{8\pi ne^4}{3m^2c^4}.$$

In this formula ϕ is independent of the wavelength of the X-rays, and it is now known that this expression applies only to elements of low atomic numbers and for X-rays of moderate wavelength (0·1–1·0 A.). This method is, however, historically important since it was applied by Barkla in 1911, when its limitations were not realized, who showed that the numbers of orbital electrons in certain atoms were equal to their respective atomic numbers. In the same year Rutherford demonstrated, by experiments on the scattering of α particles, that the charge on the nucleus of an atom was also equal to its atomic number. Measurement of the refractive indices of solids for X-rays gives more reliable estimates of the numbers of electrons per atom, but the radial distribution of electrons in atoms is best determined in the following ways.

The radial distribution of electron density in an atom such as helium or neon may be determined directly by measuring the scattering of monochromatic X-rays by the gas at various angles. The only assumptions made are that the atoms are spherically symmetrical and that all the electrons scatter according to the same law and independently of one another. Since no atomic model is assumed, such experiments provide one of the best tests of the correctness of our ideas of atomic structure, provided that we can calculate the form of the radial distribution curve from our atomic model. This becomes very difficult as the total number of orbital electrons increases and various approximate methods have to be used, e.g. those of Thomas and Fermi and of Hartree. The observed and calculated radial electron distributions in a helium atom are shown in Fig. 2. On the Bohr theory there should be in the helium atom electrons

only at the distance 0·33 A. from the centre of the atom. It is seen that although the electron density is much more diffuse than according to the old theory, Bohr's model nevertheless gives a good idea of the size of the atom. In Figs. 2 and 4 the ordinates represent the values of a function $U(r)$ which

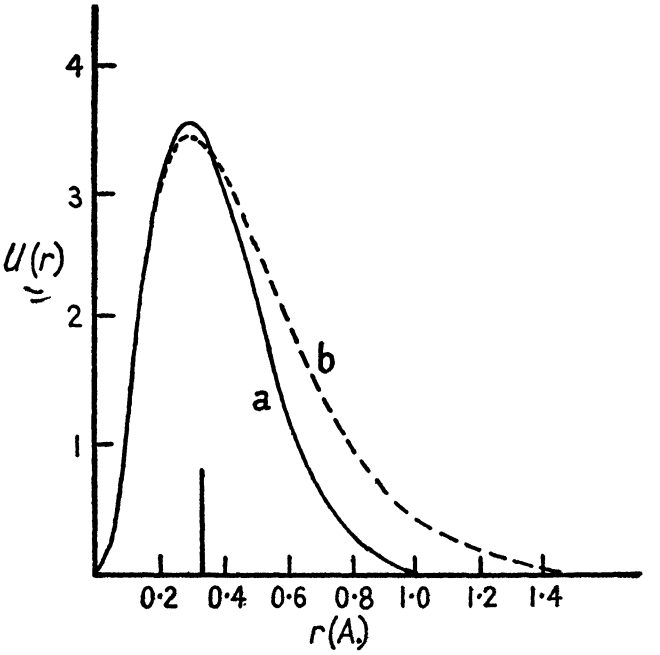


FIG. 2. Radial distribution curves for helium:
(*a*) experimental (Wollan), (*b*) theoretical (Hartree).

is defined by the relation: $U(r)\,dr$ = number of electrons at distances between r and $r+dr$ from the centre of the atom, so that $\int_0^\infty U(r)\,dr = Z$ (atomic number). This function therefore does not give a true indication of *electron density* (which would reach a maximum at $r = 0$) because as r decreases the volume of the shell ($4\pi r^2 dr$) becomes very small and vanishes at $r = 0$.

An alternative method of deriving the radial electron distribution in an atom is based on the theory of the diffraction of X-rays by crystals. Although in the elementary treatment the atoms in a crystal are represented by points situated at their centres, in actual fact the electronic system of one atom extends to meet those of its neighbours. The electron density along a line of atoms in a crystal is of the type shown in Fig. 3 (*a*) as compared with a section across a simple diffraction grating (*b*). Owing to this fact the expression for the intensity of reflection of X-rays by a crystal involves functions called the atomic structure factors f_1, f_2, etc., for the different kinds of atoms composing the crystal. The structure factor f of an atom is the ratio of the amplitude of the coherent radiation

(i.e. of the same wavelength as the incident) scattered by the atom to that scattered by a single electron. Its numerical value falls off as the angle of reflection increases, starting from a maximum value $f = Z$ at $\theta = 0$. The structure factor curves for certain atoms may be derived directly

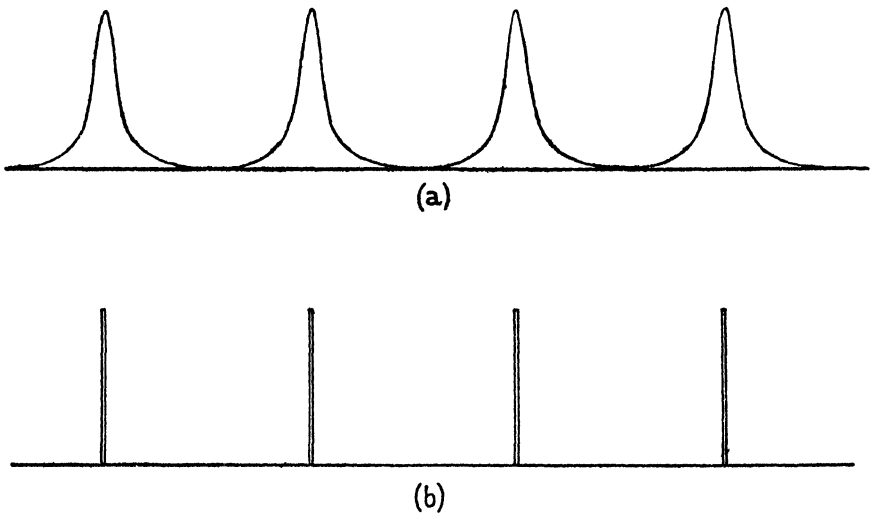


FIG. 3. The shape of the peaks in (*a*) is that of the electron density in the Cl^- ion as determined by Fourier analysis from the intensities of reflections of X-rays from rock-salt. In (*b*) is shown the variation in density of scattering matter across an *ideal* linear diffraction grating.

from the measured intensities of the X-rays reflected by sets of atomic planes in certain simple crystals (e.g. NaCl, CaF_2), and from these curves the radial electron distribution curves may be derived by the method of Fourier analysis. The area under such a curve gives the total number Z of orbital electrons. A radial electron distribution curve for a Cl^- ion in NaCl, obtained from the intensities of diffracted X-ray beams, is shown in Fig. 4.

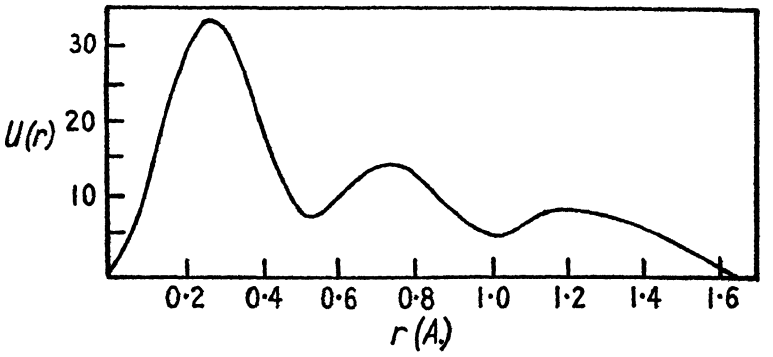


FIG. 4. Radial distribution curve for the Cl^- ion in NaCl (Havighurst). Total area under the curve corresponds to 17·85 electrons.

Our next problem is to see how the orbital electrons in atoms are arranged. Before proceeding to this, however, we shall for the sake of completeness devote a few pages to a consideration of the nucleus of the atom. This will clear up the question of the relative masses of atomic nuclei to which we referred at the beginning of this chapter in connexion with Prout's hypothesis.

THE STRUCTURE OF THE ATOMIC NUCLEUS

Nuclear Disintegration

When α particles collide with atoms of a gas (or strictly with atomic nuclei in a molecule of the gas) the effect of the collision depends on the nature of the gas and on the type of impact. In a glancing collision with a hydrogen nucleus the latter atom is ionized and projected forward with some of the energy of the α particle, which is thereby slowed down. In a head-on collision the proton (H^+, i.e. hydrogen atom minus its electron) acquires the maximum possible velocity. Largely owing to its increased velocity the proton has greater penetrating power, by means of which such elastic collisions were demonstrated by Rutherford in 1919. From a source of α particles in nitrogen gas particles were detected with a range greater than any previously known. They produced scintillations on a fluorescent screen and their deflexion in a magnetic field showed them to be protons. These result from the disintegration of nitrogen nuclei according to the equation:

$$_2He^4 + _7N^{14} \rightarrow (_9F^{18}) \rightarrow _8O^{17} + _1H^1.$$

It is conventional to represent an isotope of an element by its chemical symbol with the nuclear mass as superscript and nuclear charge, or atomic number, as subscript. The fluorine isotope $_9F^{18}$ shown above as an intermediate stage is unstable.

When α particles collide with beryllium atoms a different type of reaction takes place and rays of great penetrating power are emitted, which carry no charge. On absorption in paraffin wax, which contains a large proportion by volume of hydrogen, these particles eject high-speed protons which can, on account of their charge, be detected in a cloud-chamber. To explain these results Chadwick (1932) postulated the existence of the neutron, a particle with unit mass but no charge, and represented the collision of an α particle with a beryllium nucleus as follows:

$$_2He^4 + _4Be^9 \rightarrow _6C^{12} + _0n^1 \ (\gamma \text{ ray also emitted}).$$

The high penetrating power of the neutron is due to the fact that, having no charge, it can ionize atoms only by direct collision. Therefore its energy is lost, i.e. it is absorbed, only when it hits an atomic nucleus, and nuclei occupy only a small proportion of the volume of matter. Charged particles, α particles, protons, and electrons can ionize atoms from a distance, and since by so doing they are slowed down their penetrating power is correspondingly smaller.

We said earlier that the nucleus of an atom of atomic number Z carries a charge of $+Z$. The nucleus cannot simply consist of Z protons, since the mass of a proton is close to unity whereas the mass M of the nucleus of an element of atomic number Z is of the order of $2Z$. It was therefore first assumed that the nucleus of an atom of atomic number Z and mass M is made up of M protons and $M-Z$ electrons. The later view, following the discovery of the neutron, is that the nucleus contains Z protons and $M-Z$ neutrons. The number, Z, of orbital electrons remains, of course, unchanged. Little is known of the arrangement of the elementary particles or of the cohesive forces within the nucleus.

The Relative Masses of Nuclei

In this section we wish to consider two points. Firstly, the masses of atoms as determined in the mass spectrograph and referred to $O^{16} = 16{\cdot}000$ are not exactly integers. For example, the relative masses of the isotopes ${}_1H^1$, ${}_2He^4$, and ${}_8O^{16}$ are 1·008, 4·003, and 16·000 (standard). Before such accurate values had been determined it was thought that the discovery of isotopes had vindicated Prout's hypothesis of integral atomic masses. Of the eleven lightest atoms, excluding oxygen which is taken as standard, seven have atomic weights within 0·02 of the nearest integer, but the atomic weights of the other four are far removed from integers, viz. 6·94, 10·82, 20·18, and 24·32. These four elements were shown to be mixtures of isotopes. However, accurate determinations of the masses of isotopes show small departures from whole numbers referred to 1/16 of the mass of O^{16}. The latter unit is therefore not the mass of the fundamental particle of which nuclei are built since the lightest nucleus (H^1) has a mass of 1·008. The departures from integral masses are termed packing fractions. We must inquire into the meaning of these packing fractions.

Secondly, if we write disintegration equations of the kind already given in the previous section and insert the accurate masses of the nuclei concerned we find that the sums of the masses on the two sides of the equations do not balance.

The Equivalence of Mass and Energy

We have already seen that theory requires and experiment confirms that the mass of the electron increases with its speed. Einstein showed that there is a general relation between mass and energy which is expressed in his mass-energy equation, $E = mc^2$, in which m is mass, c the velocity of light, and E the energy-equivalence of the mass. It implies that mass and energy are interconvertible. Various forms of energy may all be equated: $E = mc^2 = h\nu = Ve = \frac{1}{2}mv^2$, a series of equalities which have been checked experimentally. Consider for example the equation $mc^2 = Ve$. The term Ve is the energy an electron acquires if accelerated by a potential V. (This provides a convenient way of stating energy, 1 million electron-volts being the energy of an electron accelerated by a potential of 10^6 volts.) If we calculate V from the known values of m, c, and e we obtain

the value 500,000 volts. The equation therefore implies that if we could annihilate one electron and give the energy to another the latter would acquire the same energy as if it had been accelerated by a potential of $\frac{1}{2}$ million volts. In order to see how this has been checked experimentally we must digress for a moment.

It has been known for some years that rays of extraordinary penetrating power are incident on the earth from outer space. They are termed cosmic rays and can penetrate as much as 2,000 feet of water. On some Wilson cloud-chamber photographs Anderson in 1932 found evidence of particles, with the same mass as the electron but with a positive charge, which had been produced by cosmic rays. Soon afterwards theoreticians predicted that if a high-energy photon (e.g. a γ ray) came sufficiently near to an atomic nucleus the photon could be annihilated and create a pair of particles, an electron and a positron, with equal masses and equal but opposite charges. Such pairs have been observed in cloud-chambers. The positron has a short life because as soon as it meets an electron the two disappear and regenerate a γ ray. It is found that when an electron is annihilated on meeting a positron two γ-ray photons of energy $\frac{1}{2}$ million electron-volts are produced, thus confirming the above relation, $mc^2 = Ve$. If the frequency of such a γ ray is calculated from the equation $mc^2 = h\nu$ we find $\nu = 1{\cdot}2 \times 10^{20}$ (vibrations/second), and in agreement with this it is found that the minimum frequency of the γ ray required to produce electron pairs (electron+positron) by collision is twice this value.

uclear Masses and Integers

We are now in a position to reconsider the masses of nuclei themselves and the differences between the sums of the nuclear masses on the two sides of a disintegration equation. The equation

$$_2\mathrm{He}^4 + {}_4\mathrm{Be}^9 \rightarrow {}_6\mathrm{C}^{12} + {}_0n^1$$

suggests that the sum of the masses of the products is equal to that of the reacting nuclei. However, the actual masses of these isotopes and of the neutron are

$_2\mathrm{He}^4$	4·0039	$_6\mathrm{C}^{12}$	12·0040
$_4\mathrm{Be}^9$	9·0150	$_0n^1$	1·0090
	13·0189		13·0130
K.E.	0·0057		
	13·0246		

To the masses on the left-hand side we have to add the mass-equivalence of the kinetic energy of the α particles, which is determined from their range in air. The surplus energy (0·0116 mass units) is either given entirely to the recoiling nuclei or partly thus and partly as γ rays. Measurement of the energy of the resultant particles in nuclear transformations confirms the accuracy of Einstein's mass-energy equation.

Consider now the mass of the nucleus of deuterium, the hydrogen

isotope $_1H^2$, which is 2·0147. The sum of the masses of the neutron and the proton, the constituents of the $_1H^2$ nucleus, is 1·0090 ($_0n^1$)+1·0081 ($_1H^1$) = 2·0171. The difference (0·0024 mass units) must be accounted for as follows. When a neutron and proton come together the interaction is so strong that the equivalent of this mass is radiated as energy. The *reason* for such interaction is unknown, but it is confirmed by the fact that γ rays of this energy will break up the deuterium nucleus into its component parts whereas rays of smaller energy will not. In other words, the 'reaction' $_0n^1+{}_1H^1 \rightleftharpoons {}_1H^2+0{\cdot}0024$ mass-units radiated is reversible; compare the photoelectric effect. The case of the helium nucleus is similar but more complex. The necessary components could be obtained in various ways, e.g.

$2\,{}_1H^1+2\,{}_0n^1 = 4{\cdot}0342$	$_1H^2+{}_1H^2 = 4{\cdot}0294$	$_1H^1+{}_1H^3 = 4{\cdot}0251$
$_2He^4 = 4{\cdot}0039$	$4{\cdot}0039$	$4{\cdot}0039$
Difference $0{\cdot}0303$	$0{\cdot}0255$	$0{\cdot}0212$

These differences are the amounts of energy which would be required to split the nucleus into the respective products. We conclude therefore that the mass of an atomic nucleus is not the sum of the masses of the fundamental component particles, the neutron and the proton (masses 1·0090 and 1·0081 respectively), because energy is emitted when these particles come together and mass is lost equivalent to this amount of energy. The difference between the two quantities, the mass of the nucleus and the sum of the masses of the component particles, is a measure of the stability of the nucleus.

We shall conclude these remarks on the nucleus by a brief reference to other types of nuclear disintegration.

Nuclear Disintegration by Protons, Deuterons, and Neutrons

Many examples have been found of disintegration processes produced by high-energy protons and deuterons. For example:

$$_1H^1+{}_9F^{19} \rightarrow {}_8O^{16}+{}_2He^4$$

and

$$_1H^2+{}_4Be^9 \rightarrow {}_5B^{10}+{}_0n^1.$$

The latter reaction is valuable since it provides an intense source of neutrons for other disintegration experiments. In some cases the primary product is radioactive, a phenomenon known as 'induced radioactivity', e.g.

$$_2He^4+{}_{13}Al^{27} \rightarrow (_{15}P^{30})+{}_0n^1$$

$$\searrow \text{ spontaneously}$$

$$\searrow {}_{14}Si^{30}+{}_1e^0 \text{ (positron)}$$

and

$$_1H^2+{}_{11}Na^{23} \rightarrow {}_{11}Na^{24}+{}_1H^1$$

$$\searrow {}_{12}Mg^{24}+{}_{-1}e^0+\gamma \text{ ray.}$$

At least 200 different kinds of radioactive atoms have been produced artificially. Some of these radioactive isotopes have very short lives; the lives of others are of useful lengths, e.g. ${}_{15}P^{32}$ with half-life 15 days and ${}_{11}Na^{24}$ with half-life 15 hours. Such isotopes are finding useful applications, as, for example, in tracing the movement of salts in plants, living bodies, etc.

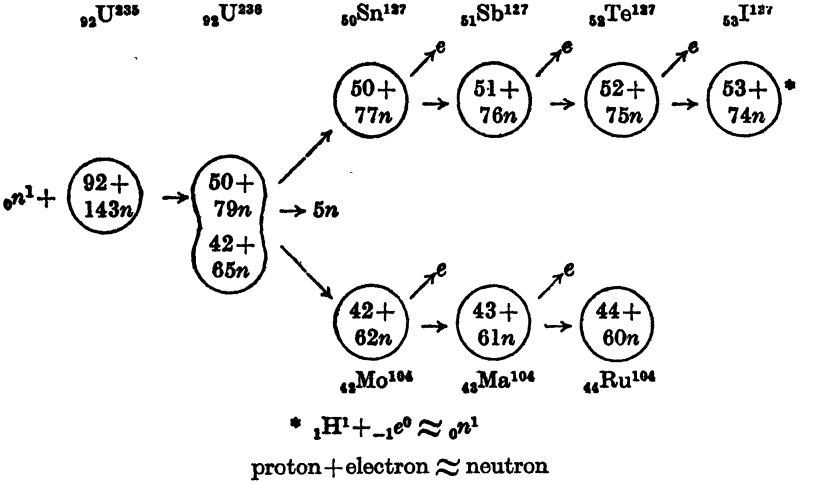
The neutron also may be used as a projectile, as in the reactions,

$${}_0n^1 + {}_7N^{14} \rightarrow {}_6C^{14} + {}_1H^1 \quad \text{and} \quad {}_0n^1 + {}_{52}Te^{126} \rightarrow ({}_{52}Te^{127}) \rightarrow {}_{53}I^{127} + {}_1e^0.$$

radioactive

Nuclear Fission

In the examples of nuclear disintegration mentioned above the products are nuclei with masses of the same order as those of the atoms bombarded together with a particle not heavier than He^4 (i.e. ${}_1e^0$, ${}_0n^1$, ${}_1H^1$, ${}_2He^4$). Another type of disintegration has been observed in the case of certain heavy elements in which the nucleus breaks up into two nuclei of comparable size. This process is called nuclear fission. When uranium is bombarded with neutrons the nuclei break up into pairs such as ${}_{50}Sn^{127}$ and ${}_{42}Mo^{104}$ with the simultaneous ejection of the surplus neutrons. The nuclei so formed are, however, very unstable and continue to emit β rays (i.e. they are radioactive) until they become stable isotopes of other elements. The whole series of processes for ${}_{92}U^{235}$ would then be as follows:



i.e. on the loss of each electron (β ray), 1 neutron → 1 proton.

THE PERIODIC TABLE

We must now consider the relations between the structures of atoms of different elements. It is generally accepted that all matter is composed of one or more of ninety-two different chemical elements. The atoms of the various elements possess different physical and chemical properties which enable us to recognize and separate them. All the atoms of a

particular element have the same arrangement of orbital electrons and therefore the same chemical properties but not necessarily the same nuclear mass. Atoms of a given element with different masses are termed isotopes. Since the isotopes of an element have the same chemical properties the chemist refers to the mixture of isotopes as the pure element, for he is always dealing with the same isotopic mixture. By chemical analyses of compounds the atomic weights of the elements relative to O = 16 may be determined. The chemical atomic weight of an element is therefore the weighted mean of the masses of the isotopes. Although the precise values of these chemical atomic weights are not of any particular physical significance they are, of course, of the greatest importance to the chemist. Long before anything was known of the structure of the atom the atomic weights of most of the elements had been determined, and from a knowledge of these values combined with the chemical properties of the elements the Periodic Classification was evolved.

A comprehensive classification of the elements was not possible until (1) the majority of the elements had been discovered, and (2) their relative atomic weights had been determined to a reasonable degree of accuracy. Lavoisier, in 1789, set out a list of some thirty elements which was increased to fifty by Berzelius in 1819, and Mendeleeff's first Table of the Elements contained some sixty or so elements. Many years of careful work were required to establish these atomic weights and the values are still being revised to the present day. We said above that atomic weights were obtained from analyses of compounds, but this is not strictly true. Analysis of water shows it to consist of hydrogen and oxygen combined in the proportions 1:8 (approximately) by mass. Early lists of 'combining weights' contained therefore not atomic weights but *equivalents*, for the atomic weight of oxygen relative to hydrogen cannot be found unless we know the relative numbers of hydrogen and oxygen atoms in the water molecule. These have to be determined in other ways (e.g. from the determination of vapour density), and the Periodic Classification of the elements was delayed until the correct formulae were assigned to molecules as a result of the resuscitation and application of Avogadro's hypothesis, enunciated in 1811, by Cannizzaro in 1858. For example, the equivalents of O, Mg, and F are 8, 12, and 19, whereas their atomic weights are 16, 24, and 19. As long as equivalents were used numerical relations could be found only between elements of the same chemical family, in which all the equivalents bear the same relation to the atomic weights.

The first of these relations was discovered by Döbereiner in 1829. He showed that in a group of chemically similar elements such as the halogens the atomic weight of bromine is approximately the arithmetic mean of those of chlorine and iodine. Other 'triads' were calcium, strontium, and barium, and lithium, sodium, and potassium. The elements were first arranged in order of their true atomic weights by Newlands in 1864, and Newlands' table was soon followed by the periodic classifications of Mendeleeff and of Lothar Meyer (1869–71). There is little point in dealing

here with the shortcomings of these early classifications and we shall deal now with the Periodic Table in its present form. It is found that if the elements, with six exceptions, are arranged in order of their atomic weights, elements with similar chemical properties recur at intervals. One form of the Periodic Table is shown on p. 30. Atomic weights increase from left to right and a new row is started when we come to an element similar to one in the preceding row. It is seen that the first two rows, the two short periods, contain 8 elements each and these are followed by two long periods of 18 elements, a long period of 32 elements (including 15 rare-earths, all placed in the same compartment), and finally an incomplete row of 6 elements. Two questions immediately suggest themselves. What determines the lengths of the various periods, or in other words, Why do elements with similar chemical properties occur separated by 8, 8, 18, 18, and 32 atoms respectively as in the case of the inert gases or the alkali metals, for example?

Inert gases . .	He		Ne		A		Kr		X		Rn
Atomic number .	2		10		18		36		54		86
Difference . .		8		8		18		18		32	
Alkali metals . .	Li		Na		K		Rb		Cs		—
Atomic number .	3		11		19		37		55		87
Difference . .		8		8		18		18		32	

Any theory of the structure of the atom must offer some explanation of these sequences, and we shall return to this problem in a later section. It is also relevant to inquire why there are only ninety-two elements, but no satisfactory answer to this question is yet possible. The fact that the elements of the last period are all radioactive (i.e. they decompose spontaneously into lighter atoms) indicates that these large nuclei are unstable, but attempts to calculate the limiting atomic number from theoretical considerations have not been successful.

Comparison of the order of the elements in the Periodic Table with the chemical atomic weights shows that in the cases of three pairs of atoms, viz. A and K, Co and Ni, Te and I, the atom of greater atomic weight has been placed before that of smaller atomic weight. Mendeleeff inverted these pairs of atoms on the grounds of chemical properties, which showed clearly that tellurium, for example, belonged to the same family as sulphur and selenium, and iodine to the halogens. When the atomic numbers of these elements were determined later by physical methods these rearrangements were fully justified, confirming the fundamental importance of the atomic number rather than the chemical atomic weight of an element. It so happens that iodine consists of the isotope 127 only, whereas tellurium has isotopes 126, 128, and 130, giving a mean atomic weight greater than that of iodine.

In the Periodic Table as set out on p. 30 we have distinguished as A and B sub-groups the vertical columns of elements of the long periods. The reason for this is that there are certain resemblances between the elements of an A and the corresponding B sub-group—for example, they often form

TABLE 1. *The Periodic Table*

	H 1·0081			He 4·003	Li 6·940	Be 9·02	B 10·82	C 12·010	N 14·008	O 16·000	F 19·00		I	SHORT PERIODS				
				Ne 20·183	Na 22·997	Mg 24·32	Al 26·97	Si 28·06	P 31·02	S 32·06	Cl 35·457		II					
A 39·944	K 39·096	Ca 40·08	Sc 45·10	Ti 47·90	V 50·95	Cr 52·01	Mn 54·93	Fe 55·84	Co 58·94	Ni 58·69	Cu 63·57	Zn 65·38	Ga 69·72	Ge 72·60	As 74·91	Se 78·96	Br 79·916	
Kr 83·7	Rb 85·48	Sr 87·63	Y 88·92	Zr 91·22	Nb 92·91	Mo 95·95	Ma	Ru 101·7	Rh 102·91	Pd 106·7	Ag 107·88	Cd 112·41	In 114·76	Sn 118·70	Sb 121·76	Te 127·61	I 126·92	LONG PERIODS
Xe 131·3	Cs 132·91	Ba 137·36	La* 138·92	Hf 178·6	Ta 180·88	W 183·92	Re 186·31	Os 190·2	Ir 193·1	Pt 195·23	Au 197·2	Hg 200·61	Tl 204·39	Pb 207·21	Bi 209·00	Po	—	
Rn 222	—	Ra 226·05	Ac	Th 232·12	Pa 231	U 238·07												
INERT GASES		[A SUB-GROUPS]						*GROUP VIII* TRIADS			[B SUB-GROUPS]							

* And the rare-earths

Ce 140·13	Pr 140·92	Nd 144·27	Il	Sm 150·43	Eu 152·0	Gd 156·9	Tb 159·2	Dy 162·46	Ho 163·5	Er 167·2	Tu 169·4	Yb 173·04	Lu 175·0

[NOTE. Atomic Weights are those given in the *Eighth Report of the Committee on Atomic Weights of the International Union of Chemistry*, 1938.]

compounds of the same formula type or in other words exhibit the same valency. There are, however, important differences between the properties of the A and B sub-group elements of a particular periodic group, some of which we shall note in later chapters. The groups of three elements Fe, Co, and Ni, Ru, Rh, and Pd, and Os, Ir, and Pt, occurring in the middle of the long periods between the A and B sub-group elements, were termed the transition elements. This term is now applied to a much larger group of elements characterized by certain peculiarities in their electronic structures. Finally we should mention that a few of the ninety-two elements have not yet been isolated. When the Periodic Classification was first put forward many more were unknown, and the chemical properties and approximate atomic weights of some of these (e.g. Sc, Ga, Ge) could be predicted since there were obvious gaps in some of the vertical families of elements. The absence of a whole family of elements could not, however, be detected, for the atomic weights of the elements do not rise by constant increments for unit increase in atomic number. The inert gases were in fact not discovered until some twenty-five years after the Periodic Table was first drawn up. The periodic variation with atomic weight of many physical properties of the elements showed that the Periodic Classification had a sound physical basis, but in order to confirm that no further families of elements could exist and to clear up the anomalies of the atomic weights of argon and potassium, cobalt and nickel, and of tellurium and iodine it was necessary to find some property of the elements which varies, not periodically, but continuously with atomic number.

Periodic and Non-periodic Properties

In support of the Periodic Classification Lothar Meyer showed that if the atomic volumes of the elements (atomic weights/densities) are plotted against the atomic weights they show a periodic variation. Some other physical properties show a similar variation, e.g. compressibility, coefficient of thermal expansion, the reciprocal of the melting-point, magnetic susceptibility, and atomic heat at low temperatures. At ordinary temperatures (i.e. over the range 20°–100° C.) the atomic heats of most elements lie close to the value 6 (Dulong and Petit Law of Atomic Heats). Boron, atomic heat 2·9, and carbon, atomic heat of graphite 2·39 and of diamond 1·84, are notable exceptions. At low temperatures, on the other hand, the atomic heats show large differences and vary in much the same way as the atomic volumes. Compare, for example, the following values:

	Atomic heat 20°–100° C.	*Atomic heat* −253° to −195° C.
Mg	6·1	1·74
P	6·2	1·34
Zn	6·1	2·52
Cd	6·2	3·46
Pb	6·4	4·96

We have seen that with a few exceptions the atomic weights of the elements increase regularly, and this was the only non-periodic property

of the elements known until the investigation of X-ray spectra and radioactivity. Actually we now know that an element of atomic number Z may have heavier isotopes than the element of atomic number $Z+1$, as for example in the case of ${}_{27}Co^{59}$ and ${}_{28}Ni^{58}$ and ${}_{28}Ni^{60}$, and the number of isotopes per element varies quite irregularly. Of the properties which vary steadily as Z increases we may mention the scattering of α particles by the elements, the absorption and scattering of X-rays and the wavelengths of the characteristic X-rays of a given series (i.e. K, L, etc. radiation). Moseley in 1914 showed that the square-roots of the frequencies of a given type of characteristic radiation, e.g. the K lines, vary approximately linearly with the atomic numbers over a wide range of elements. This linear relation between $\sqrt{\nu}$ and Z does not extend all the way down to $Z = 1$ for each type of characteristic X-radiation (K, L, M, etc.), but only to the point where the shell concerned becomes the outer shell of the atom. The determination of these frequencies established without doubt the atomic numbers of the elements such as argon and potassium and the other pairs whose order in the Periodic Table does not correspond with their atomic weights. The total number of the rare-earth elements was also finally settled.

We have now quoted examples of properties which vary periodically and of others which vary regularly with atomic number. The property of radioactivity falls into neither of these categories; it is a distinctive property of the nuclei of certain elements. Concerning the periodic and non-periodic properties we may make the following generalization. The former depend on the state of aggregation (solid, liquid, or gas) and on the state of chemical combination, whereas the latter do not. For example the same characteristic X-ray frequencies are emitted by the free elements or by the elements when chemically combined in compounds, and the large-angle scattering of α particles obeys the same laws whether the element be a solid or a gas. The periodic properties are therefore to be associated with the outer electrons of the atoms, for these electrons, as we shall see later, are responsible for the forces between the atoms. The type of interaction between the atoms is different in the different states of aggregation, so that properties such as compressibility or the coefficient of thermal expansion are quite different for the solid, liquid, and gaseous phases. The non-periodic properties, on the other hand, must either be associated with parts of the atoms more shielded from outside influences, such as the inner electron levels in the case of characteristic X-rays or the nucleus itself (scattering of α particles), or they must depend, as does the power of the atom to scatter X-rays, on the total number of orbital electrons.

THE ARRANGEMENT OF THE ORBITAL ELECTRONS IN ATOMS

In previous sections we have seen that optical and X-ray spectra and the photoelectric effect with X-rays provide good evidence for the arrangement of the orbital electrons of an atom in shells, though the electrons are not

now regarded as particles moving in plane orbits as in the original atomic model of Bohr. We have now to discuss the precise numbers of electrons in each shell, how far the arrangement of the electrons can be predicted from theory, and how the electronic structures of the atoms are related to their chemical and physical properties. A brief introduction to the wave-mechanical atom was given in an earlier section. On this model the states of the electrons of an atom are defined by four quantum numbers, n, l, s, and j. The principal quantum number n of the electronic orbit has already been mentioned. The various integral values of n correspond to the successive shells, e.g. for the K shell $n = 1$, for the L shell $n = 2$, and so on. The second quantum number l is involved in the wave-mechanical expression for the permitted energy states of an electron. A state of energy E_n defined by the quantum numbers n and l has orbital angular momentum of magnitude $\sqrt{\{l(l+1)\}}(h/2\pi)$ where l may have any one of the n values from zero to $n-1$. This expression gives the angular momentum due to the orbital motion of the electron. In addition to the angular momentum due to its orbital motion the electron also possesses intrinsic angular momentum due to its spinning about an axis of its own. Evidence for the spin of the electron comes from the behaviour of spectral lines when the radiating gas or vapour is placed in a magnetic field and from the Stern-Gerlach experiment mentioned below. Each electron therefore contributes to the total angular momentum of the atom in two ways: first by its motion around the nucleus, and secondly by its own motions around its own centre. The angular momentum of the electron spinning about its own axis is $\sqrt{\{s(s+1)\}}(h/2\pi)$ where s, the spin quantum number, has the value $\frac{1}{2}$. The projection of this angular momentum along the direction of an applied field is $\pm\frac{1}{2}(h/2\pi)$. The magnetic moment of the electron due to its spin is $2(eh/4\pi mc)\sqrt{\{s(s+1)\}}$ or $\sqrt{3}eh/4\pi mc$, the projection of which along the direction of an applied field is $\pm eh/4\pi mc$, which is taken as the unit—the Bohr magneton.

The resultant angular momentum of all the electrons in an atom is obtained by compounding vectorially the orbital and spin momenta of all the electrons, and this quantity is quantized and defined by the quantum number j. It has the value $\sqrt{\{j(j+1)\}}$. Theory predicts that in a magnetic field an atom can adopt only a limited number (actually $2j+1$) of discrete orientations. This prediction was confirmed for a number of atoms by the experiments of Stern and Gerlach and their pupils. For hydrogen and the elements of Group I of the Periodic Table the magnetic moment is simply that of the single spinning electron in the outer (valence) shell. The orbit of this electron makes no contribution to the moment since $l = 0$, and in the case of the elements other than hydrogen the orbits and spins of the other electrons are so oriented as to produce no resultant magnetic moment. For sodium, for example, j can have values $l\pm\frac{1}{2}$. For the valence electron ($l = 0$) $j = \frac{1}{2}$, so that $2j+1 = 2$. A beam of Na atoms, produced by vaporizing the metal, is accordingly split into two discrete beams by an inhomogeneous magnetic field (see also p. 220).

For our present purpose, which is to find the numbers of electrons in the various shells, it is convenient to consider the behaviour of an atom in a strong magnetic field since the quantum number j is not characteristic of a single electron but of a number of electrons. In a strong magnetic field each electron orients itself with its axis of rotation parallel to the field. The projection of its angular momentum in the direction of the field has the value $\pm\frac{1}{2}(h/2\pi)$ or $m_s(h/2\pi)$ where m_s, the magnetic quantum number of the electron, is equal to $\pm\frac{1}{2}$. Also, in such a field the orbit of the electron is subject to a further restriction. If we represent the component of l along the field as m_l then m_l must lie between $+l$ and $-l$, having therefore $2l+1$ possible integral values. We have now for each electron of an atom in a strong magnetic field five quantum numbers with the following possible values:

$$\begin{aligned} n &: 1, 2, 3, \ldots, \infty \\ l &: 0 \text{ to } n-1 \\ s &: \tfrac{1}{2} \\ m_l &: -l \text{ to } +l \\ m_s &: \pm\tfrac{1}{2}. \end{aligned}$$

We require to find how many electrons an atom may have for each value of n. This number is limited by Pauli's principle, which states that no two electrons may have all of their quantum numbers identical. Since s is always $\frac{1}{2}$ in a strong magnetic field we need not consider it here. For $n = 1$ there are clearly only the two possibilities

$$\begin{aligned} l = 0 &: m_s = +\tfrac{1}{2} \\ l = 0 &: m_s = -\tfrac{1}{2} \end{aligned}$$

and for $n = 2$

l	m_l	m_s
0	0	$-\frac{1}{2}$
0	0	$+\frac{1}{2}$
1	-1	$-\frac{1}{2}$
1	-1	$+\frac{1}{2}$
1	0	$-\frac{1}{2}$
1	0	$+\frac{1}{2}$
1	1	$-\frac{1}{2}$
1	1	$+\frac{1}{2}$

Electrons with the same value of l constitute a sub-shell, and it will be noticed that the sub-shells consist of one or more pairs of electrons with $m_s +\frac{1}{2}$ and $-\frac{1}{2}$. These are pairs of electrons with spins in opposite senses. The association of electrons in pairs with opposed spins is termed the pairing of electrons, and we shall meet this again when we come to consider the nature of the covalent bond. The electrons in a given shell are distinguished as s, p, d, etc. electrons according as $l = 1$, 2, 3, and so on. In any sub-shell there are $2(2l+1)$ electrons since m_l has $2l+1$ values and m_s always two possible values. The number of electrons in the nth shell is therefore

$$\sum_{l=0}^{l=n-1} 2(2l+1) = 2n^2$$

and the values of $2n^2$ are 2, 8, 18, 32 for $n = 1$, 2, 3, and 4. We might

therefore expect to find periods containing these numbers of elements in the Periodic Table, each period concluding with an inert gas in which all the shells are filled. The atomic numbers of the inert gases are not, however, 2, 10, 28, and 60 (i.e. 2, 2+8, 2+8+18, 2+8+18+32) but 2, 10, 18, 36, 54, and 86, that is 2, 2+8, 2+8+8, 2+8+8+18, 2+8+8+18+18, and 2+8+8+18+18+32. We assumed above that each sub-shell and shell is completed before the next is started, as in the scheme:

Shell	*n*,	*l*	2(2*l*+1)	$2n^2$	*Nomenclature*
K	1	0	2	2	1*s*
L	2	0	2	8	2*s*
	2	1	6		2*p*
M	3	0	2	18	3*s*
	3	1	6		3*p*
	3	2	10		3*d*
N	4	0	2	32	4*s*
	4	1	6		4*p*
	4	2	10		4*d*
	4	3	14		4*f*

etc.

What actually happens is that the first 18 electrons do go in as shown in the table, up to argon ($Z = 18$), but at the element potassium the first departure occurs. The 19th electron in potassium goes, not into the 3*d* but into the 4*s* sub-shell, and the 20th electron (in Ca) similarly goes into the *N* shell. After this the electrons continue to fill up the incomplete *M* shell, the two 4*s* electrons remaining in the *N* shell. This sequence of electronic structures shows (1) that the Pauli principle alone does not determine the sizes of the most stable electron groups, and (2) that the sub-shells have a certain completeness and stability even though the shell is not complete. It is reasonable to suppose that the observed configuration of an atom is that which makes its energy a minimum and this configuration is not always that derived simply from the application of the Pauli principle. The stability of the *s* sub-group of 2 electrons is very marked in certain heavy metals. Such a pair of *s* electrons has been termed an 'inert pair' and is discussed in a later chapter. The structures of the atoms following argon are as follows:

	K	*L*	*M*	*N*
A . . .	2	8	8	
K . . .	2	8	8	1
Ca . . .	2	8	8	2
Sc . . .	2	8	8+1	2
to				
Ni . . .	2	8	8+8	2
Cu . . .	2	8	8+10	1
Zn . . .	2	8	8+10	2

TABLE 2

The Electronic Structures of the Elements

		K	*L*		*M*			*N*				*O*				*P*			*Q*
		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*
H	1	1																	
He	2	2																	
Li	3	2	1																
Be	4	2	2																
B	5	2	2	1															
C	6	2	2	2															
N	7	2	2	3															
O	8	2	2	4															
F	9	2	2	5															
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12				2														
Al	13				2	1													
Si	14				2	2													
P	15		10		2	3													
S	16	Neon Core			2	4													
Cl	17				2	5													
A	18				2	6													
K	19	2	2	6	2	6		1											
Ca	20							2											
Sc	21						1	2											
Ti	22						2	2											
V	23						3	2											
Cr	24		18 Argon Core				5	1											
Mn	25						5	2											
Fe	26						6	2											
Co	27						7	2											
Ni	28						8	2											
Cu	29	2	2	6	2	6	10	1											
Zn	30							2											
Ga	31							2	1										
Ge	32							2	2										
As	33		28 Copper Core					2	3										
Se	34							2	4										
Br	35							2	5										
Kr	36							2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38											2							
Y	39									1		2							
Zr	40									2		2							
Nb	41									4		1							
Mo	42		36 Krypton Core							5		1							
Ma	43									6		1							
Ru	44									7		1							
Rh	45									8		1							
Pd	46									10									

		K	*L*		*M*			*N*				*O*				*P*			*Q*
		1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*
Ag	47	2	2	6	2	6	10	2	6	10		1							
Cd	48											2							
In	49											2	1						
Sn	50											2	2						
Sb	51				46 Silver Core							2	3						
Te	52											2	4						
I	53											2	5						
Xe	54											2	6						
Cs	55	2	2	6	2	6	10	2	6	10		2	6			1			
Ba	56															2			
La	57				54 Xenon Core									1		2			
Ce	58	2	2	6	2	6	10	2	6	10	1	2	6	1		2			
Pr	59										2			1		2			
Nd	60										3			1		2			
Il	61										4			1		2			
Sm	62										5		8	1		2			
Eu	63										6	5*s*, 5*p*		1		2			
Gd	64										7			1		2			
Tb	65				46 1*s* to 4*d*						8			1		2			
Dy	66										9			1		2			
Ho	67										10			1		2			
Er	68										11			1		2			
Tu	69										12			1		2			
Yb	70										13			1		2			
Lu	71										14			1		2			
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
Ta	73													3		2			
W	74													4		2			
Re	75				68 Hafnium Core									5		2			
Os	76													6		2			
Ir	77													9					
Pt	78													9		1			
Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
Hg	80															2			
Tl	81															2	1		
Pb	82															2	2		
Bi	83				78 Gold Core											2	3		
Po	84															2	4		
—	85															2	5		
Rn	86															2	6		
—	87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
Ra	88																		2
Ac	89																	1	2
Th	90				86 Radon Core										1			2	2
Pa	91														2			3	2
U	92														3			4	2

It is seen that in the elements from Sc to Ni the penultimate shell is incomplete. It is apparently completed in Cu, but one of the M electrons of Cu can be easily removed (in the formation of the cupric ion), so that we can say that the first element with a stable completed M shell is zinc. The elements Sc to Cu have a number of characteristic properties which are to be associated with the incomplete penultimate shell, such as variable valency and the formation of coloured, paramagnetic ions. They are called transition elements, a term previously restricted to the triads Fe, Co, and Ni, Ru, Rh, and Pd, and Os, Ir, and Pt. From Zn to Kr ($Z = 36$) the $4p$ sub-shell is completed in the normal way giving the B sub-group elements with electronic structures from 2, 8, 18, 2 (Zn) to 2, 8, 18, 7 (Br). After Kr the same process occurs as happened after argon, one and two electrons going into the fifth shell in Rb and Sr respectively and then from Y onwards the filling of the fourth shell is completed. Then in the next set of B sub-group elements, In, Sn, Sb, Te, and I, the $5p$ electrons are added until we reach xenon, with the structure 2, 8, 18, 18, 8. We should note that from Rb onwards the $4f$ sub-shell has never been filled; the first electron enters this sub-shell at Ce. Then from Ce to Lu the fourth shell is built up from 18 to 32 electrons. The fourteen elements in which this process takes place all have 2 electrons in the outermost (6th or P) shell, 9 in the fifth shell, and from 19 to 32 electrons in the fourth shell. Since the two outer shells are similarly constituted in all of these fourteen elements, the rare-earths, the atoms are extraordinarily alike in chemical behaviour and their separation by chemical methods has been one of the most difficult problems in preparative chemistry. There is no point in proceeding further with this discussion of the electronic structures of the elements, for these are given in Table 2. The detailed assignments of the electrons to particular sub-shells are based on spectroscopic studies.

PROCESSES INVOLVING ORBITAL ELECTRONS

We may conveniently end this chapter with a few remarks on certain processes, some of which have already been mentioned, involving the orbital electrons of atoms. We have seen that the movement of an electron from an orbit of energy E_1 to another of energy E_2 is accompanied by the emission or absorption of an amount of energy $E_1 \sim E_2 = h\nu$, light of frequency ν being emitted or absorbed in the process. The emission of characteristic X-rays by atoms is accounted for by electronic transitions of this kind, but there is an important difference between optical and X-ray spectra. The latter result from the movement of electrons between levels which are occupied by electrons in the atom in its normal state, whereas optical spectra arise when electrons, previously raised to outer levels (normally unoccupied) in the process called excitation, fall back to orbits of lower energy. Since the energies of the outer electrons vary from element to element, only atoms with similar arrangements of these outer electrons have optical spectra of similar types. Thus the optical spectra of elements of one periodic family resemble one another in many cases.

Those of the alkali metals, for example, are all of the same type and different from those of the alkaline earths. The X-ray spectra of the elements, however, show no such periodic resemblances since the inner electrons are arranged similarly in all but the very light elements.

The limit of the process of excitation is the complete removal of the electron from the atom. This is termed ionization. Just as there are the two types of spectra, X-ray and optical, involving inner and outer electronic levels respectively, so an electron may be completely removed from either an inner or an outer shell. In the photoelectric effect with X-rays we saw that electrons could be removed from the various shells. The removal of an inner (say, K) electron is followed by the emission of characteristic X-rays as the vacancy in the K shell is filled by an L electron, that in the L shell by an M electron, and so on until the outermost shell is reached. The positive ions with which we are familiar in chemistry are atoms deficient in one or more outer electrons. Just as certain atoms attain a stable electronic configuration by the loss of a number of electrons, so others do so by gaining electrons and forming negative ions. Ionization may be brought about in a variety of ways. It does not occur when a crystal of sodium chloride is dissolved in water, for the ions were already present in the crystal. If the sodium chloride was made directly from the elements, the ionization took place when the sodium and chlorine combined. When, however, some solids, liquids, or gases are dissolved in water or other solvents with high dielectric constants ionization may accompany the process of dissolution, as when HCl gas dissolves in water. The photoelectric effect is an example of ionization caused by light, and other methods of ionizing atoms include the heating of solids (and sometimes liquids and gases), particularly metals, and collision processes. If a gas is heated, atoms may be ionized by collision with other atoms, so that when thermal equilibrium is reached we have a system containing atoms, ions, and electrons—the processes of ionization and the recombination of ions with electrons to form neutral atoms taking place continuously. A method of ionization of particular importance is that in which the atoms of a rarefied gas are ionized by a beam of electrons. Since the kinetic energy of the electrons may be determined, the method yields much information about the energy required to remove one or more electrons from an atom, though there are a number of experimental complications. It is found that for a given atom ions are formed only if the energy of the electrons exceeds a certain value, I_0, the ionization potential of the atom (which is usually expressed in electron-volts). Typical ionization potentials are

H	He	Ne	Na	Cs	Mg	Hg	
13·54	24·5	21·5	5·12	3·9	7·6	10·4	electron-volts.

More than one electron may be removed simultaneously from an atom. For caesium the corresponding ionization potentials are

Cs^{+} 3·9, Cs^{2+} 27·4, Cs^{3+} 62, Cs^{4+} 113 electron-volts.

The fact that further electrons after the first are removed only with great expenditure of energy is consistent with the electronic structure and chemical behaviour of the atom. It is interesting to consider what happens if the energy of the electrons is less than I_0, and we find two possibilities. The first is that 'elastic' collisions take place in which the atom recoils from the impact with only sufficient energy to assure conservation of momentum. Collisions of this type need not concern us further. In the second type of collision, termed 'inelastic', more than this amount of energy is taken up with the result that the internal structure of the atom is altered. We have already seen that electrons of energy 10·4 E.V. are required to ionize the mercury atom. It is found, however, that if the energy of the electron is only 4·66 E.V. this amount of energy is taken up by the atom and, moreover, various other discrete amounts of energy, 4·86, 5·43, 6·7, etc. E.V. can be absorbed. After absorption of energy in this way the atom is said to be in an excited state and it re-emits the energy by returning, either directly or in stages, to the normal state. The energy W of 4·86 E.V. corresponds to the 2536 A. line of mercury ($W = hc/\lambda$), so that mercury vapour bombarded by electrons of this energy emits the spectral line of this wavelength. Excitation to the same state may alternatively be brought about by illuminating the vapour by light of this wavelength, but there is an interesting difference between excitation by electrons and by photons. Whereas electrons with energy between two values W_1 and W_2 ($W_2 > W_1$), corresponding to two excited states, can give up energy W_1 and retain the difference, light of wavelength corresponding to energy between W_1 and W_2 in general will not excite the atom. The photons must give up all or none of their energy. Thus mercury vapour absorbs the 2536 A. line but not light of wavelength in the immediate vicinity. There are exceptions to this general rule in the case of groups of atoms (molecules and crystals), where we find that in certain cases light of energy $h\nu > W$ does cause excitation to the state W. The difference in energy, $h\nu - W$, is emitted as scattered light of frequency ν' given by

$$\nu' = \nu - \frac{W}{h}.$$

This is the Raman (or Smekal-Raman) effect which has found considerable application in chemistry (see Chap. VI). The normal and excited states of an atom are referred to collectively as the stationary states of an atom, and it is conventional to refer the energies of these states to that of the ionized atom, which is taken as zero. For the mercury atom we have:

	Energy value (E.V.)
Ionized atom	0·0
Excited states	−3·7
	−4·97
	−5·54
	−5·74
Normal atom	−10·4

After determining the stationary states of an atom we find that not all the spectral lines which could arise as the result of transitions between these states do actually occur. The different states are distinguished by particular values of the various quantum numbers and the reason for the non-appearance of certain spectral lines is that the quantum numbers may change only by certain amounts in such electronic transitions. The permitted changes constitute the so-called 'selection principles'. For example, the quantum numbers n and l may change their values only by ± 1, and j by ± 1 or zero.

All the periodic properties of atoms which we mentioned earlier are functions of the number and arrangement of the orbital electrons, and we have seen that the radial electron distribution of an atom can be calculated from measurements of the X-rays scattered by a gas. In the gas there is little interaction between the orbital electrons of one atom and those of another. These determine the size of the atom, and when two atoms collide prevent the approach of the nuclei beyond a certain distance —the effective atomic diameter. In condensed phases, liquids and solids, the atoms are much closer together, and the properties of these phases depend not only on the structures of the individual atoms but also on their arrangement in space relative to one another and on the extent to which the electronic systems of the different atoms interact with one another. So far we have been discussing the behaviour of individual atoms without paying much attention to the relation of the atom to its neighbours. We must now consider how the orbital electrons of one atom interact with those of its neighbours. We cannot give any detailed treatment of the various kinds of interatomic forces such as would be required if we wished to account for the physical and chemical properties of substances. Our chief concern in this book lies with the geometrical arrangement of atoms rather than with the reasons why certain arrangements are more stable than others and why the resulting system of atoms has certain properties. Our treatment of interatomic forces will therefore be descriptive.

CHAPTER II

FORCES BETWEEN ATOMS

TYPES OF BONDS BETWEEN ATOMS

So far we have dealt with the structure and some of the properties of isolated atoms. In practice we shall seldom meet with such atoms since for most elements the monatomic state (i.e. the existence as free atoms) is not the most stable under ordinary conditions. The inert gases exist in this form and show little or no tendency to unite either with one another or with other atoms. In other cases more or less vigorous treatment is required to produce a monatomic vapour. If an inert gas is cooled sufficiently it eventually liquefies and finally solidifies. In these condensed states there are clearly weak interatomic forces of some kind operating—their weakness is evident from the extremely low melting- and boiling-points, very little thermal energy being needed to separate the atoms from one another. Furthermore, the structure of the crystals shows that the atoms are arranged in the most closely packed way possible for equal spheres, each having twelve equidistant neighbours, indicating that the interatomic forces from a given atom are not directed preferentially towards any particular neighbour. Such forces are called van der Waals forces.

Suppose now that we cool the vapour of the metal sodium. In the vapour the sodium is present in the form of atoms.* It condenses to a liquid and then to a solid. In the latter the atoms are arranged in the same way as in a crystalline inert gas, each atom being equidistant from twelve others. The physical properties of crystalline sodium are, however, very different from those of, say, crystalline argon. The latter is transparent and a very poor conductor of heat and electricity, whereas sodium is opaque, except in very thin layers, has a brilliant metallic lustre, and is a good conductor of heat and electricity. Properties such as these are characteristic of the metallic state and suggest that the atoms in sodium are bound together in quite a different way from those in crystalline argon. In this book we shall not have occasion to consider in any detail the nature of the metallic bond, but something will be said of the structure of metals and alloys in the last chapter.

Let us now turn to another element, chlorine. At a sufficiently high temperature we should find in this case also that the gas was largely in the form of discrete atoms. On cooling, these unite in pairs to form molecules,

* This is true at high temperatures. At lower temperatures the atoms combine to form diatomic molecules, as shown by the Stern-Gerlach experiment. The molecules have no magnetic moment and are therefore not deflected in the magnetic field. The interatomic distances in the alkali-metal molecules have been determined from studies of band spectra.

in which form the element normally exists. Considerable energy is required to separate the atoms of such a molecule. On further cooling liquefaction and solidification take place and both the liquid and the solid consist of the same molecules Cl_2 as are present in the gas at ordinary temperatures. These cohere in the same way as the atoms of an inert gas, by van der Waals forces. The interatomic bonds within the molecules are clearly much stronger than these weak intermolecular forces since the crystal melts at $-102°$ C. whereas only 0·04 per cent. of the molecules are split into atoms even at 1794° C. (The molecules of bromine and iodine are more easily split up, these elements being respectively 6·3 per cent. and 25·5 per cent. dissociated at about 1050° C.) The force between the two chlorine atoms in a Cl_2 molecule is called a homopolar or covalent bond.

This attraction between two similar chlorine atoms to form a stable diatomic molecule has to be explained in terms of the atomic model already described. The number (17) of electrons in each atom is one less than that in the stable argon atom. Each atom can attain the argon structure if it shares one of the electrons of the other atom, i.e. if two of the thirty-four electrons were considered the common property of both the atoms. These two electrons would then constitute the bond between the atoms. This suggestion was made by Lewis in 1916, though at that time it was not at all clear how the two electrons could satisfy both atoms at the same time. The modern view of the electron-pair bond will be given later.

We have seen that the Cl atom is not the most stable form of the element under ordinary conditions and that it prefers to acquire the argon configuration by forming one electron-pair bond with a second atom. It can also do this by forming a similar bond with an atom of another element, so that we find chlorine combining with many elements by means of electron-pair bonds. It is evident that there is an alternative way of attaining the argon configuration, namely by acquiring an extra electron to form the ion Cl^-. An atom like sodium, on the other hand, can also acquire an inert gas configuration by losing an electron. Accordingly if sodium is placed in chlorine gas there is an interchange of electrons from sodium to chlorine with the formation of Na^+ and Cl^- ions. Between such oppositely charged ions there is a strong attractive force, the ionic bond, and the ions together form a stable solid in which they behave, to a first approximation, as spherically symmetrical charged bodies. The geometrical arrangement of the ions in ionic crystals will be dealt with later.

If we have two ionic crystals A^+B^- and C^+D^- it is possible to change the partners to form A^+D^- and C^+B^-. To do this it is necessary to reduce the strength of the ionic bonds between the ions so that separation of the oppositely charged ions can take place and so make rearrangement possible. The usual method of effecting this is to place the ionic crystals in a medium of high dielectric constant (e.g. water), and many chemical processes involve the mixing of ions in aqueous solution. The possibility of separating the products AD and CB depends on the relative solubilities

of the four salts, AB, CD, AD, and CB. Such *double decompositions* may also be effected, though usually less conveniently, in the molten state.

Of the four main types of interatomic bond, van der Waals, metallic, covalent, and ionic, we shall consider only the last two in any detail. The van der Waals bond is responsible for the feeble attraction between atoms with stable electronic configurations and is not of importance in chemical reactions. It is responsible for the cohesion of molecular crystals.

It is interesting to consider now what types of interatomic binding were recognized by the chemist as a result of the studies of the chemistry of the elements. All atoms other than those of the inert gases have the power of combining with those of other elements, though not necessarily of all other elements. The hydrogen atom is usually found attached to only one other atom in simple molecules and is said to have a valency of one. The halogens and the alkali metals are also univalent in many of their compounds. Early work on the electrolysis of fused salts and of salt solutions indicated the close connexion between electricity and interatomic forces and also showed that some atoms could be differentiated as electropositive and others as electronegative. The former, H, Na, K, etc., are evolved at the negative electrode in electrolysis and the latter, the halogens, O, etc., at the positive electrode. Berzelius therefore suggested, in 1812, that the forces between atoms in their compounds were electrostatic, but this view was dropped towards the middle of the century as it appeared incompatible with the facts of organic chemistry, the chemistry of carbon compounds. For example, the electropositive H atom in a hydrocarbon molecule such as CH_4 could be replaced by the electronegative Cl without any radical change in properties, suggesting that the bonds in such compounds were non-polar rather than electrostatic bonds between oppositely charged atoms. With the advent of the theory of electrolytic dissociation of Arrhenius (1887) the electrostatic theory of valency was revived and it came to be recognized that there were two different kinds of interatomic force, the electrostatic bond in salts, acids, and bases, solutions of which could be electrolysed, and the non-polar bonds in organic and other molecules which could not be broken in this way. To these a third type had to be added to account for the existence of the 'coordination compounds' of Werner. These compounds are discussed elsewhere in this book, and it must suffice to say here that a characteristic feature of these compounds is that the central metal atom is attached by non-ionizable bonds to a number, usually 4 or 6, of atoms or molecules, this number being independent of the Periodic Group to which the metal atom belongs. Typical coordination compounds are

$$[Al(NH_3)_6]Cl_3, \quad [Cr(NH_3)_6]Cl_3, \quad \text{and} \quad [Co(NH_3)_6]Cl_3.$$

When these compounds dissolve in water they ionize like salts AX_3 yielding the complex ion $[M(NH_3)_6]^{3+}$ and 3 Cl^-, the bonds between the metal atom and the NH_3 molecules remaining intact. The fact that the numbers of such bonds formed by elements of different Periodic Groups is

the same and the fact that the NH_3 molecule, already a stable molecule, can form such bonds, seemed to indicate that these bonds must be of quite a different type from those in simple salts or molecules. The formulae of the fluorides of the elements of the second short period, for example, are simply related to the positions of the elements in the Periodic Table:

$$NaF,\ MgF_2,\ AlF_3,\ SiF_4,\ PF_5,\ SF_6.$$

There is, however, a further complication. In their hydrides the elements do not all exhibit the same maximum valency as in their fluorides, as is seen from the formulae of the highest hydrides of Si, P, S, and Cl:

$$SiH_4,\ PH_3,\ SH_2,\ \text{and}\ ClH.$$

In these cases the elements apparently have two valencies, the sum of which is eight (Abegg's rule of eight, 1904). These are some of the facts which have to be explained by our atomic model. It has to account for the two main types of bond in chemical compounds, the polar binding between the oppositely charged ions in salts and the non-polar binding in organic and other non-ionizable molecules. This non-polar binding is apparently of two kinds, the first occurring in molecules like CH_4 and NH_3, in which the number of such bonds is related to the position of the element in the Periodic Table, and the second in the Werner coordination compounds. The chemist is not primarily concerned with the relatively feeble forces between atoms whose primary valencies are already satisfied—the van der Waals bonds.

No real development of the theory of valency was possible until after 1913, when the significance of atomic numbers was established, and in 1916 Kossel and Lewis laid the foundations of the modern theory of chemical bonds. Kossel pointed out that elements with numbers of electrons close to those of the inert gases could, by losing or gaining the appropriate number of electrons, acquire the stable electronic configuration of the inert gas. Sulphur and chlorine, for example, would require to take up 2 electrons and 1 electron respectively, whereas Ca and K could reach the argon structure by the loss of 2 electrons or 1 electron, giving the ions S^{2-}, Cl^-, K^+, and Ca^{2+}. The bonds in salts like KCl and CaS would then be due to the electrostatic attraction between the constituent ions. This was quite satisfactory for elements not far removed from the inert gases, for such ions were already known to exist, but it was obviously not so plausible to regard a molecule like CH_4 as $C^{4+}(H^-)_4$. The properties of methane are very different from those of a salt like KCl. The theory of Lewis was complementary to that of Kossel and, as we have already mentioned, postulated that electrons could be *shared* between atoms, a pair of shared electrons constituting a chemical bond between them.

IONS AND IONIZATION

We have already met with the process of ionization as the limit of the optical excitation of an atom and have seen that in a simple case like caesium the ease with which electrons can be removed from an atom (or

added to it) depends on the electronic structure of the atom. In chemical operations we are chiefly interested in ions which are stable in solution, and it is necessary to see how ionization is related to the structures of atoms and hence to their positions in the Periodic Table. First we may say that ions carrying high charges are rare, and whereas some positive ions with charges as high as 4 are stable in solution, no negative ion with a charge greater than 2 exists in aqueous solution. This difference between positive and negative ions is to be expected since in the formation of negative ions of increasingly greater charge there is an increasing excess of negative charge over the positive charge of the nucleus, leading to instability, whereas in positive ions the electrons are held by the positive nuclear charge which exceeds the total charge of the electrons. Also, in forming a negative ion the atom acquires electrons to form a stable electronic group and this may be done in other ways besides ionization.

In the case of K and Ca the formation of ions is easily understood. In other cases the arrangement of the orbital electrons is less simple and as regards electronic structure we may distinguish four types of atom, as follows:

(1) The inert gases, which have outer groups of electrons of considerable stability, though as we saw in Chapter I these are not necessarily complete shells of $2n^2$ electrons.

(2) Atoms with all except the outer shell complete. These include the elements of the first and second short periods, the pairs of elements following the inert gases A, Kr, X, and Rn, and the B sub-group elements. The ions formed by these elements are colourless if, as is usual, the atom has acquired by ionization a stable outer group of 8 or 18 electrons. Certain of the B sub-group elements can form in addition to such normal ions others in which either (*a*) one or more electrons of the next quantum group are given up, or (*b*) the two *s* electrons of the outermost shell remain. Thus the normal ion of Cu is the cuprous ion Cu^+ (2, 8, 18), but the cupric ion Cu^{2+} is also formed with the structure (2, 8, 17). Such an ion resembles those of the next class. Other examples of this behaviour are the ions Ag^{2+} and Au^{3+}. An example of (*b*) is the thallous ion Tl^+ (2, 8, 18, 32, 18, 2).

(3) Atoms with the two outermost electron groups incomplete. These elements exhibit variable valency, forming coloured paramagnetic ions which often possess catalytic activity. They are termed the transition elements and in the Bohr presentation of the Periodic Table are enclosed in a single frame. The first group of transition elements have the following structures:

			3*s*	3*p*	3*d*	4*s*
Sc					1	2
Ti					2	2
V					3	2
Cr					5	1
Mn	2	8	2	6	5	2
Fe					6	2
Co					7	2
Ni					8	2

central atom in a simple molecule AB_n acquires a share in one electron for each bond formed. If then the most stable electronic configuration for the atoms C, N, O, and F is that of the inert gas neon (with a completed shell of 8 electrons) we see why the formulae of the simple hydrides are CH_4, NH_3, OH_2, and FH, and similarly for the elements of the second short period, SiH_4, PH_3, SH_2, and ClH with the argon configuration. The formulae of the fluorides PF_5 and SF_6, in which the elements show a different valency, could be accounted for if we assumed that instead of forming only sufficient bonds to complete the octet of valency electrons the elements formed a number of bonds equal to the number of their valency electrons. In this way we could explain Abegg's 'rule of eight'. Later we shall see that the problem is not quite so simple as this.

In the above formulae we assumed that to form a covalent bond one electron came from each of the atoms. There is also the possibility that both the electrons might come from the same atom. When we examine the electronic formula of ammonia, for example, we see that the N atom still has a pair of electrons which are not being used for bond formation. This offers an explanation of the fact that a molecule like NH_3 can, although its octet is already completed, still form a further bond to another atom provided that this atom is willing to acquire a share in two electrons. This could account for the formation of the Werner coordination compounds (hence its name the 'coordinate link') and compounds such as amine oxides, sulphoxides, and sulphones. Sidgwick gave the coordinate link the symbol $\rightarrow$ to indicate that one atom provides the electrons, and typical formulae involving coordinate links are

$[Co(\leftarrow NH_3)_6]Cl_3$, $O\leftarrow NR_3$, $O\leftarrow SR_2$ and $O\leftarrow SR_2\rightarrow O$

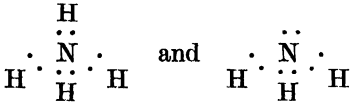
Stereochemical considerations showed that the coordinate link could not be distinguished from a single covalent bond once it had been formed, but if in the latter the two electrons are shared symmetrically between the atoms then the coordinate link must have a polar character. The N atom in $O\leftarrow NR_3$ would now have a share in seven electrons instead of eight as in NR_3, so that it should be the positive end of a dipole. Measurements of the dipole moments of such bonds will be dealt with later. The charges which would arise as the result of the symmetrical

$O^-\leftarrow N^+R_3$

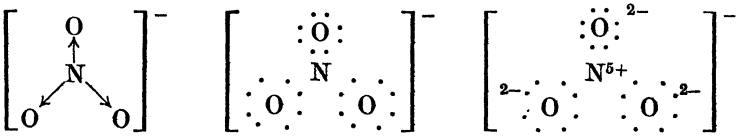
sharing of the electrons have been called 'formal charges'. Owing to the polar nature of the coordinate link it is sometimes alternatively referred

to as a 'semi-polar double bond', being in a sense a combination of a single covalent bond and an ionic bond. With these two types of covalent bond and the ionic bond the early electronic theory of valency was able to relate the formulae of most inorganic compounds to the electronic structures of the component atoms. In certain exceptional cases, such as the boron hydrides, one-electron bonds had to be assumed. In a molecule like B_2H_6 there are not sufficient valency electrons for the required number of covalent bonds. We must, however, note a number of important limitations to this early theory.

First, it offered no explanation of the angles between the bonds formed by an element. The tetrahedral distribution of four, and the octahedral arrangement of six, bonds had been firmly established for a number of elements by classical stereochemical studies, but these and other less symmetrical arrangements of bonds could not be predicted theoretically. However, assuming the tetrahedral arrangement of four bonds formed by four pairs of electrons constituting a stable octet, as in the elements of the first two short periods, the spatial distribution of three and two bonds was consistent with the assumption that unshared pairs of electrons behaved like bonds in occupying one or two of the tetrahedral bond positions. Thus while the NH_4^+ ion has a tetrahedral configuration the NH_3 molecule is pyramidal, the unshared pair of electrons occupying the fourth tetrahedral position:



In the NO_3^- ion, on the other hand, we have a different state of affairs. If we regard the bonds in this ion as covalent, then they must be coordinate links as in (*a*). The electronic formula is shown at (*b*). Each O atom completes its octet by acquiring a share in two additional electrons. The N atom has now no pair of unshared electrons as was the case in the NH_3 molecule and the three bonds are accordingly arranged symmetrically in a plane. Of course, on this simple electronic theory there was no reason



why the bonds should not be regarded as ionic (*c*), when the same planar arrangement would be expected if we assume, as is reasonable, that ionic bonds will be arranged in the most symmetrical manner possible. This brings us to the second point we have to make. That there was no way of deciding whether a complex ion or molecule should be formulated with ionic or covalent bonds must be attributed to the fact that we have been

considering only the number of electrons available, i.e. the outer electronic structures of the atoms, without regard to other characteristic properties of the elements concerned. For example, the elements fluorine and chlorine have similar arrangements of outermost electrons, but there are considerable differences between the chemical properties of the two elements. Fluorine does not always form compounds analogous to those of chlorine. In particular there are very few fluorine oxy-compounds whereas there are many oxy-compounds of chlorine, and much of the chemistry of fluorine is not paralleled by the other halogens. It is clear that any satisfactory treatment of interatomic bonds must also take account of factors other than the mere distribution of the orbital electrons.

As the early electronic theory of valency was developed by chemists no serious attempt was made to extend it to crystalline solids, and as a result it was not at all obvious that the structure of, say, a cuprous iodide crystal was consistent with the ordinary chemistry of copper and iodine. In the crystal every Cu atom is attached to four I atoms and every I atom to four Cu atoms, hence the following bond picture could have been given:



and for ZnS with the same structure:



On the other hand, an attempt *was* made to formulate compounds such as hydrates, which exist only in the crystalline state, with covalent bonds attaching the water molecules to anions or cations, and this led to difficulties which are discussed in Chapter XI. As the study of crystals progressed it became evident that the bonds in many simple crystalline salts could not be described as purely ionic or purely covalent bonds, although the well-marked differences between some of the physical properties of certain sets of compounds appeared to support the view that bonds intermediate in type between ionic and covalent were extremely rare if they existed at all. At this stage it is relevant to inquire

(*a*) whether such bonds of intermediate type are of frequent occurrence. If not, then they are of relatively small importance and should be treated as exceptional cases;

(*b*) whether the intermediate bonds represent only small departures from the extremes, or whether bonds of all types from those with 100 per cent. covalent to those with 100 per cent. ionic character are found.

In the latter case our treatment of bonds must be of such a nature as to allow for all intermediate types. In the former it would be sufficient to

deal with the extremes and merely to recognize that small departures from 100 per cent. pure bond types are permissible. This latter was the viewpoint first adopted. The extreme bond types, ionic and covalent, were recognized and intermediate cases were approached from the ionic standpoint, using the concept of polarization which we must now examine briefly. We may anticipate our later conclusions by saying here that in fact all kinds of intermediate bonds are found and that the treatment in terms of polarization of ionic bonds which we shall first describe is unsatisfactory except for essentially ionic crystals.

POLARIZATION

The retarding of light waves on passing through a medium is due to the interaction of the electromagnetic waves with the electronic systems of the atoms. This results in their distortion or polarization. Since an atom is polarized when placed in an electric field we may expect a similar effect when two oppositely charged ions come close together. The total effect will depend on (*a*) the susceptibility of each ion to distortion, its polarizability, and (*b*) the power of each ion to distort the other, i.e. its polarizing power. In discussing the ionic bond we assumed that ideally each ion is unaffected by the presence of the other but any treatment of actual bonds must take account of polarization. The essence of this treatment of bonds is as follows. For a bond between two atoms A and B let us assume that the ions A^{m+} and B^{n-} are brought together to their equilibrium distance. The problem is to discover the nature of the bond between them. As we have said, this will be determined by the polarizabilities and the polarizing powers of the two ions. We should expect the polarizability of a negative ion to be greater than that of a positive ion since in the former the negative charge is greater than the positive charge on the nucleus, so that the outer electrons are less firmly bound than in a positive ion, in which the number of orbital electrons is less than the nuclear charge. Also, for a series of ions carrying the same charge we should expect the polarizability to increase with the size of the ion, this effect being more marked for negative than for positive ions. Thirdly, for a series of isoelectronic ions such as Mg^{2+}, Na^{+}, F^{-}, and O^{2-} the polarizability should increase steadily throughout the series. As for polarizing power, this should be greater the greater the positive charge and the smaller the size of the ion. These relations are sometimes referred to collectively as 'Fajans' Rules'. Now if we regard as the limit of the distortion of the negative ion in a bond A^{+}—B^{-} the complete sharing of electrons between the atoms, i.e. the formation of a covalent bond, it appears reasonable to use the above relations to account for facts such as the following: Ionization in solution is restricted to elements of low valency and extends to elements of higher valency in later than in earlier periodic groups. Thus in the case of the typical and A sub-group elements we may draw a rough line of demarcation between those elements which

are known to form ions stable in aqueous solution and those which do not (Be, Al, and Zr show only a weak tendency to ionize).

Li	Be	B	C
Na	Mg	Al	Si
K	Ca	Sc	Ti
Rb	Sr	Y	Zr

We must note, however, that it is strictly not sound to relate the nature of the bond A—B in a salt to the tendency of the salt to ionize in solution, for, as we have seen, there are no bonds between A^+ and B^- ions in a dilute solution of the salt, and there is no justification for assuming that only ionic bonds can be disrupted in the process of dissolution of a crystal. (Compare, for example, the dissolution of HCl in water.)

This method of dealing with bonds in terms of polarization is unsatisfactory for a number of reasons. When extended to bonds between atoms such as C or P it becomes artificial in postulating ions of high charge which cannot exist under ordinary conditions. A more serious objection is that this method does not provide a quantitative treatment of bonds of intermediate type. So far we have talked of polarizability and polarizing power without defining these terms. The former may be precisely defined as the dipole moment induced in an ion by unit electric field, and values of the polarizabilities of atoms and ions may be determined from spectroscopic, optical, and other data. The Lorenz-Lorentz equation connects the polarizability α of the atoms of an elementary monatomic gas with the refractive index (n) for waves of infinite wavelength:

$$\alpha = \frac{p}{I} = \frac{3}{4\pi N}\frac{n^2-1}{n^2+2}\frac{M}{\Delta} = \frac{3}{4\pi N}R_\infty,$$

where p is the polarization, I the strength of the electric field, and R the molar refractivity. The value of n is obtained from measurements of the refractive index for various wavelengths in the visible region which, combined with a knowledge of the dispersion (variation of the refractive index with wavelength), give by extrapolation the value of the refractive index for infinite wavelength. This method is applicable to the inert gases and, with slight modification, to ions in solution. The effect of the interaction of the ions is eliminated by determining the refractive index at a series of concentrations and then extrapolating to infinite dilution. The value of R_∞, the molar refractivity, so obtained is, however, the sum of the refractivities of the separate ions and to obtain these individual values we need to know the value of the refractivity for one particular ion—compare the determination of ionic radii, p. 91. It is assumed that the polarizability of H^+ is zero, since this ion consists of a single proton with no orbital electrons. Approximate corrections for the effect of the hydration of various ions are made. The molar refractivities of a number of ions are given below, grouped according to the total number of orbital

electrons in the atoms or ions—the Effective Atomic Numbers (E.A.N.). We may note the rapid increase in R_∞ with increasing size of the ion and the large effect of increasing negative charge for a given E.A.N.

Refractivities of some Atoms and Ions

E.A.N.	*Charge*					
	−2	*−1*	*0*	*+1*	*+2*	*+3*
10	O	F	Ne	Na	Mg	—
	7·0	2·4	1·0	0·5	0·3	
18	—	Cl	A	K	Ca	Sc
		9·0	4·2	2·2	1·3	0·9
36	—	Br	Kr	Rb	Sr	—
		12·6	6·3	3·6	2·2	
54	—	I	Xe	Cs	Ba	La
		19·0	10·3	6·1	4·2	3·3

In order to determine the polarization of an ion in a bond we should need not only the values of the polarizabilities of the ions but also those of the polarizing powers, but no satisfactory way of assessing this latter property has been suggested. Goldschmidt calculated the 'field strengths' of positive ions as the ionic charge divided by the square of the ionic radius, giving values such as the following:

+1		*+2*		*+3*	
Li	1·7	Be	17·3	—	
Na	1·0	Mg	3·3	Al	9·2
K	0·6	Ca	1·8	Sc	4·4
Rb	0·5	Sr	1·2	Y	2·7
Cs	0·4	Ba	1·0	La	1·0

but such values do not in general provide a criterion for estimating the nature of bonds since the 'field strength' makes no distinction between ions with an outer shell of 8 and those with an outer shell of 18 electrons. For example, the radii of the Cu^+ and Na^+ ions are very nearly the same (and similarly for the pairs K^+ and Au^+, Ca^{2+} and Cd^{2+}), but the bonds in the cuprous and sodium halides have certainly not the same degree of ionic character.

The use of the concept of polarization led to a strange inconsistency in the description of bonds. It was assumed that there was a clear-cut distinction between ionic and covalent bonds in spite of the fact that polarization implied bonds intermediate in nature between the two extremes. This was in a large measure due to the misinterpretation of physical data. The nature of the bond between two atoms A and B in a solid or in a molecule cannot necessarily be deduced from the properties of the substance AB when it is dissolved in water, fused, or vaporized. For example, the conductivities of certain fused halides (to which we refer later) show that ions are formed when the solid has been broken down by fusion, but the formation or non-formation of ions in this way does not

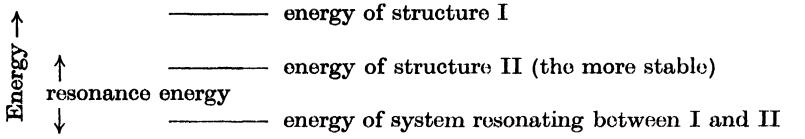
mean that the bonds in the solid were 100 per cent. ionic or 100 per cent. covalent. The relation between the structure of a compound in different states of aggregation will be discussed in more detail in Chapter IV.

The conception of polarized ionic bonds is convenient when dealing with crystals in which the bonds are essentially ionic. The term 'ionic crystal' cannot in practice be restricted to those with 100 per cent. ionic bonds, since few, if any, crystals would satisfy such a criterion. The interpretation of ionic crystal structures in terms of polarization was developed by Goldschmidt and has thrown considerable light on the changes in structure type in series of compounds with analogous chemical formulae. It will be realized, however, that this treatment of bonds has many limitations as a method of dealing with all the gradations of bonds between ionic and covalent. An alternative and later method, resulting from the application of wave-mechanics, starts from a different standpoint. Adopting the view that few, if any, bonds are 100 per cent. ionic or 100 per cent. covalent and that bonds of all intermediate types are possible, the new method would consider, in the ideal case, all the possible electronic configurations of the system of atoms and describe the actual nature of a given bond in terms of the contributions made by the various configurations. In practice it is not feasible to consider all the possible electronic configurations of a system of atoms and we take account only of the most likely and reasonable possibilities, but this limitation is not inherent in the method and is imposed only for reasons of practical convenience. We shall now consider a bond between two atoms from this point of view.

RESONANCE

In the Bohr atom each electron was regarded as a charged particle moving in a fixed orbit. Transitions between one orbit and another were possible and involved the gain or loss of an integral number of quanta of energy. In the later wave-mechanical theory of the atom the idea of a particle confined to a plane orbit was replaced by a probability function which has a maximum at a distance from the nucleus corresponding to the radius of the Bohr orbit. Just as an atom has a number of discrete energy states, referred to as stationary states and distinguished by a set of quantum numbers, so a molecule has a normal state and a system of stationary states. The normal state is that corresponding to the lowest value of the total energy of the molecule and therefore to the greatest stability. Each state of the molecule, like that of the atom or individual electron, is represented by a wave-function ψ from which the energy of the system can, at least in theory, be calculated. Let us suppose that a system of atoms has in the normal state two possible structures I and II represented by wave-functions ψ_{I} and ψ_{II}. Theory postulates that the function $\psi = a\psi_{\mathrm{I}} + b\psi_{\mathrm{II}}$ is also a possible wave-function of the system. Now the most stable configuration of the system could be found if we could determine the value of the ratio b/a which gives the wave-function

ψ corresponding to minimum energy. In the extreme cases, when b/a is found to be either very small or very large, then the most stable structure is I or II respectively. If, however, b and a are of comparable magnitude, the normal state of the system *involves* both structures I and II, or is said to resonate between these two structures. The word 'involves' is used because the resulting structure of the system is not simply intermediate between the structures I and II. The fundamental idea in resonance is that the minimum energy corresponding to the wave-function ψ is smaller than that corresponding to either ψ_{I} or ψ_{II}, i.e. by resonating between two structures the system becomes more stable than either of the simple structures. In the above argument we have assumed only two possible structures, but any number of reasonable structures may be taken into account subject to the following restrictions: Resonance is possible between structures only if they have (*a*) the same number of unpaired electrons in each structure and (*b*) the same general configuration of the nuclei.



We cannot review here the experimental evidence for the existence of resonance, but the relevant data for some resonating systems will be given when these compounds are described in later chapters. The principle of resonance has many applications in chemistry. The simplest is to the problem of bonds intermediate in type between ionic and covalent bonds. Its most important application, however, is to molecules or other groups of atoms for which alternative arrangements of bonds are possible and where the properties of the molecule are not explained satisfactorily by any single structural formula. Benzene is the classic example of a molecule of this sort. Provided that the conditions for resonance are satisfied we may regard the actual state of such a molecule to be the result of resonance between a number of structures with different arrangements of bonds, the contributions of the various structures being such as to make the resonance energy a maximum. The experimental evidence for resonance may be summarized under the following heads:

(1) Chemical properties not those to be expected for any single structural formula.

(2) Abnormal interatomic distances; these are best discussed in individual cases.

(3) Resonance energies. The contention that the energy of the resonating system is less than that of the most stable of the contributing systems by an amount termed the resonance energy can obviously be verified if we can determine these energy quantities. These calculations are dealt with in a later section (see Bond Energies, p. 70), but we may say here that they provide good evidence in support of the idea of resonance.

Other experimental evidence comes from

(4) The force-constants of bonds.
(5) The values of interbond angles.
(6) Electric dipole moments.

We have said that the structure of a resonating system is not simply intermediate between the structures of the forms involved. Equally a resonating system is not to be regarded as a mixture of these forms, as is the case in tautomerism. If we regard resonance as an electronic process with a definite frequency, then resonance and tautomerism differ only in degree, and whereas tautomeric forms can be separated by chemical or physical means, the time involved in the resonance process is so small that no separation of the resonating forms is possible. The difference between the physical properties of a resonating molecule and a tautomeric mixture may be illustrated by a simple example. If we have a molecule ABC which resonates between two polar forms $A—B^+—C^-$ and $A^-—B^+—C$, then its electric dipole moment will be close to zero if both forms are involved to approximately equal extents. In a tautomeric mixture of the two forms, on the other hand, the molecule would have an apparent dipole moment as large as that of either polar form, since each type of molecule can orient itself in the field (compare the molecular structure of N_2O, p. 406).

We have seen that the ordinary single covalent bond is formed by the sharing of two electrons between the atoms it joins. Other types of covalent bonds, involving one, three, four, and six electrons, are also known, the first two being rare. However, despite the fact that the 1-electron bond is of relatively little importance from the practical point of view as compared with the normal electron-pair bond, we shall consider it first on account of its simplicity.

The 1-electron Bond

The simplest possible group of atoms is the so-called hydrogen 'molecule-ion', H_2^+, consisting of two hydrogen nuclei and one orbital electron which must constitute the bond between them. According to Bohr the hydrogen atom consisted of a nucleus around which an electron revolved with constant speed in a circular orbit of radius 0·529 A. On the wave-mechanical model the behaviour of the electron is represented by a wave-function ψ and the circular orbit is replaced by a probability function $\psi^2(4\pi r^2 dr)$ which gives the probability of finding the electron at a distance between r and $r+dr$ from the nucleus. The variation of ψ and of $\psi^2(4\pi r^2 dr)$ with the distance r is shown in Fig. 5 (*a*). The probability function rises to a maximum value at a distance of about 0·5 A. from the nucleus, which was the radius of the circular orbit in the earlier atomic model. The essential difference between this picture and the Bohr atom lies in the fact that the electron *may* be found at other distances, but will

most probably be found at the distance 0·5 A. from the nucleus. The procedure for finding the stable configuration of H_2^+ is as follows:

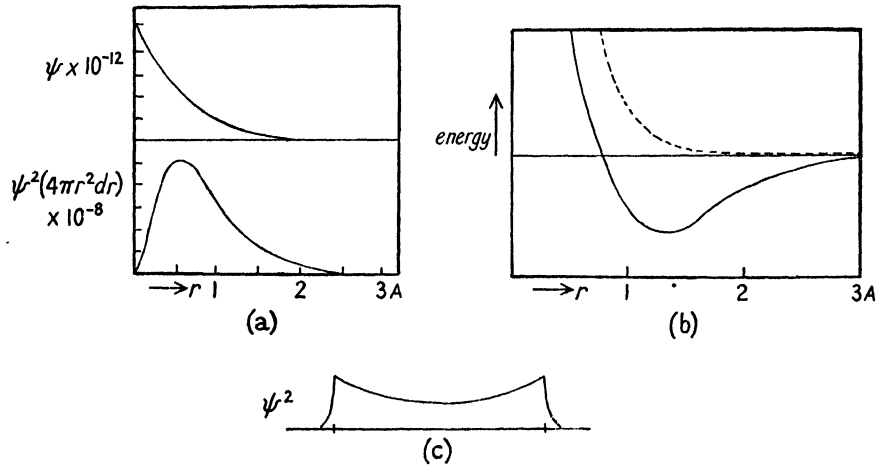


FIG. 5. (*a*) The wave-function ψ and $\psi^2(4\pi r^2\,dr)$ for the hydrogen atom. (*b*) The energy of interaction of a hydrogen atom and a proton. (*c*) Section through the hydrogen molecule-ion showing the electron distribution (after Pauling and Burrau).

If we consider a hydrogen atom and a hydrogen ion to approach one another and plot the energy of interaction against the distance between the nuclei we obtain a curve like the upper one in Fig. 5 (*b*). There is no minimum, showing that they do not combine to form a stable system. According to quantum mechanics, however, we must consider the possibility of resonance between the two equivalent arrangements

$$\begin{array}{lll} H_A & H_B^+ & \psi_1 \\ H_A^+ & H_B & \psi_2. \end{array}$$

Each of these two systems has exactly the same energy, so that there is complete resonance. If we now plot the energy of interaction calculated with the wave-function $\psi_1+\psi_2$ instead of ψ_1 (or ψ_2) we obtain the lower curve of Fig. 5 (*b*), showing the formation of a stable H_2^+ ion with interatomic distance about 1·06 A. This is a rather over-simplified picture, but it is adequate for the present purpose. The electron spends practically all its time between the two nuclei as shown in Fig. 5 (*c*), where the ordinates represent the probability of finding the electron at a given position. In the case of $H\cdot H^+$ the resonance energy which stabilizes the system is large because the two forms have exactly the same energy. If the two possible forms of a system have different energies then resonance is less complete, resulting in smaller stability. Thus if we have a 1-electron bond between two different atoms the two forms are

$$\begin{array}{ll} A\cdot & B^+ \\ A^+ & B\cdot \end{array}$$

which have different energies. In general 1-electron bonds between atoms

of different kinds are not likely to be stable. Probably the only compounds in which bonds of this sort occur are the hydrides of boron. The existence of 1-electron bonds even in these molecules is not, however, definitely established and their structures are discussed in Chapter XV.

The Electron-pair Bond

The treatment of the simplest case, that of the H_2 molecule, is quite analogous to that given above for H_2^+, except that the two possible structures are

$$H_A{\cdot}^1 \quad {}^2{\cdot}H_B \quad \text{and} \quad H_A{\cdot}^2 \quad {}^1{\cdot}H_B$$

corresponding to interchange of the two electrons (labelled 1 and 2) between the two H atoms. Two other structures

$$H_A{:}^- \quad H_B^+ \quad \text{and} \quad H_A^+ \quad H_B{:}^-$$

also have to be considered but are relatively unimportant. As before, the energy of interaction shows no minimum corresponding to molecule formation unless resonance between the two forms is taken into account. The curves are similar to those in Fig. 5 (*b*), the internuclear distance for H_2 being 0·75 A. The stability of the electron-pair bond so formed is largely due to the resonance energy arising from the interchange of the two electrons between the two nuclei.

In addition to mass and charge the electron has other properties which are attributed to the spin of the electron. Arising from its spin the electron has angular momentum $\sqrt{3}h/4\pi$. This angular momentum can be oriented by an external magnetic field either with or against the field and the electron is said to have positive or negative spin and values $\pm\frac{1}{2}$ for the spin quantum number m_s. This interaction with an external magnetic field means that the electron has a magnetic dipole moment. The Pauli exclusion principle states that not more than two electrons can occupy a given orbit and that the two electrons must have opposite spins, so that their magnetic moments are neutralized. We now see how wave-mechanics accounts for the fact, previously impossible to explain, that two electrons are required for the formation of a stable covalent bond. The presence of an unpaired electron gives rise to paramagnetism, and we shall see later that this relation of magnetism to the electronic structure of atoms is of great importance in structural problems. In the H atom there is only one electron, so that the *monatomic* gas is paramagnetic (under ordinary conditions hydrogen is diatomic). In the He atom there are two electrons occupying the same (1*s*) orbit, hence the gas is diamagnetic. The pairing of the electron spins in H_2 makes this molecule also diamagnetic.

When discussing the 1-electron bond it was pointed out that the two systems $A{\cdot}\ B^+$ and $A^+\ B{\cdot}$ have different energies so that complete resonance is not possible, with the result that in general such bonds between atoms of different kinds are not stable. In the case of the electron-pair bond, however, the two forms, $A{\cdot}^1\ {}^2{\cdot}B$ and $A^2{\cdot}\ {}^1{\cdot}B$, have the same energy,

the only difference being that the electrons have been interchanged. Complete resonance is possible with the result that the electron-pair bond is stable between unlike atoms, accounting for its widespread occurrence. We noted above that in a full treatment of the electron-pair bond in the H_2 molecule the ionic forms $H_A^- H_B^+$ and $H_A^+ H_B^-$ had to be considered but were of minor importance. With unlike atoms these ionic structures (A^+B^-, A^-B^+) may contribute appreciably to the structure of the molecule, particularly if one atom is much more electronegative than the other (see p. 68). This wave-mechanical approach to the nature of the covalent bond therefore provides a method of dealing with the transition from covalent to ionic bonds. Its merit lies in the fact that all reasonable structures for the bond are considered and the contributions from the various structures are deduced from the properties of the atoms concerned.

The 3-electron Bond

There are only a few stable molecules or complex ions (other than those containing transition elements) in which the total number of electrons is odd. We should expect such 'odd' molecules to polymerize and in this way pair up the unpaired electrons. The stability of odd molecules is to be attributed to the presence of 3-electron bonds, arising from resonance between two forms A: ·B and A· :B. Assuming that each atom has one stable orbital, then two (paired) electrons occupy one of the orbitals and the third electron the other. As in the case of the 1-electron bond the resonance energy will be large only if the atoms A and B are identical or closely similar in electronegativity. Pauling represents the 3-electron bond by the symbol A···B and points out that since the strength of this bond is about one-half that of an electron-pair bond, the total bond energy of two molecules A···B is approximately the same as that of the dimer Ä—B—B—Ä. Thus the dimer is not necessarily more stable than the odd molecule. In agreement with this we find that the molecule NO is stable and forms no dimer, whereas NO_2 polymerizes to the dimeric form N_2O_4. It is also consistent with the above view of the 3-electron bond that it is found only between atoms of similar electronegativity, as in NO, NO_2, O_2^-, and ClO_2.

$$:N \equiv N:$$

THE PHYSICAL PROPERTIES OF CRYSTALS IN RELATION TO BOND TYPE

We have expressed the view that bonds intermediate in character between the extreme types do exist and that in fact pure bonds are the exception rather than the rule. For this reason we have decided to adopt a method of describing bonds which will allow for possible types of intermediate bonds. We have, however, produced little evidence in support of our view—indeed we have stated that the physical properties of certain sets of compounds would appear to indicate that solids containing ionic

bonds can be sharply differentiated from those containing covalent bonds. It is necessary therefore to consider briefly this aspect of the physical properties of crystals. Let us first see to what extent distinctive properties are associated with the four extreme types of solid—metallic, molecular, homopolar, and ionic crystals.

Metals have a number of characteristic properties, dependent on the presence of free electrons, which place them in a class apart from all other solids. They possess good electrical and thermal conductivities, they are opaque to light except when in very thin layers, and they have high reflecting powers. The property of thermionic emission has already been mentioned in Chapter I. These electrical and optical properties are generally very similar in the liquid and solid metal. Another set of physical properties, including hardness, melting-point, thermal expansion, and compressibility, show very large variations from one metal to another, being dependent on the properties of the individual atoms and the way in which they are packed together in the crystal. Thus the melting-point of mercury is $-39°$ C. and that of tungsten $+3{,}300°$ C., while compressibility varies from values around unity to as much as 60 and the coefficient of thermal expansion also has widely different values for different metals. Malleability is an important property peculiar to metals.

The simplest molecular crystals are composed of non-polar molecules (see Chap. IV) held together by the relatively weak van der Waals bonds. Their properties should therefore be considered in two sets: first, those which are characteristic of the molecule itself, such as magnetic, electrical, and optical properties; and secondly, those which arise only in the assembly of molecules forming the crystal, i.e. hardness, melting-point, compressibility, and thermal expansion. Since there is in general little interaction between the molecules in a molecular crystal the properties dependent on the electronic structure of the molecule are essentially the same for the molecule in the crystal as for the free molecule, and therefore the magnetic properties of the crystal, for example, are simply the vector resultants of the properties of the individual molecules, which may be inclined to one another at various angles in the crystal. The properties of the first set may therefore differ greatly for different molecular crystals. Those of the second set, on the other hand, are much more characteristic of molecular crystals as a class. They are usually soft and have low melting- and boiling-points, large compressibilities and thermal expansions. These properties arise from the feeble cohesion between the molecules.

The typical ionic crystals (e.g. NaCl, CaF_2) are composed of ions of highly electropositive and electronegative elements in proportions determined by the charges on the ions. Normally they are moderate insulators, but at high temperatures they possess considerable ionic conductivity and they conduct well in the molten state. They are usually transparent to visible light but absorb strongly in the infra-red. Colour is determined by the electronic structures of the constituent ions and is generally the same as the colour of the free ions in solution. Ionic crystals often

exhibit good cleavage and for the most part have fairly high melting-points and moderate hardness. We can make only very general remarks about the properties of ionic crystals since, as we shall see shortly, there are comparatively few crystals in which the bonds are even approximately 100 per cent. ionic.

Homopolar or covalent crystals, in which all the interatomic bonds are essentially covalent, are comparatively few in number. They are insulators both in the solid and molten states (see, however, semi-conductors, p. 163), are usually hard, and exhibit poor cleavage. Their melting-points are often high, as are their refractive indices (e.g. diamond). Some possess a characteristic resinous lustre (zinc-blende). They are mostly formed by the lighter elements of the middle columns of the Periodic Table.

From these brief remarks we see that while some properties are characteristic of a certain type of crystal others are not. Whereas softness and low melting-point are characteristic of molecular crystals, we can make no such generalization about the hardnesses or melting-points of metals, homopolar or ionic crystals. Since such properties have been invoked as evidence of bond type this is a convenient point at which to deal with the old controversy concerning ionic and covalent bonds. The early electronic theory of valency provided simple mechanisms for the formation of ionic and covalent bonds, i.e. the complete transfer of one or more electrons or the sharing of two (four or six) electrons for the ionic and covalent bonds respectively. It was difficult to see how a bond could be intermediate in character between these extremes apart from the small departures from ionic character arising from the polarization of the ions, and it was therefore suggested that bonds intermediate between ionic and covalent should be rare if they occurred at all. Although in some ways this matter is now only of historical interest, it is worth while considering some of the arguments adduced in favour of this view, since they may still appear convincing unless carefully analysed. We shall take them in turn.

(i) The number of covalent bonds which an atom can form is limited in accordance with its position in the Periodic Table whereas the number of ionic bonds is, of course, not restricted in this way. Moreover, the disposition of the covalent bonds from an atom is often not the most symmetrical in space as is the case in typical ionic crystals. These characteristics of 'covalent' bonds are not, however, inconsistent with their having some ionic character, for if the bond is assumed to be the result of resonance between various electronic configurations of the system of atoms, then the number and spatial arrangement of the bonds must depend on the orbitals available, even though there is resonance with ionic structures. We shall be discussing interbond angles and interatomic distances in the next chapter.

(ii) The melting-and boiling-points of the alkali halides fall steadily from the fluoride to the iodide, whereas the reverse effect is observed for the silicon tetrahalides. The former are typical salts and the latter non-ionized compounds. It was argued that the halides of a metal with

chemical properties intermediate between a metal and a non-metal should show intermediate behaviour if the bonds in such halides were intermediate between ionic and covalent bonds. In fact it is found that the boiling-points of the halides of aluminium and tin vary as shown in Fig. 6,

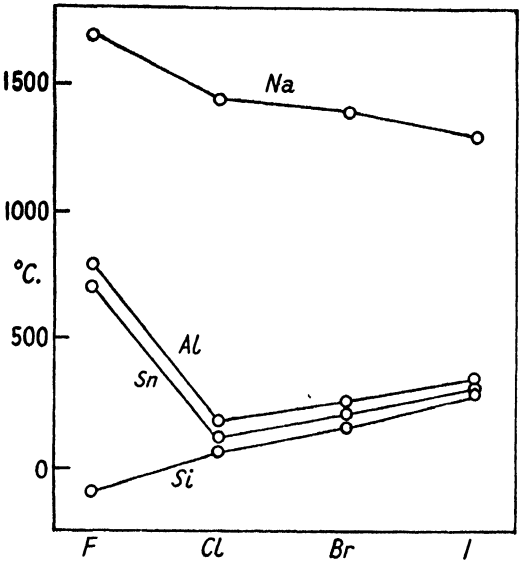


FIG. 6. Boiling-points of halides.

the fluorides having high boiling-points and the others much lower boiling-points which increase from chloride to iodide. In the same way it might be argued that the following series of melting-points indicates a sudden change in bond type between Al and Si:

NaF	MgF_2	AlF_3	SiF_4	PF_5	SF_6
980	1400	1040	−77	−83	−55° C.

Actually these sudden changes in series of melting- or boiling-points correspond to changes in structure type and not to abrupt changes in bond type. The fluorides of Si, P, and S form molecular crystals, while those of Na, Mg, and Al are infinite 3-dimensional assemblages of ions, but the fact that the crystal of SiF_4 contains discrete molecules does not necessarily mean that the Si—F bonds are less ionic in character than the Al—F bonds, for example. The relative sizes of the Al^{3+} and F^- ions are such that the most stable arrangement is one in which every Al is surrounded by six F ions. It follows that every F ion must be linked to two Al ions in order to obtain the ratio Al:3F. This is possible only in an infinite array of Al and F ions. The Si^{4+} ion, however, is only large enough to have four F neighbours, and each F can therefore belong to one Si only, since the formula is SiF_4. Thus the SiF_4 molecules are discrete units in the crystal, bonded to one another only by van der Waals forces. AlF_3 and SiF_4 therefore differ in this important respect, that in the former all

the bonds in the crystal are essentially ionic bonds between Al and F ions, whereas in the latter there are two different kinds of bonds, the Si—F bonds within SiF_4 molecules (which are probably as nearly ionic as the Al—F bonds) and the feeble van der Waals bonds between the F atoms

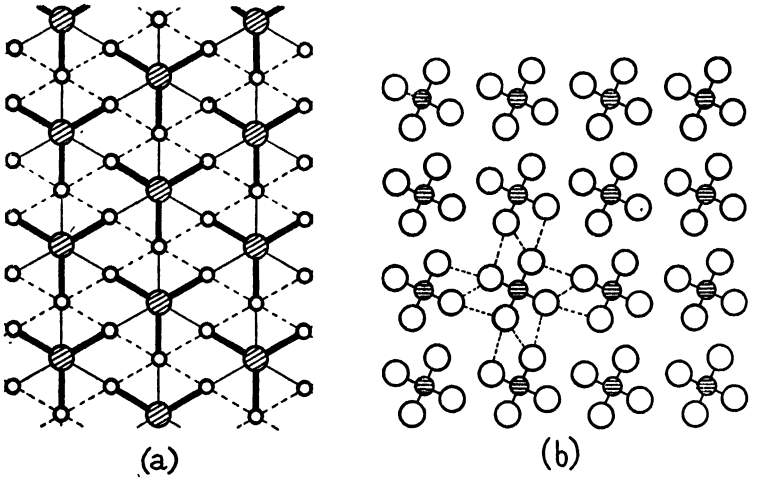


FIG. 7. Possible structure types for halides (*a*) MX_3 and (*b*) MX_4. In (*a*) the M and X atoms are linked into an infinite array and breakdown of the crystal involves the breaking of M—X bonds (light full lines) in addition to the X—X bonds (broken lines). In (*b*) there are discrete molecules MX_4, to separate which it is necessary to break only the weak X—X bonds (broken lines).

of different molecules. The latter are the only bonds which are broken when the crystal is melted or vaporized, whereas when AlF_3 melts Al—F bonds are broken. This point is illustrated by the 2-dimensional analogy shown in Fig. 7. Structural differences of the same general kind exist between many metallic fluorides and the chlorides, bromides, and iodides. The change from the infinite 3-dimensional M—F—M linking in the fluorides to layer, chain, or molecular lattices in the other halides must be associated with increasing covalent character of the metal-halogen bonds. Further discussion of the structures of halides must be postponed until we reach Chapter VIII.

(iii) A study of the electrical conductivities of some sixty chlorides just above their melting-points showed that about half had values lying between 10 and 0·1 ohm^{-1} cm. while most of the remainder had conductivities below about 2×10^{-6} ohm^{-1} cm. Only three had intermediate values, these being $BeCl_2$, $ZnCl_2$, and $HgCl_2$ (certain other halides also show such intermediate behaviour). The following considerations will make it apparent that these facts do not indicate, as was at first thought, that bonds are either pure covalent or pure ionic bonds. If a crystalline halide contains an infinite array of atoms (3-, 2-, or 1-dimensional), this must break down on melting to form either finite molecules, ions, or possibly a mixture of both. Low conductivity implies the presence of

molecules in the melt, but on the one hand these were not necessarily present in the crystal and on the other the bonds in molecular halides are not necessarily covalent bonds. Thus the presence of ions in the melt, leading to high conductivity, does not prove that the bonds in the crystal were 100 per cent. ionic bonds. A crystal containing bonds intermediate between ionic and covalent must yield molecules or ions or both, so that deductions about the nature of the bonds in a crystal cannot be made from the nature of the products which arise when the lattice is destroyed.

(iv) Many compounds AX crystallize with the zinc-blende structure (p. 83) in which each atom is surrounded tetrahedrally by four of the other kind. If the element A belongs to the Nth periodic group, then X comes from the $(8-N)$th group. In addition to the elements of the fourth periodic group (C, Si, Ge, and Sn) the compounds containing pairs of elements on either side of these also crystallize with the zinc-blende structure. We have therefore a series of compounds with the same structure for which the sum of the atomic numbers of A and X is the same, and it was found that in many cases the distance A—X is constant throughout the series:

	Atomic numbers	*Distance A—X*
Ge—Ge	32+32	2·44 A.
Ga—As	31+33	2·44
Zn—Se	30+34	2·45
Cu—Br	29+35	2·46
Sn—Sn	50+50	2·80
In—Sb	49+51	2·79
Cd—Te	48+52	2·80
Ag—I	47+53	2·80

If, on the other hand, we compare the interatomic distances in compounds AX with the rock-salt structure, where the sum of the atomic numbers of A and X is the same, we find a very different result:

	Atomic numbers	*Distance*
Na—F	11+9	2·31 A.
Mg—O	12+8	2·10
K—Cl	19+17	3·14
Ca—S	20+16	2·84
Rb—I	37+53	3·66
Sr—Te	38+52	3·32

There is a difference of some 10 per cent. (of the smaller) between the distances in each pair. This was taken to mean that the bonds in these two types of structure were essentially different in nature, those in the zinc-blende structure being covalent and in the rock-salt structure ionic. Now there is good reason to believe that the bonds between atoms of the same element (C—C, etc.) are genuine covalent bonds, and it will be noticed that in the first table above we have chosen elements immediately before and after Ge and Sn respectively. If, however, for a given atomic

number we choose a light and a heavy element, we immediately find larger A—X distances in many cases. In Fig. 8 we have plotted the distance A—X against the sum of the atomic numbers of A and X and the points for C, Si, Ge, and Sn are joined by the full line (SiC falls on

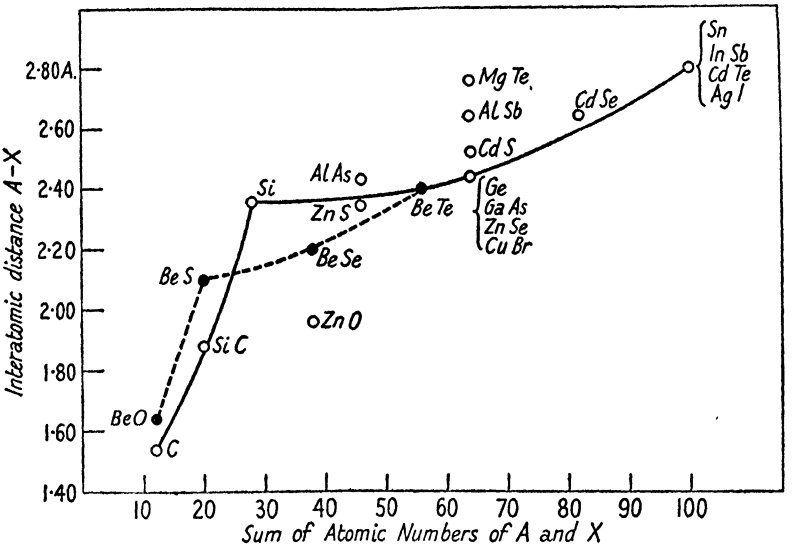


FIG. 8. Interatomic distances in crystals with the zinc-blende structure.

this line). It is seen that the points for BeO, BeS, and BeSe fall well off this line, as do those for a number of other compounds. A more representative list of A—X distances for atomic number sum 64 is given below.

	Atomic numbers	*Distance*
Mg—Te . . .	12+52	2·76 A.
Al—Sb . .	13+51	2·64
S—Cd . . .	16+48	2·52
Cu—Br . . .	29+35	2·46
Zn—Se . . .	30+34	2·45
Ga—As . . .	31+33	2·44
Ge—Ge . . .	32+32	2·44

Clearly then we cannot make deductions about bond type from the supposed constancy of interatomic distances in such structures. In fact the 'abnormal' distances are found in cases where we have reason to believe that the bonds are not pure covalent bonds.

We must now indicate some of the positive evidence for the existence of bonds intermediate between the four main types. Bonds intermediate between covalent, metallic, and van der Waals bonds are not of great interest in chemistry. We have mentioned that low resistivity is a characteristic property of metals. Some metals, however, have much higher resistivities than others and there is reason to believe that in these the bonds are partially covalent in character. This is supported by the

nature of the crystal structures, which will be described later. Compare, for example, the resistivities of the following metals: Cu, 1·56, Ag, 1·49, Au, 2·04, Ge, $8{\cdot}9\times10^{4}$—that of diamond is 10^{20} (all times 10^{-6} ohm/cm.). Germanium has the same type of crystal structure as diamond. Gallium has a high resistivity compared with Al, In, or Tl, but on the other hand the fact that the resistivity of bismuth is higher than that of arsenic would not appear to be directly related to change in bond character since the general properties of bismuth and the geometry of its crystal structure (compared with that of As) indicate that it is more metallic than arsenic. Many metallic sulphides have pronounced 'semi-metallic' character, e.g. PbS, FeS_2, and it is difficult to draw a hard-and-fast line between certain types of covalent compounds and alloys (see Chap. XVII).

In some molecular crystals the distances between atoms of different molecules suggest that the inter-molecular bonds are not pure van der Waals bonds, and further evidence on this point comes from physical properties. In selenium and tellurium the atoms are joined into infinite chains in which each atom forms two bonds. The simplest view of such a structure would be that the bonds within the chains are covalent and those between the chains van der Waals bonds, but the metallic properties of the crystals show that the bonds are not of these pure types. Care must be taken in interpreting physical properties. For example, while the heats of sublimation of simple molecular crystals are usually low, a high heat of sublimation does not necessarily mean that the inter-molecular bonds are stronger than simple van der Waals bonds. Thus the sublimation of rhombic sulphur or selenium involves not only the separation of S_8 molecules or Se_∞ chains respectively but also the breaking up of these structural units into simpler (diatomic) molecules. Accordingly the heats of sublimation of rhombic S and Se are much higher than those of crystals which contain molecules of the same degree of complexity as exist in the vapour, as may be seen from the following values: heats of sublimation in k.cals./mole, $S_{rhombic}$ 20, Se 30, O_2 1·74, CH_4 2·40, and HCl 4·34.

Evidence for the intermediate ionic-covalent nature of many bonds comes from various sources. The most direct is the determination of the electric dipole moment of a bond. The bond between two chlorine atoms is non-polar, i.e. there is no separation of positive and negative charges at the ends of the bond, which may be described as a normal covalent bond. On the other hand, a bond such as H—Cl has a dipole moment which indicates that the bond does not consist of a pair of electrons shared equally between the two atoms but instead results from resonance between ionic and covalent states of the HCl molecule (see the next section). Less direct evidence comes from the detailed structure of crystals, determined by X-ray diffraction, and of free molecules, studied by electron diffraction, leading to accurate information about interatomic distances and interbond angles. We shall examine data of this sort in later chapters. Some physical properties of crystals provide informa-

tion about bond type: for example, molecular refractivities and elastic constants. We can do no more than mention here the very important theoretical work on the calculation of lattice energies leading to estimates of the relative importance of homopolar, van der Waals, and ionic attractions between the ions in crystals such as those of the alkali halides.

We have seen that there are bonds intermediate between ionic and covalent bonds and that in resonance we have a way of accounting for a bond being partly ionic and partly covalent. The questions now arise: Is it possible to relate the nature of the bond between any pair of atoms to other properties of the atoms and to make any sort of quantitative estimate of the amount of ionic character of a particular bond? Pauling has attempted to answer these questions, and his treatment of the subject will be outlined in the following section.

ELECTRONEGATIVITY AND BOND TYPE

The obvious property with which to relate bond type is the electronegativity of the atoms forming the bond. An atom is said to be more or less electronegative than another according to the relative positions of the two atoms in the 'electromotive series', which is derived as follows:

K	−2·56
Na	−2·39
Ba	−2·2
Sr	−2·07
Al	−1·28
Zn	−0·76
Cd	−0·40
Pb	−0·12
H	0·00
O	+0·39
I	+0·54
Br	+1·08
Cl	+1·36
F	+1·9

Electromotive Series.

Measurements are made at room temperature of the E.M.F. developed between a normal hydrogen electrode and an electrode of the metal M surrounded by electrolyte containing M^{n+} ions in a concentration of one gram ion per litre. (For non-metals other methods have to be adopted.) Some of these E.M.F.s in volts are shown in the accompanying table. The alkali metals are described as highly electropositive and the halogens are electronegative, and the bonds between such extreme elements are the most ionic bonds found. In order to give some more quantitative meaning to the term electronegativity Pauling derives numerical values for the electronegativities of elements from considerations of bond energies. The electronegativity is defined as the attraction of a neutral atom in a molecule for electrons, and its relation to ionization energy and electron affinity is mentioned later. (The electrode potential in the electromotive

series expresses the difference in free energy of the element in the electrode and in ionic solution.)

If the bond between two atoms can be formulated as covalent A:B or ionic A^+B^- and provided that both structures contain only paired electrons and have essentially the same configuration of the atomic nuclei, then resonance between A:B and A^+B^- is possible. Accordingly the structure of the molecule can be represented by the wave-function $a\psi_{A:B}+b\psi_{A^+B^-}$. The contributions of the covalent and ionic structures are proportional to a^2 and b^2 respectively, and the relative magnitudes of these quantities will be determined by the properties of the atoms A and B. For example, the greater the difference between the electronegativities of A and B, the greater is b, i.e. the more ionic the bond. As already pointed out, the nature of such a bond is not exactly intermediate between A:B and A^+B^- because the resonance energy will make the bond energy greater than that of either A:B or A^+B^-. For simplicity we have just assumed that the two structures involve no unpaired electrons. We saw in an earlier section that resonance is possible between two structures only if they both contain the same number of unpaired electrons. There are therefore two possibilities:

(1) The possible extreme ionic and covalent structures have the same number of unpaired electrons, leading to resonance and the possibility of a continuous transition from one to the other.

(2) The extreme ionic and covalent structures contain different numbers of unpaired electrons. Resonance is not possible and the transition between the two structures would be discontinuous. This is the case with certain complex ions of transition metals in which, on this view, the bonds in a given ion must be either purely ionic (as in $[FeF_6]^{3-}$) or purely covalent as in $[Fe(CN)_6]^{3-}$.

These two possibilities replace the old Sidgwick–London view of the essential distinctness of ionic and covalent bonds. We have now to consider how numerical values can be assigned to the 'coefficients of electronegativity'.

It is likely that the bond between two atoms of the same element is a more or less purely covalent bond. If we write its wave-function in the form: $a\psi_{A:A}+b\psi_{A^+A^-}+b\psi_{A^-A^+}$ to allow for the hypothetical ionized structures, we should presumably find, if we could calculate it, that the ratio b/a would be very small. We shall call such a bond a *normal covalent bond*. For a bond between two different kinds of atoms A and B the corresponding expression is $a\psi_{A:B}+c\psi_{A^+B^-}+d\psi_{A^-B^+}$ in which allowance must be made for the different contributions of the ionic forms A^+B^- and A^-B^+ on account of their different stabilities. Unless the atoms A and B have very similar electronegativities, the actual bond A—B will be appreciably different in character from the hypothetical normal covalent bond A:B. The actual state of the bond would be known if we knew the values of the ratios c/a and d/a. When we talk of the ionic character of bonds we shall imply resonance with the possible ionic

structures leading to additional ionic resonance energy over and above the energy which would be possessed by the normal covalent bond between the same two atoms. This idea, that a bond with partial ionic character is stabilized by additional ionic resonance energy, could easily be tested if we knew the energies of both the actual bond A—B and of the hypothetical normal covalent bond A:B. The energy of the actual bond A—B can, of course, be determined experimentally, but that of the (non-existent) normal covalent bond can only be estimated indirectly.

Determination of Single-bond Energies

In the case of diatomic molecules AB the energy of the bond A—B is directly obtainable from the energy of dissociation of the molecule into atoms. This may be found either by spectroscopic or by thermochemical methods. For polyatomic molecules, however, we can determine only the total energy of dissociation into atoms and hence find only the average amount of energy required to break one bond in the molecule. If we take this average energy (e.g. 1/8 of the heat of formation of the S_8 molecule from atoms) to be the energy of a single bond, we are assuming that the energy required to form (or break) successive bonds is the same. This is probably not true, but the assumption must be made for the present. The process of decomposing e.g. NH_3 into nitrogen and hydrogen involves first the breaking of a N—H bond in NH_3, then of a N—H bond in NH_2, and so on, assuming that the reaction proceeds in this simple way. The energy required to remove H from NH_3 is not necessarily the same as that for removing H from NH_2. In complex molecules containing bonds of more than one kind the further assumption has to be made that bond energies are additive. Moreover, these single-bond energies can be derived only from molecules containing simple electron-pair bonds (not coordinate links) in which there is no resonance between structures with different electronic configurations. In fact resonance energies may be determined as the differences between the actual heats of formation of molecules and the sums of the appropriate single-bond energies.

The Energies of Normal Covalent Bonds between atoms of different kinds cannot, of course, be determined experimentally since the bonds are non-existent and in general they cannot be calculated. The simplest assumption to make is that the energy of the normal bond (E_{A-B}) is the arithmetic mean of the bond energies E_{A-A} and E_{B-B}. Then the additional ionic resonance energy E_r is given by

$$E_r = E_{A-B} - \tfrac{1}{2}(E_{A-A} + E_{B-B})$$

and clearly E_r must be either zero or positive. In fact E_r was found to be negative in some cases (Li—H, Na—H, K—H), showing that the above assumption is certainly not generally true. As an alternative Pauling tried the geometric mean of the bond energies:

$$E'_r = E_{A-B} - \sqrt{(E_{A-A} E_{B-B})},$$

and this is more satisfactory in some cases. In practice, however, the quantity E_r was used for drawing up the electronegativity scale, since on the one hand there is no theoretical justification for using either the arithmetic or the geometric mean of E_{A-A} and E_{B-B}, and on the other hand E_r can often be obtained directly as the heat of the reaction $\frac{1}{2}A_2+\frac{1}{2}B_2 \rightarrow AB$, whereas the calculation of E'_r requires a knowledge of the individual bond energies E_{A-A} and E_{B-B}. The values of E_r (and of E'_r) for the hydrogen halides are

	H—F	H—Cl	H—Br	H—I	
E_r . .	64·0	22·1	12·5	1·6	k.cals./mole.
E'_r . .	66·5	25·4	18·3	10·2	

Electronegativity Values

It will be seen that these values of the ionic resonance energy increase with the difference in electronegativity of the two atoms H and X. If we

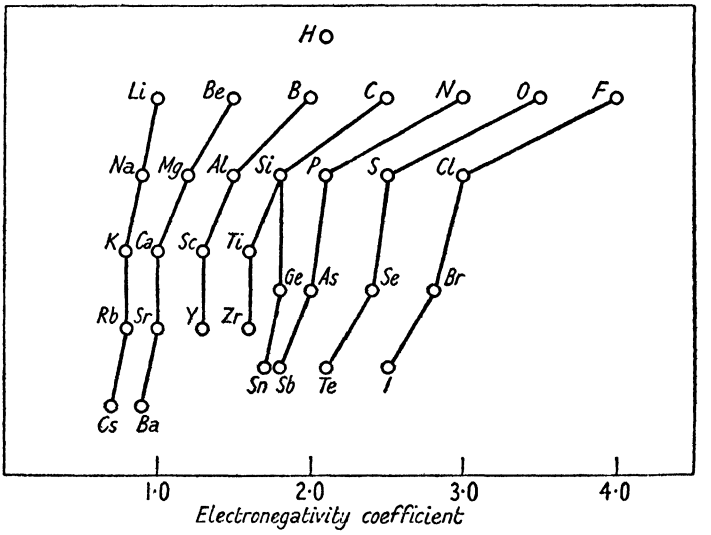


FIG. 9. Relative electronegativities of some elements (after Pauling).

calculate E_r for various bonds we obtain a set of values which are some function of the difference in electronegativity between the atoms of the bonds. It should therefore be possible to assign to each atom a number representing its electronegativity, on some arbitrary scale, so that the differences between any pairs of these numbers are related to the values of E_r for the bonds between the atoms concerned. The electronegativity values given in Table 4 and shown in relation to the Periodic Table in Fig. 9 are such that the difference x_A-x_B between the values for any pair of elements is equal to the square root of E_r, the ionic resonance energy of the bond A—B expressed in electron-volts. From the values of

$\sqrt{E_r}$ only differences $x_A - x_B$ are obtained and it is necessary to assign an arbitrary value of x to one element. The choice of the absolute value of x was determined by the relation of electronegativity to ionization energy and electron affinity. If we regard the first ionization energy, that is, the energy of the process $X \rightarrow X^+ + e^-$, as the average of the electron attraction of the atom and the corresponding positive ion, and the electron affinity, the energy involved in the reaction $X + e^- \rightarrow X^-$, as the mean of the electron attraction of the atom and the negative ion, then the arithmetic mean of these two quantities should be a measure of the electronegativity.

TABLE 4

Electronegativities of the Elements

			H					
			2·1					
Li	Be	B	C		N	O	F	
1·0	1·5	2·0	2·5		3·0	3·5	4·0	
Na	Mg	Al	Si		P	S	Cl	
0·9	1·2	1·5	1·8		2·1	2·5	3·0	
K	Ca	Sc	Ti	Ge	As	Se	Br	
0·8	1·0	1·3	1·6	1·8	2·0	2·4	2·8	
Rb	Sr	Y	Zr	Sn	Sb	Te	I	
0·8	1·0	1·3	1·6	1·7	1·8	2·1	2·5	
Cs	Ba							
0·7	0·9							

For the simple univalent ions the values of x agree well with the mean of the ionization energy and the electron affinity, though H, as in much of its behaviour, is rather abnormal (Table 5). For multivalent ions the interpretation of the numerical values of these quantities is more complex.

TABLE 5

	Ionization energy	*Electron affinity*	*Sum/130*	x
F . . .	429·0	98·5	4·06	4·0
Cl . . .	298·9	92·5	3·01	3·0
Br . . .	272·1	87·1	2·76	2·8
I . . .	240·8	79·2	2·46	2·5
H . . .	312·0	16·4	2·52	2·1
Li . . .	123·8	assumed zero	0·95	1·0
Na . . .	117·9		0·91	0·9
K . . .	99·7		0·77	0·8
Rb . . .	95·9		0·74	0·8
Cs . . .	89·4		0·69	0·7

There is also in some, but by no means all, cases a general correlation between electronegativity values and the dipole moments of bonds.

From Fig. 9 it is seen that the dividing line between metals and non-metals corresponds to an electronegativity value about 2, though there is no sharp division—Te for example having $x = 2{\cdot}1$ and the less metallic carbon having $x = 2{\cdot}5$.

Pauling has gone further in suggesting approximate numerical values of percentage ionic character of bonds. This can obviously be done if we

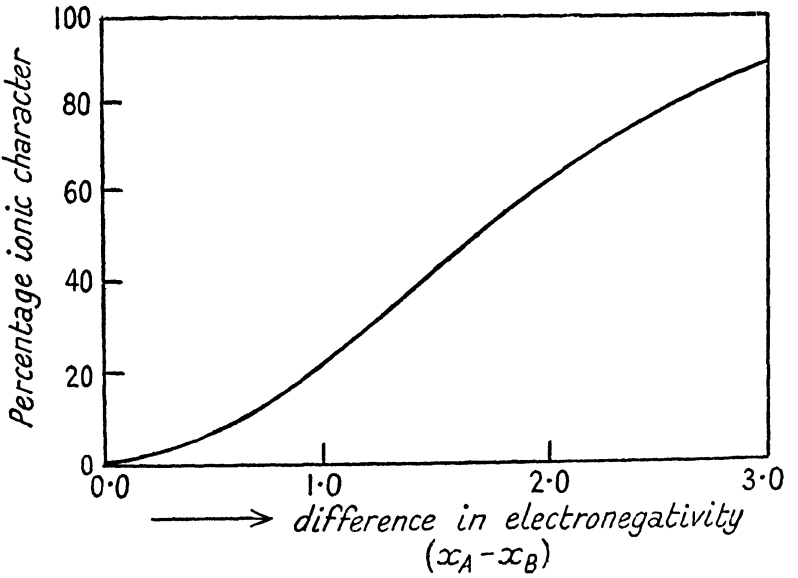


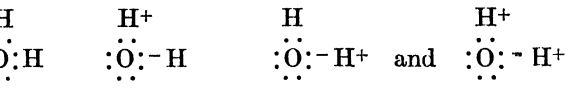
FIG. 10. Relation between percentage ionic character of a bond and the difference between the electronegativities of the atoms (after Pauling).

adopt values for a number of bonds, since we may then plot these percentages against the values of $x_A - x_B$ for these bonds. The values 5 per cent., 11 per cent., 17 per cent., and 60 per cent. were adopted for the bonds H—I, H—Br, H—Cl, and H—F respectively, and the curve in Fig. 10 relates the percentage ionic character to the electronegativity differences of the pairs of atoms. The values for the H—X bonds are derived directly from the electric dipole moments of the hydrogen halide molecules. The interatomic distances used were those determined from the absorption spectra of the gases. For HCl this distance is 1·273 A., so that the completely ionized molecule would have a moment

$$1{\cdot}273 \times 4{\cdot}774 \times 10^{-18} = 6{\cdot}08 \times 10^{-18} \text{ e.s.u.}$$

The observed moment is $1{\cdot}03 \times 10^{-18}$ e.s.u., which is 17 per cent. of the former value. The values for HI and HBr were obtained in a similar manner, while that for HF is an estimated value. In connexion with these values for percentage ionic character of bonds two points should be noted. First, the fact that a bond has some ionic character means that there is resonance between covalent and ionic forms, and the number of these forms which

must be taken into account may be quite large. For example, for H_2O we have the possibilities:



Secondly, for molecules in which there are 'formal charges' on any of the atoms (i.e. molecules containing coordinate links) the electronegativity values must be adjusted, but we cannot enter here into such refinements.

Some of the conclusions to be drawn from Fig. 10 may be briefly summarized. The bonds between alkali metals and all non-metals are more than 50 per cent. ionic. Magnesium and the alkaline earths form essentially ionic bonds with the more electronegative elements. The bonds from Al, Be, B, and Si are of some interest in connexion with the structures of their compounds, and Pauling gives the following figures:

Al or Be—F	79% ionic	B—H	100% covalent		
O	63	F	63	ionic	
Cl	44	O	44		
Br	35	Cl	22		
I	22				

Si—F	70% ionic
Cl	30
O	50.

The value (50 per cent.) for the percentage ionic character of Si—O bonds is of particular interest, as we shall see when we come to discuss the structures of silica and of silicates (Chap. XIV). The most ionic carbon bond is C—F, with 44 per cent. ionic character. The bonds from fluorine and oxygen to all metals are essentially ionic. The application of these ideas to multiple bonds is much more difficult and, so far, less successful.

We have devoted a considerable amount of space to this admittedly empirical method of assessing the amount of ionic character of bonds because, although we shall not have much occasion to refer to the particular numerical values of percentage ionic character of bonds, it is essential to have some idea of what we mean when we talk of bonds intermediate between ionic and covalent bonds.

Before proceeding further it will be as well to summarize our conclusions regarding interatomic bonds. We recognize four extreme types, ionic, covalent, van der Waals, and metallic bonds, and the chemist is primarily interested in the first two. The early electronic theory of valency accounted for the existence of ionic and covalent bonds, but it was unsatisfactory for a number of reasons. It did not take account of the differences between individual atoms with the same outer electronic structure. It offered no explanation of the angles between a number of bonds formed by an atom, and there was no way of deciding whether to formulate a given molecule or complex ion with ionic or covalent bonds. Moreover, this simple theory was not capable of extension to solid salts, in which it was

soon apparent that bonds are not all simple ionic or covalent bonds. To account for the existence of bonds intermediate between ionic and covalent the concept of resonance has been introduced, and to determine the amount of ionic character in such mixed bonds we have utilized the electronegativities of the elements. Crystals in which all the bonds are essentially ionic or covalent are comparatively few in number. The ionic salts include most metallic oxides and fluorides and all the halides of the alkali metals except LiI, but the metallic sulphides, chlorides, bromides, and iodides, in which the bonds have less ionic character, adopt other kinds of structures. In molecular crystals adjacent molecules are held together by van der Waals forces, but the nature of the bonds within the molecule depends on the electronegativities of the atoms concerned. The bonds in most molecules composed of non-metals other than O or F are essentially covalent, but in non-metallic oxides and fluorides the bonds may have appreciable ionic character. According to Pauling's treatment of intermediate bonds the percentage ionic character of the bond between any particular pair of atoms can be determined by means of Table 4 and Fig. 10.

So much for the nature of interatomic bonds. We now have to consider the arrangement in space, relative to one another, of atoms linked by covalent and by ionic bonds. This involves a study of the distances between atoms and the angles between the various bonds. In the case of covalent bonds experimental data come from the study of molecules (in the vapour or solid state) and of a few covalent crystals, but data on ionic bonds are necessarily obtained from the crystalline state.

CHAPTER III

THE SPATIAL ARRANGEMENT OF ATOMS

We may conveniently define the positions of atoms in space relative to a given atom by stating the interatomic distances and the angles between the various bonds formed by the atom. For various reasons we shall deal separately with covalent and ionic bonds. One is that the stereochemistry of ions must be studied in the solid state, there being few finite molecules or complex ions containing essentially ionic bonds. Also, although the number of electrons acquired or lost by an atom in forming an ion depends on the electronic structure of the atom, once the ion is formed geometrical factors and the condition of electrical neutrality alone determine the way in which the ions pack together with other ions in a crystal. We find a large variation in the number of neighbours of, say, an O^{2-} ion in different crystals, e.g. 3 Ti^{4+} ions in TiO_2, 4 Th^{4+} in ThO_2, 6 Mg^{2+} in MgO, and 8 K^+ in K_2O, and we shall see later that the effective radius of an ion varies with its coordination number. In the case of covalent bonds, however, the maximum number an element can form is strictly limited because the electrons serving as bonds also function as part of the orbital electronic system of the atom and there is a definite limit to the number of electrons which can occupy the outer shell of an atom. Although the maximum number of covalent bonds is limited, less than this number may be formed. We shall therefore have to inquire first whether we can draw up a set of covalent radii the sums of which give the lengths of the covalent bonds between the respective pairs of atoms, and secondly if this covalent radius depends on the number of bonds formed. Before we can do this it will be necessary to see precisely which electrons are involved in the formation of various numbers of bonds. When discussing the lengths of covalent bonds and the angles between them we shall not deal separately with molecules and crystals. Classical stereochemistry was limited to the study of groups of atoms in solution or in the liquid or vapour phases, i.e. of finite, and usually small, groups of atoms forming relatively stable complex ions or molecules. The study of the solid state has now extended the scope of structural chemistry to embrace the infinite groups of atoms which constitute crystals. The crystal structure of diamond is a better demonstration of the spatial arrangement of the four bonds from a carbon atom than was the resolution of various optically active compounds. We shall return to this point in Chapter VI, where we outline some of the experimental methods of structural chemistry.

COVALENT BOND ANGLES AND BOND LENGTHS

In Chapter I we indicated some of the evidence for the distribution of the orbital electrons of atoms in various shells, *K*, *L*, *M*, etc., distinguished

by different values of the principal quantum number. We also saw that the electrons in a given shell (except the K shell, which contains only two electrons) can be divided into sub-groups designated s, p, d, and so on. The L shell, for example, can contain 2 s and 6 p electrons, making a total of 8 as in neon, with the structure $1s^2 2s^2 2p^6$. In this atom the electrons are associated in pairs, with opposed spins, so that in the L shell there are four pairs of electrons rather than eight independent electrons. Now the probability of finding a given electron in a particular part of the negative cloud around the nucleus is given by the square of the orbital, or wave-function, associated with the orbital motion of the electron. Owing to the association of the electrons in pairs there are four orbitals defining the behaviour of the electrons in the L shell.

In general, orbitals may differ from one another in two ways: first in the way in which they vary with the distance from the nucleus, which variation is equivalent to saying that the orbits of the corresponding electrons are of different sizes, and secondly, these functions have different angular distributions. The $1s$ and $2s$ orbitals differ in the first way, whereas the three $2p$ orbitals differ from one another only in their angular distribution. Whereas an s orbital is spherically symmetrical, the three $2p$ orbitals are mutually perpendicular and are accordingly distinguished as $2p_x$, $2p_y$, and $2p_z$ orbitals. In an atom or simple ion the electrons tend first to occupy the more stable orbitals in pairs, but when several orbitals of the same energy are available the electrons go one into each orbital with their spins parallel. Thus the nitrogen atom has the electronic structure $1s^2 2s^2 2p_x 2p_y 2p_z$, with three unpaired electrons. In oxygen the additional electron goes into one of the p orbitals, leaving two unpaired electrons, and similarly in fluorine there is one unpaired electron and in neon no unpaired electron. For the formation of a simple electron-pair bond, to which each atom contributes one electron, we require in each of the atoms a stable orbital which can accommodate a second electron. We see therefore why nitrogen forms NH_3, oxygen OH_2, and so on.

We pointed out in the previous chapter that the early electronic theory of valency gave no information about angles between bonds. Wave-mechanics enables us to calculate the angular distribution of the various orbitals, and since bonds will tend to be formed in the directions in which the orbitals are concentrated, theoretical predictions of interbond angles become possible. Moreover, wave-mechanical calculations give the relative strengths of the bonds formed when particular orbitals or combinations of orbitals are used. We must note, however, an important limitation to these advances. The angles between bonds can in many cases be predicted, assuming certain orbitals to be used, but there may be a number of possible ways of forming, say, three bonds from a given atom (using different combinations of orbitals) and the calculated stabilities of the various configurations may not differ greatly. Then the bond angles for these configurations may be predicted, but theory does not necessarily tell us which combination of orbitals is actually being used in the particular

case under consideration. We shall meet an example of this difficulty shortly.

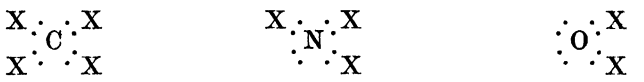
Let us consider first the simplest case of covalent bond formation—the formation of 8—N bonds by the elements of the later Periodic Groups, C to F, Si to Cl, etc. Nitrogen, oxygen, and fluorine have respectively 3, 2, and 1 unshared $2p$ electrons and could form these numbers of p bonds. The angles between such bonds should be 90°. What happens in the case of carbon, which forms four bonds ? If the s and p orbitals retain their individuality we might expect to find this element forming three p bonds and a weaker s bond in some arbitrary direction. Theoretical calculations show, however, that a new type of bond—stronger than either s or p bonds—can be formed by a combination of the s and p orbitals, and that these four sp^3 bonds are directed towards the corners of a regular tetrahedron. Such bonds formed by the combination of two or more orbitals are described as hybrid bonds, and the process of combination is

Bond angle	*Compound*	*Value*
	H_2O	105°
	OF_2	100°
	OCl_2	115°
	$O(CH_3)_2$	111°
	H_2S	92° 20′
	S_8 (crystal)	106°
	S_8	100°
	BaS_3 (crystal)	103°
	$K_2S_3O_6$ (crystal)	103°
	SCl_2	103°
Se	Se (crystal)	105°
Te	Te (crystal)	102°
N	NH_3	108°
	$N(CH_3)_3$	108°
P	in all the following: crystalline black P, $P(CH_3)_3$ and PF_3, $PFCl_2$, PCl_3, PBr_3, PI_3, but not P_4 molecule	101±3°
		60°
As	in the following: crystalline As, $As(CH_3)_3$ and $AsCl_3$, $AsBr_3$, AsI_3, but	100±4°
	As_4 molecule	60°
Sb	in the following: crystalline Sb, $SbCl_3$, $SbBr_3$, SbI_3	100±4°
Bi	in metallic Bi	94°

termed hybridization. The tetrahedral arrangement of four bonds from a carbon atom had been deduced from the stereochemistry of its compounds. However, the optical activity of a compound C *abcd*, for example,

does not imply that the interbond angles are very close to the tetrahedral angle of 109° 28′, whereas wave-mechanical calculations show that any appreciable departure from this angle will weaken the bonds considerably. In symmetrical molecules such as CH_4 and CCl_4 it has been shown that the bond angles are very close to the value 109° 28′, but in CH_2F_2 and CH_2Cl_2 the angles between the carbon-halogen bonds lie between 110° and 113°. The elements of the later Periodic Groups can also form these tetrahedral sp^3 bonds, and the possibility arises that when they are forming less than four bonds these might also be sp^3 bonds rather than simple p bonds as suggested above. In the one case we should expect angles of 109° 28′ and in the other 90°. In fact the experimentally determined angles lie in many cases between these two values, as may be seen from the selection given on p. 78, though for some compounds of nitrogen and oxygen the angles are close to, or slightly greater than, the tetrahedral angle. The compounds were studied in the vapour state by electron diffraction or spectroscopically unless otherwise stated.

Various suggestions have been made to account for these intermediate values of bond angles. If on the one hand we assume the 8—N bonds to be p bonds, then the values greater than 90° might be due to partial ionic character of the bonds, the charge on the H atoms in H_2O, for example, causing some repulsion. Alternatively if large atoms or groups are attached to the central atom, the size of these atoms might account for the increased bond angle. On the other hand, if we assume the 8—N bonds in, say, OH_2 or OF_2 to be sp^3 bonds, it would mean that the orbitals of both shared and unshared pairs of electrons have been hybridized. In the formation of sp^3 bonds by C all the four orbitals are occupied by pairs of shared electrons, but this is not the case in NX_3 or OX_2 molecules:



Owing to the fact that the s orbital is more stable than the p orbitals, an unshared pair of electrons may prefer this orbital. For oxygen, however, there are two unshared pairs and only one s orbital, hence the suggestion that the unshared pairs have orbitals intermediate between s and sp^3, and the shared electrons orbitals intermediate between sp^3 and p. This ingenious *ad hoc* explanation is hardly consistent with the bond angles of 108° in NH_3 and $N(CH_3)_3$.

Normal and Tetrahedral Covalent Radii

The assignment of covalent radii to atoms is possible because (1) the length of a simple covalent bond between a given pair of atoms is constant in a series of molecules or covalent crystals, and (2) the length of a covalent bond A—B is the arithmetic mean of the lengths of the bonds A—A and B—B. The C—C distance, for example, is found to be $1{\cdot}54 \pm 0{\cdot}02$ A. in diamond and in normal and cyclic paraffins, which contain

series of CH_2 groups linked together. This constancy of bond length in fact enables us to say with certainty that C—C bonds of length appreciably different from 1·54 A. are not simple electron-pair bonds. For example, in $H_3C—C{\equiv}C—CH_3$ the length of the $C—CH_3$ bonds is 1·46 A. The Si—Si distance in the element is 2·34 A. The arithmetic mean of 1·54 and 2·34 A. is 1·94 A., and the C—Si distance in carborundum is 1·93 A. It should therefore be possible to assign to the elements covalent radii, the sums of which give the lengths of the covalent bonds between pairs of atoms. There are two points to note here. First we may expect to have to use different radii according to whether the elements are forming $8-N$, tetrahedral, or other kinds of bonds (see below). Secondly we must be sure that the bonds from which we deduce our covalent radii are actually single covalent bonds, i.e. electron-pair bonds with very little ionic character.

Pauling has drawn up sets of normal (for $8-N$ bonds) and tetrahedral radii for a number of elements, and we shall examine briefly the origins of these radii with particular reference to the second point mentioned above. Clearly the best values of the radii would be obtained from the interatomic distances in the elements themselves, for then no question of appreciable ionic character due to electronegativity differences arises. This is possible only for a limited number of elements. For the fourth group elements, C, Si, Ge, and Sn (grey form), for which the normal and tetrahedral radii are of course equal, the radii are directly obtainable from the interatomic distances in the crystalline elements, in which each atom is surrounded tetrahedrally by four others. Elementary nitrogen and oxygen, however, consist of diatomic molecules containing multiple bonds, $:N:::N:$ and $:\ddot{O}::\ddot{O}:$ and their radii must therefore be derived from bond lengths in other molecules. The $8-N$ radii of the halogens may be derived from the molecules of the elements. Many of the elements in which we are interested form methyl derivatives $M(CH_3)_n$ where $n = 8-N$ and the M—C distances in these molecules have been used both in deriving and as a check on the $8-N$ covalent radii of the elements.

If we compare the electronegativity values of the elements concerned with that of carbon, we find that the bonds in many of these methyl derivatives must be appreciably ionic (see Table 6 below). The use of certain of these distances, particularly C—O and C—F, in fixing covalent radii is therefore unsound. The fact that the original covalent radii of Pauling and Huggins gave, by simple addition of the appropriate pairs, the observed N—C, O—C, and F—C distances in $N(CH_3)_3$, $O(CH_3)_2$, and $F.CH_3$ respectively indicates that those radii were not really covalent radii. This was also evident from the discrepancy between the observed O—F distances in OF_2 and $FO.NO_2$ (1·41 and 1·42$\pm$0·05 A. respectively) and the sum (1·30 A.) of the Pauling–Huggins radii. Owing to the smaller difference between the electronegativities of O and F than between those of C and F, the O—F bond length should agree better with the sum of the

covalent radii than should the C—F bond length. The normal covalent radii for N, O, and F have since been amended using values derived from the molecules $H_2N—NH_2$, HO—OH, and F—F, and these later values are included in Table 6. The value given for H is one-half the spectroscopic value (0·74 A.) found in the H_2 molecule. Whereas the original radii of Pauling and Huggins gave by simple addition the interatomic distances in 'covalent' molecules and crystals, the amended values do so only if the bond under consideration is very nearly 100 per cent. covalent.

TABLE 6

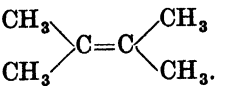
Electronegativities					*Normal covalent radii*			
C	N	O	F	H	C	N	O	F
2·5	3·0	3·5	4·0	0·37	0·77	0·74	0·74	0·72 A.
Si	P	S	Cl		Si	P	S	Cl
1·8	2·1	2·5	3·0		1·17	1·10	1·04	0·99 A.
Ge	As	Se	Br		Ge	As	Se	Br
1·7	2·0	2·4	2·8		1·22	1·21	1·17	1·14 A.
Sn	Sb	Te	I		Sn	Sb	Te	I
1·7	1·8	2·1	2·4		1·40	1·41	1·37	1·33 A.

In general a correction, so far purely empirical, must be made to allow for the partial ionic character of the bond, and the expression for the length r_{AB} of a bond between two atoms with normal covalent radii r_A and r_B and electronegativities x_A and x_B is

$$r_{AB} = r_A + r_B - \beta(x_A \sim x_B),$$

where β is a constant with the value 0·09.

Except for a brief account of 1-electron and 3-electron bonds in the section on resonance we have confined our attention so far to single covalent, or electron-pair, bonds. In some molecules there are bonds consisting of 4 or 6 electrons, double and triple bonds. Evidence for the existence of such bonds comes from interatomic distances, bond angles, and the general chemical properties of the molecules. For the elements of the first Periodic Row, C, N, O, and F, the 'double-bond radii' are about 13 per cent. and the triple-bond radii about 22 per cent. less than the normal single-bond covalent radii, as seen from the distances C=C in ethylene (1·34 A.) and C≡C in acetylene (1·20 A.), compared with 1·54 A. for C—C in diamond. For heavier atoms the percentage decreases for double and triple bonds are probably rather smaller. The use of four of the eight shared electrons of a carbon atom for a double bond permits the formation of only two other (single) bonds, and the angles between the double and single bonds should have the value 125° 16′ (i.e. ½(360°—109° 28′)). Values close to this have been found in a number of molecules such as

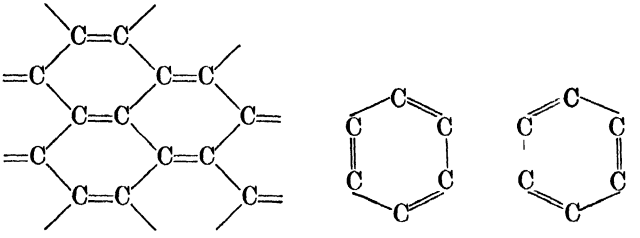


The characteristic 'unsaturated' properties of multiple bonds are of great importance in organic chemistry.

In addition to the values

1·54 A.	for	C—C
1·34		C=C
1·20		C≡C

intermediate bond lengths are found in certain cases. In graphite, for example, the C—C distance is 1·42 A. and in the benzene molecule, 1·39 A. The graphite crystal is built up of planes of carbon atoms forming a hexagonal network (see p. 436). Assuming only van der Waals forces between atoms of adjacent layers, it is reasonable to suppose that the four bonds from each atom are utilized in the plane and that there is resonance between structures of the type shown at (*a*) and the others with similar arrangements of the double bonds in the other possible positions. Such resonance would give each bond one-third double-bond character. In the benzene molecule resonance between the forms (*b*)



(*a*) (*b*) (*c*)

and (*c*) would similarly give each bond one-half double-bond character. In fact if we plot the C—C distance against percentage double-bond character a smooth curve can be drawn through the points for 1·54 A., 0 per cent., 1·42 A., 33 per cent., 1·39 A., 50 per cent., and 1·34 A., 100 per cent. This curve may usefully be employed in discussions of resonance in organic molecules.

The *tetrahedral* covalent radii of Pauling and Huggins were derived from interatomic distances in crystals in which the atoms form four tetrahedral bonds.* Two important crystal structures of this type are those named after the polymorphic forms of zinc sulphide—the zinc-blende (or sphalerite) and wurtzite structures, illustrated in Fig. 11. The meaning to be attached to such radii is doubtful. For the elements of the fourth Periodic Group they have the same values as the normal $(8-N)$ covalent radii already given in Table 6, and in these cases may certainly be taken as one-half of the lengths of the true covalent bonds C—C, Si—Si, etc. We have already commented on the interatomic distances in crystals with the zinc-blende structure in the previous chapter, where we concluded

* The value for F was obtained from spectroscopic data and is now known to correspond to an excited state of the fluorine molecule. The radii for N and O were interpolated between those of C and F.

that in many cases the bonds must have appreciable ionic character. This is also evident from the fact that if ZnO, for example, is represented as a purely covalent crystal, then there are formal charges of +2 and −2 respectively on the O and Zn atoms, since each atom would be forming

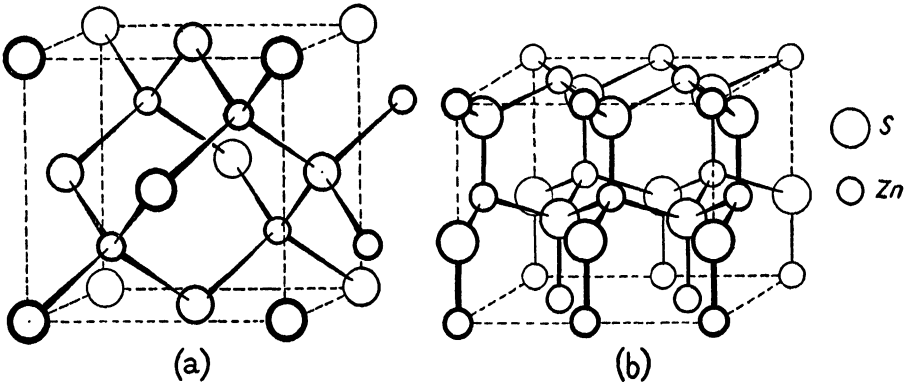


FIG. 11. The crystal structures of (*a*) zinc-blende and (*b*) wurtzite.

four electron-pair bonds. If the eight electrons around each atom are shared equally with its four neighbours, then Zn has effectively 4 valency electrons as compared with 2 in the normal atom, and O has 4 as compared with 6 in the neutral atom. Nevertheless, although these tetrahedral radii cannot (except for the elements of Group IV) be covalent radii, they do give by addition the actual bond lengths in crystals in which the elements form four tetrahedral bonds. They are tabulated in Table 7.

TABLE 7

Tetrahedral Radii

	Be	B	C	N	O	F
	1·06	0·88	0·77	0·70	0·66	0·64
	Mg	Al	Si	P	S	Cl
	1·40	1·26	1·17	1·10	1·04	0·99
Cu	Zn	Ga	Ge	As	Se	Br
1·35	1·31	1·26	1·22	1·18	1·14	1·11
Ag	Cd	In	Sn	Sb	Te	I
1·53	1·48	1·44	1·40	1·36	1·32	1·28
Au	Hg	Tl	Pb	Bi		
1·50	1·48	1·47	1·46	1·46		

Linear and Triangular Bonds

When 8−*N* bonds are formed by C the octet of electrons around the atom consists of four pairs of shared electrons. For N forming three bonds there is one unshared pair. When B forms three covalent bonds, however, the group of valency electrons consists of three shared pairs. The nature of these bonds is not known, but they presumably utilize

s and p orbitals, for they are distributed symmetrically in a plane. The boron compounds of this type readily take up neutral molecules such as NH_3 and CH_3CN as in $(CH_3)_3B.NH_3$ and $BCl_3.NC.CH_3$, the boron atoms thereby forming a fourth bond. In these latter molecules the bonds are presumably the usual tetrahedral sp^3 bonds. The boron radius derived from the B—C distance in $B(CH_3)_3$ is 0·79 A.

In certain compounds of the metals of the first and second B sub-groups of the Periodic Table the metal atom forms two bonds, and here again all the electrons of the valency group (now 4 in number) are shared. A linear arrangement of such bonds is found in the complex ions $[NC—Ag—CN]^-$, $[Cl—Au—Cl]^-$, in the molecules of $HgCl_2$, $HgBr_2$, and HgI_2, and in crystalline Cu_2O and Ag_2O. These bonds are also presumably sp bonds. With regard to the '2-covalent radii' of Cu^I and Ag^I in the latter crystals, 1·18 and 1·39 A. respectively, there is the same difficulty as in ZnO. If the bonds are assumed to be covalent bonds, there would be a formal charge of −1 on each Cu atom and of +2 on each O atom, so that it is unlikely that these bonds are pure covalent bonds.

So far we have been discussing bonds involving only s and p orbitals. For the atoms of the first Periodic Row only s and p orbitals are available, but in heavier atoms d orbitals are used, in combination with s and p, for the formation of more than four bonds and also in a limited number of cases for forming four planar bonds. There is some evidence that even the atoms of the second Periodic Row may utilize d orbitals when exhibiting covalencies of five and six, as in the pentahalides of phosphorus, in the $[PF_6]^-$ ion, and in SF_6.

Octahedral Bonds and Radii

Calculations show that six strong bonds directed towards the corners of an octahedron can be formed using two d with one s and three p orbitals. This combination of orbitals is normally available, so that octahedral bonds are formed by very many elements, but we may distinguish between d^2sp^3 bonds using two d orbitals of the penultimate shell and sp^3d^2 bonds which are formed by hybridization of s, p, and d orbitals of the same (valency) shell. In the transition metals the d orbitals of the penultimate shell have about the same energy as the s and p orbitals of the outer shell, with the result that 6-covalent complexes of these elements are numerous and in some cases possess extraordinary stability. For example, in the hexamminocobaltic ion, $[Co(NH_3)_6]^{3+}$, the thirty-six electrons of the Co atom are made up as follows:

		$3s$	$3p$	$3d$	$4s$	$4p$
(2)	(8)	2	6	6+ 4	2	6

those within the rectangle being the twelve shared electrons forming the six d^2sp^3 bonds. In the ferrocyanide ion, $[Fe(CN)_6]^{4-}$, the shared electrons are also $3d^24s4p^3$, while in $PdCl_6^{2-}$ and $PtCl_6^{2-}$ they are $4d^25s5p^3$ and $5d^26s6p^3$ respectively. We shall have more to say about the transition

metal complexes in Chapters VI and XVI. If a transition metal forms six octahedral bonds in one of its compounds, it must not be assumed that these are necessarily covalent d^2sp^3 bonds. For example, FeI_2 crystallizes with the CdI_2 structure (see p. 101), in which each metal atom is surrounded by six I atoms, but the observed Fe—I distance and the paramagnetism ($\mu = 5{\cdot}4$ Bohr magnetons) of the compound (see p. 214) show that the bonds are essentially ionic. This is also the case in the halides of Mn, Co, and Ni.

Many disulphides, diselenides, and ditellurides crystallize with the pyrites or marcasite structures, illustrated on p. 390. In the pyrites structure each Fe atom is attached to six S atoms which form an approximately regular octahedron around it. The sulphur atoms are linked in pairs, and the nearest neighbours of a S atom are the S atom of its own S_2 group and three Fe atoms. Accordingly octahedral radii for Fe and similar atoms can be derived by deducting from the metal–S distance the tetrahedral radius of sulphur. The other octahedral radii for Group VIII elements have been obtained from related structures, NiAsS, CoAsS, and that for Au from $AuSb_2$. For these d^2sp^3 bonds in the covalent complexes of the transition metals the two d orbitals used are those of the penultimate shell, but in some cases two d orbitals of the outer shell have to be used. This is so when (*a*) there are no d orbitals in the penultimate shell, as in SF_6 or (*b*) the d orbitals in the penultimate shell are fully occupied by unshared electron pairs as, for example, in the $[SnCl_6]^{2-}$ ion. Octahedral radii for a few elements forming bonds of this sort are included in Table 8, the values for Ti and Zr being derived from the disulphides, which crystallize with the CdI_2 structure. The values for Se^{IV}

TABLE 8

Octahedral Radii (*Pauling and Huggins*)

	Fe^{II}	1·23	Ru^{II}	1·33	Os^{II}	1·33	Co^{II}	1·32 A.
d^2sp^3	Co^{III}	1·22	Rh^{III}	1·32†	Ir^{III}	1·32	Ni^{III}	1·30 A.
							Ni^{II}	1·39 A.
	Ni^{IV}	1·21*	Pd^{IV}	1·31	Pt^{IV}	1·31	Fe^{IV}	1·20 A.
							Au^{IV}	1·40 A.
sp^3d^2	Ti^{IV}	1·36	Sn^{IV}	1·45	Se^{IV}	1·40 A. (p^3d^2s ?)		
	Zr^{IV}	1·48	Pb^{IV}	1·50	Te^{IV}	1·52 A.		

* Extrapolated. † Interpolated.

and Te^{IV} call for some comment. In the ion $[SeBr_6]^{2-}$ we have a different state of affairs from that in the cases previously discussed, since there is here a valency group of 14 electrons consisting of 12 shared and 2 unshared electrons. There is some doubt as to which orbital is occupied by the unshared pair. Of the two possibilities:

Shared	*Unshared*
$4s4p^34d^2$	$4d$
$4p^34d^25s$	$4s$

the second appears preferable, since the use of the 5*s* orbital might account for the very high value of the Se^{IV} octahedral radius, which is some 23 per cent. greater than the tetrahedral radius of Se as compared with a difference of only 3 per cent. between the octahedral and tetrahedral radii of Sn (see Table 7).

Trigonal Prism Bonds

A less symmetrical disposition of six bonds is found in a few crystals. In MoS_2 and WS_2 each metal atom is surrounded by six S atoms arranged at the apices of a trigonal prism around it (see p. 145). The grouping of Ni atoms around As in NiAs (p. 387) is similar. These are hybrid $d-s-p$ bonds of other types. The following 'trigonal prism radii' correspond to the interatomic distances in MoS_2 and WS_2: Mo^{IV}, 1·37 A., and W^{IV}, 1·44 A.

Other examples of the use of *d*, *s*, and *p* orbitals are the formation of 4 (planar), 5 (trigonal bipyramidal), and 8 (duodecahedral) bonds. In the two latter cases little is known of the orbitals involved. Among compounds with the trigonal bipyramidal configuration are PF_5, PF_3Cl_2, PCl_5, $MoCl_5$, $Fe(CO)_5$, and the pentafluorides and pentachlorides of Nb and Ta. It is by no means certain, however, that the bonds in molecules like pentafluorides are essentially covalent bonds. In a number of molecules and complex ions there is a group of ten valency electrons one or more pairs of which are unshared, and the arrangement of the bonds in these cases is simply related to the bipyramidal configuration of the AX_5 molecules in which all the ten valency electrons of A are shared. For examples see the stereochemistry of iodine (p. 270). For the structure of the $Mo(CN)_8^{4-}$ ion see p. 448.

Four Planar Bonds

The configuration most commonly found for four bonds is the tetrahedral one using the hybrid sp^3 orbitals. In the case of a few elements, stronger bonds than these can be formed when a *d* orbital of the penultimate shell is available. Consider what happens if a nickel atom, for example, acquires a share in six extra electrons, which it may do by forming four normal covalent bonds in a doubly charged complex ion such as $[Ni(CN)_4]^{2-}$, or by forming two normal and two 'coordinate' covalent bonds as in the glyoxime derivatives (p. 524). The atom has then 26 unshared and 8 shared electrons, and the former occupy the following orbitals:

Orbital	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*
Number available	1	1	3	1	3	5	1	3
Number of electrons	2	2	6	2	6	8	—	—

There is clearly still one 3*d* orbital left for use by the shared electrons. According to wave-mechanical calculations the strongest bonds can be formed by the combination of one 3*d*, one 4*s*, and two 4*p* orbitals, and

these bonds should be coplanar. This arrangement of four bonds has been verified experimentally for the following elements: Ni^{II}, Pd^{II}, Pt^{II}, Au^{III}, Cu^{II}, and Ag^{II}. Confirmatory evidence comes from magnetic measurements which will be discussed in Chapter VI. It is important to specify the valency of the metal when discussing the configuration of the covalent bonds it forms. For example, Cu^{I} or Ag^{I} forms four tetrahedral bonds, and the molecule $Ni(CO)_4$ has a tetrahedral configuration. If the four atoms attached to Ni themselves supply all the eight electrons required for the bonds, then there is no longer an unoccupied $3d$ orbital and accordingly the $4s$ and three of the $4p$ orbitals would be used for ordinary sp^3 bonds, i.e. we should have:

	1s	*2s*	*2p*	*3s*	*3p*	*3d*	*4s*	*4p*
Ni (28) 8	2	2	6	2	6	10	2	6

instead of

Ni (26) 8	2	2	6	2	6	8+	2	2	4

as in $[Ni(CN)_4]^{2-}$. The 'square' covalent radii of the Group VIII elements are the same as the octahedral d^2sp^3 radii. Details of the actual compounds in which the metals form bonds of the various types mentioned will be given in later chapters.

We may summarize here the conclusions from wave-mechanics regarding the configuration and strengths of bonds using orbitals of various kinds.

TABLE 9

Number of bonds	*Orbitals used*	*Angular distribution of bonds*	*Relative strengths*
1	s		1·000
3	p	Mutually perpendicular	1·732
4	sp^3	Tetrahedral	2·000
3	$s-p$	Planar (120°)	1·991
2	$s-p$	Linear	1·932
6	d^2sp^3 or sp^3d^2	Octahedral	2·923
6	$d-s-p$	Trigonal prism	2·983
4	dsp^2	Square	2·694

For bonds involving s and p orbitals and a completely shared valency group of six or eight electrons the configuration is the most symmetrical possible, i.e. linear, triangular, or tetrahedral respectively. When d orbitals are available other less symmetrical arrangements arise such as the four square and six trigonal prism bonds. As a general rule, if we know the configuration of the bonds formed by a fully shared group of electrons, then for the same valency group the arrangement of a smaller

number of bonds may be deduced assuming that the unshared pairs occupy some of the bond positions. In a few cases, such as the $[SeBr_6]^{2-}$ and $[SbBr_6]^{3-}$ ions, which are octahedral, the unshared pairs apparently have no effect.

IONIC CRYSTALS

We shall start with a simple picture of an ionic crystal and then see in what respects it has to be modified. Suppose that we have a crystal consisting of simple ions A^+ and X^- which have different sizes (X being larger than A). The problem is to find the most stable way of packing together these ions, which we shall regard as charged rigid spheres. It is reasonable to expect that each ion will surround itself with the greatest possible number of oppositely charged neighbours. Since the A and X ions each carry unit charges, there must be equal numbers of these ions in the crystal in order that the crystal shall be electrically neutral. Therefore the number of A ions around an X ion (the coordination number of X) must equal the number of X ions around any A ion, assuming that the environment of every A ion is the same, and similarly for the X ions. It is clear that this coordination number will be the maximum number of the larger X ions which can pack around an A ion so that all are in contact with the latter—provided that there is a simple symmetrical way of packing this number of X ions around the A ion. Many more of the smaller A ions could, of course, pack around an X ion, but this coordination number would be impossible for the A ions. The arrangement of the X ions around an A ion will in general be the most symmetrical in three dimensions, i.e. 3, 4, 6, or 8 ions will be arranged at the apices of a triangle, tetrahedron, octahedron, or cube around the central ion. Before proceeding any further we must consider how the coordination number is related to the relative sizes of the ions.

Radius Ratio

Suppose that we have a number of X ions surrounding an A ion—we may take triangular coordination first. The condition for stability is that the X ions are each in contact with A so that the limiting case arises when the X ions are also in contact with one another. It is easy to see that the following relation exists between r_A and r_X, the radii of A and X respectively: $r_A/r_X = 0{\cdot}155$. (Calling the radius of X a we have

$$r_A = \tfrac{2}{3}\sqrt{3}a - a = 0{\cdot}155a.)$$

It will be apparent that if the radius ratio $r_A:r_X$ falls below this value, then the X ions can no longer all touch the central A ion and this arrangement becomes unstable. For tetrahedral coordination the limiting value of the radius ratio is 0·225, so that for values of $r_A:r_X$ between 0·225 and 0·155 we should expect to find each A ion surrounded by three X ions.

The radius ratio ranges for certain highly symmetrical coordination groups are given below:

	C.N.	*Radius ratio limits*
Triangular . . .	3	0·155
Tetrahedral . .	4	0·225
Octahedral . . .	6	0·414
Cubic	8	0·732

We shall postpone further discussion of radius ratio until after we have dealt with the sizes of ions.

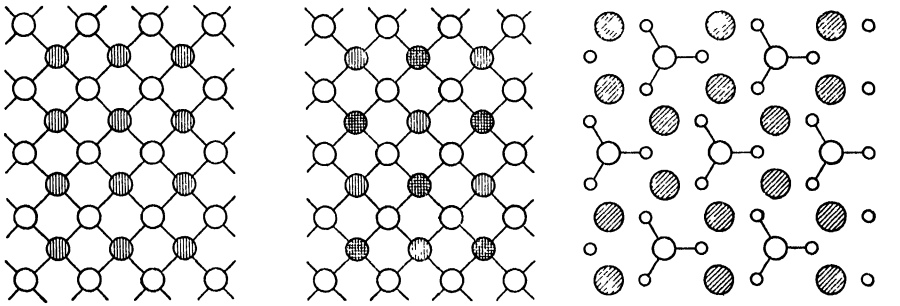


FIG. 12. Simple types of ionic crystals (diagrammatic).

In our simple ionic crystal with the composition AX every A ion is surrounded by a number of X ions, this number being determined by the ratio of the radii of A and X. The coordination number of X is necessarily the same. The X ions forming the coordination group AX_n around a particular A ion must also belong to the coordination groups around other A ions since every X ion is in contact with n A ions. The A and X ions thus form an extended array as shown diagrammatically in Fig. 12(*a*), which may be regarded either as a 2-dimensional analogue of an ionic crystal or as a projection of, or section through, such a crystal. There are no discrete molecules AX in such an arrangement. More complex formulae would result if some of the A or X ions were replaced in a regular manner by ions of other kinds, and Fig. 12 (*b*) shows how a compound A_2XY could arise by replacement of half the X ions by Y ions. In crystals of the kind illustrated in (*a*) and (*b*) all the interatomic bonds are essentially ionic in character. There are also more complicated structures in which some or all of the structural units are charged groups of atoms—complex ions. Such complex ions may be either finite groups, (*c*), such as CO_3^{2-} or NH_4^+, or they may be infinite chain or layer ions. We shall return to complex ions later in this chapter, but the various geometrical possibilities will be discussed in more detail in Chapter IV, where we consider

the classification of crystals. The bonds holding together the atoms of a complex ion may be, and generally are, quite different in character from the essentially ionic bonds operating between the complex ion and neighbouring ions. We must now see how our simple picture of an ionic crystal requires modification, and we shall deal first with the question of the sizes of ions.

Ionic Radii

If we imagine two oppositely charged ions to be brought together, the only appreciable force at first acting between them is the electrostatic

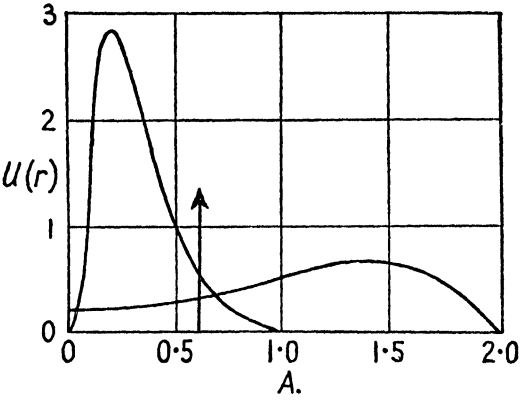


FIG. 13. Charge distributions of Li^+ and H^- ions (after Hylleraas and Bethe).

attraction due to the opposite charges. As they approach close to one another, however, this attractive force is opposed by a repulsive force due to the electron systems of the two ions and at some point these two forces will balance one another. The ions therefore do not approach closer together than this equilibrium distance. By X-ray methods we can determine such distances, which may be regarded as the sums of the radii of pairs of positive and negative ions. Ionic radii are fractions of interionic distances which have been divided up in such a way that the radii so assigned to the various ions may be used to predict the interionic distances and coordination numbers in other crystals.

As we shall see shortly, the radius of a given ion is not constant but varies with the coordination number. On the wave-mechanical model of the atom the discrete shells of electrons of the Bohr atom have been replaced by a radial distribution of electrons to which we have already referred (p. 20). As we move out from the centre of the ion beyond the point corresponding to the radius of the outermost shell in the Bohr model the electron density does not fall suddenly to zero but decreases much more gradually, as seen in an *f*-curve (p. 21). For this reason the term atomic or ionic radius has no precise physical significance. Fig. 13 shows the radial electron distributions for Li^+ and H^- ions, the distance apart of the centres of the ions corresponding to that in a LiH crystal.

The vertical line indicates the relation of the Pauling ionic radius of Li^+ to the actual electron distribution in the isolated ions.

Since it is clear that the effective radii cannot be calculated theoretically, they must be determined from observed interionic distances. The distances between pairs of positive and negative ions are the sums of pairs of radii and to obtain absolute values it is necessary to fix one ionic radius. Two early methods were:

(1) To start with the radii of the halogen ions derived from the X—X distances in the lithium halides, assuming that in these crystals these ions are in contact (Landé, 1920), or to take the radius of O^{2-} as half the distance apart of oxygen ions in silicates (*c.* 2·7 A.), making a similar assumption (Bragg, 1927). This method may be illustrated by giving the cation–anion distances in the following crystals, all of which have the rock-salt structure (see p. 98):

	AB		*AB*
MgO	2·10 A.	MnO	2·24 A.
MgS	2·60	MnS	2·59
MgSe	2·73	MnSe	2·73

From the constancy of the M—S and M—Se distances in the sulphides and selenides respectively it is reasonable to assume that in these crystals the anions are in contact with one another and to deduce the radii of S^{2-} and Se^{2-} ions as 1·84 $(2{\cdot}60/\sqrt{2})$ A. and 1·93 $(2{\cdot}73/\sqrt{2})$ A. respectively ($\frac{1}{2}CB$, Fig. 14).

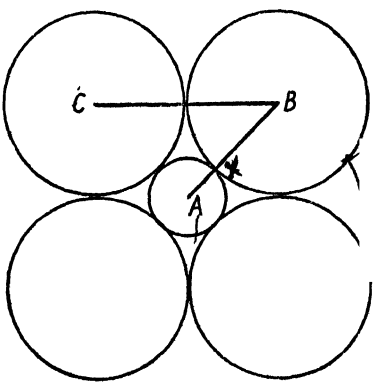


FIG. 14. Calculation of ionic radii from interatomic distances in crystals with the rock-salt structure.

(2) Wasastjerna (1923) divided the interionic distances in the alkali halides and alkaline-earth oxides in the ratios of the molar refractivities of the ions, taking the molar refractivity of an ion to be roughly proportional to its volume. Goldschmidt adopted Wasastjerna's values for F^- (1·33 A.) and O^{2-} (1·32 A.) and extended the list of radii by using the observed interionic distances in many other essentially ionic crystals.

Now we shall find that the apparent radii of ions are dependent not only on coordination number but also on the radius ratio. When the radius ratio is near to or below the critical limit then the repulsive forces between X ions in a coordination group AX_n lead to interionic distances larger than the sums of the appropriate ionic radii. To allow for this radius ratio effect Pauling derived a set of ionic radii from the A—X distances in the halides NaF, KCl, RbBr, and CsI, for which the radius ratio is in all cases about 0·75, and from the Li—O distance in Li_2O, taking the radius of O^{2-} as 1·40 A. Pauling's radii, like those of Goldschmidt, will not reproduce by simple addition the observed interionic distances in

certain crystals in which the radius ratio effect is appreciable, but they have the advantage that a perfectly definite correction may be applied for this effect, as will be shown later. Pauling starts from the following interionic distances:

Na—F	2·31 A.
K—Cl	3·14
Rb—Br	3·43
Cs—I	3·85
Li—O	2·00

The first three halides have the NaCl structure. Caesium iodide does not crystallize with this structure, therefore the Cs—I distance of 3·85 A. is that observed in CsI (with the 8-coordinated CsCl structure, p. 98), reduced by 2·7 per cent. to give the value for 6-coordination (see below). The absolute radii of the ions Na, K, Rb, and Cs and of the halogens are obtained by a semi-empirical method which is rather analogous to that of Wasastjerna. Instead of dividing up a distance such as Na—F in the ratio of the refractivities of the ions, Pauling divides it in the inverse ratio of the *effective* nuclear charges. The effective nuclear charge which, it is assumed, determines the distribution of the outer electrons and hence the size of the ion, is defined as the actual nuclear charge Ze less the screening effect Se of the remaining electrons in the ion. For the methods of estimating the screening constants we must refer the reader to the original papers. For the simple univalent ions with inert gas configurations the radii so obtained will reproduce the interionic distances in crystals other than the exceptional cases already noted. For multivalent ions, however, with inert gas structures, this is not the case, and the values obtained are 'the radii which the multivalent ions would possess if they were to retain their electron configurations but enter into Coulomb interaction as if they were univalent'. These are the 'univalent radii' of Pauling, which are convertible into 'crystal radii' by the relation

$$R_0 = R_1 z^{-2/n-1},$$

where R_0 and R_1 are the crystal and univalent radii respectively.

(This relation is easily derived from the simplest form of the Born equation for the potential energy of two ions taking into account only the electrostatic (Coulomb) attraction and the repulsive force due to overlapping of the electronic systems of the two ions, viz.

$$v = \frac{-Ae^2z^2}{r} + \frac{Be^2}{r^n},$$

in which A and B are constants for a particular crystal, ze is the charge on each ion, and the value of $n \sim 9$. Differentiating with respect to r and equating to zero (for minimum potential energy) we have

$$\frac{Ae^2z^2}{r^2} = \frac{nBe^2}{r^{n+1}} \quad \text{whence} \quad r = \left(\frac{nB}{Az^2}\right)^{1/n-1}.$$

If the Coulomb forces were to correspond to $z = 1$, i.e. the ions behaved as if

univalent, and the repulsion coefficient is unchanged we have for the sum of the univalent radii

$$r_1 = \left(\frac{nB}{A}\right)^{1/n-1}; \quad \text{hence} \quad r = r_1 z^{-2/n-1}.)$$

The crystal radii of some important ions according to Pauling are set out in Table 10. A number of points may be noted here. Com-

TABLE 10

Ionic Radii ('Crystal' radii of Pauling)

Typical and A sub-group elements

−3	*−2*	*−1*	*+1*	*+2*	*+3*	*+4*	*+5*	*+6*
—	—	(H	Li	Be	B	—	—	—
—	—	2·08)	0·60	0·31	0·20	—	—	—
N	O	F	Na	Mg	Al	Si	—	—
1·71	1·40	1·36	0·95	0·65	0·50	0·41	—	—
P	S	Cl	K	Ca	Sc	Ti	V	Cr
2·12	1·84	1·81	1·33	0·99	0·81	0·68	0·59	0·52
As	Se	Br	Rb	Sr	Y	Zr	Nb	Mo
2·22	1·98	1·95	1·48	1·13	0·93	0·80	0·70	0·62
Sb	Te	I	Cs	Ba	La	Ce	—	—
2·45	2·21	2·16	1·69	1·35	1·15	1·01	—	—

B sub-group elements

	+1	*+2*	*+3*	*+4*	*+5*
	Cu	Zn	Ga	Ge	As
	0·96	0·74	0·62	0·53	0·47
	Ag	Cd	In	Sn	Sn
	1·26	0·97	0·81	0·71	0·62
	Au	Hg	Tl	Pb	Bi
	1·37	1·10	0·95	0·84	0·74

Ions with (18+2) outer electrons

		Tl^+	Pb^{2+}						
		1·44	1·21						

Ions of transition elements

Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}
0·80	0·75	0·72	0·69	(1·01)*	0·69	0·66	0·64	0·62	0·60

* Goldschmidt.

Miscellaneous

NH_4^+
1·48

parison of ionic radii with covalent radii or metallic radii (see p. 549) shows that a positive ion is appreciably smaller than the neutral atom of the same element owing to the excess of nuclear charge over that of the orbital electrons, whereas the radius of a negative ion is much larger than the covalent radius:

Li	1·52 A.; cf.	Cl^-	1·81 A.
Li^+	0·60	Cl	0·99

In a series of isoelectronic ions (i.e. ions with the same configuration of orbital electrons) the radii decrease rapidly with increasing positive charge:

Na^+	Mg^{2+}	Al^{3+}
0·95	0·65	0·50 A.

There is no large difference in radius between pairs of ions such as O^{2-} and F^- or S^{2-} and Cl^-, for the increased attraction between ions of higher charge masks the increase in size which we might expect with increasing negative charge. The radii of the trivalent rare-earth ions show an interesting decrease with increasing atomic number, falling from 1·18 A. for Ce^{3+} to 0·99 A. for Lu^{3+}. A similar effect is found in the metallic radii of these elements (p. 549). As a result of this 'lanthanide contraction', so called because it is observed in the elements following lanthanum, certain pairs of elements in the same Periodic Group have practically identical ionic (and atomic) radii, viz.

	4+		*5+*
Zr	0·87	Nb	0·69
Hf	0·84	Ta	0·68

Table 2 shows the similarity in electronic structure of atoms such as Zr and Hf, and the remarkable similarity in chemical behaviour of such pairs of elements is well known. The elements of the second Group VIII triad are much more closely related to those of the third triad than to Fe, Co, and Ni. Within a given triad there is little or no variation in ionic radius.

The dependence of ionic radii on coordination number makes it necessary to specify the coordination number when ionic radii are quoted and it is usual to adopt the radii for C.N. 6 as standard. The apparent ionic radius increases with coordination number, and the following ratios, determined empirically, show the order of magnitude of the change:

	Coordination number		
	4	*6*	*8*
Radius	0·93-0·95	1·00	1·03

These ratios may be calculated from the simple Born equation already given if we assume that the repulsion coefficients B_1 and B_2 for the two structures of different coordination numbers are proportional to these C.N.s (i.e. to the number of contacts between positive and negative ions) and also that the Madelung constants A_1 and A_2 may be neglected on the grounds that their ratio is much nearer unity than the ratio B_2/B_1. We have

$$\frac{r_2}{r_1} = \left(\frac{A_1 B_2}{A_2 B_1}\right)^{1/(n-1)} \quad \text{which becomes} \quad \frac{r_p}{r_m} = \left(\frac{p}{m}\right)^{1/(n-1)},$$

where r_p and r_m are the apparent radii for coordination numbers p and m. Thus for a change from 6 to 8 coordination the radius is increased in the ratio $(8/6)^{1/8}$, taking $n = 9$, which equals 1·036, and for a change from 6 to 4 coordination in the ratio $(4/6)^{1/8} = 0{\cdot}950$.

We have said that a set of ionic radii such as those of Pauling or of

Goldschmidt are not consistent with the interionic distances in certain crystals owing to the 'radius ratio effect'. If our simple picture of an ionic crystal were sound, then the differences between the following pairs of distances should be equal, since they should be the difference between the radii of iodine and fluorine ions:

	Li—I	3·02	K—I	3·53	Rb—I	3·66 A.
	Li—F	2·01	K—F	2·67	Rb—F	2·82 A.
Difference		1·01		0·86		0·84 A.

We must inquire into this large discrepancy in the case of the lithium salts.

So far we have taken account only of the simple attractive and repulsive forces between ions of opposite charges, represented by terms of the form Ae^2z^2/r and Be^2/r^n respectively. This simple picture requires elaboration in various ways. The repulsive term Be^2/r^n is replaced by one of the form $w(r) = Ae^{-r/\beta}$ (where β is a constant), as the result of quantum-mechanical calculations, and three further terms are introduced. The first allows for the homopolar attraction which occurs to some extent in all 'ionic' crystals owing to the fact that the electronic systems of the ions do not remain completely independent of one another. The use of the wave-mechanical concept of resonance in describing bonds with some covalent character has already been mentioned in the previous chapter. Calculations of the lattice energies of the alkali halides show that allowance must be made also for the van der Waals attraction between the ions, though in these crystals this amounts to only some 2–3 per cent. of the total. Finally the zero-point energy must be included. An idea of the relative importance of the electrostatic attraction, the 'overlap' repulsion, and the homopolar attraction in an ionic crystal with a small amount of covalent character may be obtained from Fig. 15. We have therefore in general five terms in the expression for the lattice energy of an essentially ionic crystal.

In crystals for which the radius ratio has a value near to or below the lower limit the repulsive forces between ions of similar sign must also be taken into account. In addition therefore to the single term $w(r)$ for the overlap repulsion between ions of opposite sign, which we may write w_{+-}, we must add terms w_{++} and w_{--} for the repulsion between ions and their neighbours of like sign. The modified equation for the lattice energy is now a function not only of a single interionic distance $(r_+ + r_-)$ but also of r_+ and r_- in separate terms. The expression for the equilibrium interionic distance obtained from this equation accordingly involves the radius ratio and may be expressed in the form

$$r_0 = (r_+ + r_-)F(\rho),$$

where $F(\rho)$ is some function of the radius ratio which may be calculated and plotted against ρ. Pauling has calculated in this way the interionic distances for the lithium halides. Comparison of the simple radius sums with the observed interionic distances and with those calculated with allowance for the radius ratio effect shows the importance in such crystals

of anion-anion and cation-cation repulsions in determining the equilibrium separation of the ions. (In calculating the values given in Table 11 Pauling used radii slightly different from the crystal radii given in

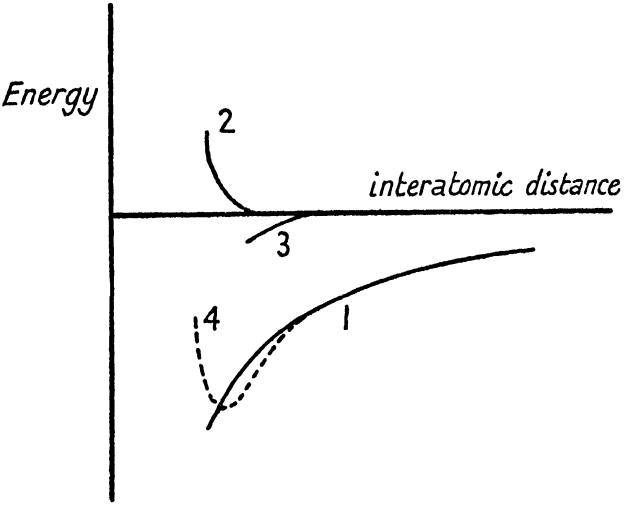


FIG. 15. Energy of a semi-polar crystal (after Mott and Gurney):
(1) electrostatic attraction, (2) overlap repulsion,
(3) homopolar attraction, (4) total energy.

Table 10, viz. Li^+ 0·607, F^- 1·341, Cl^- 1·806, Br^- 1·951, and I^- 2·168 A., but the result would have been sufficiently striking without this minor adjustment of radii.)

TABLE 11

	LiF	LiCl	LiBr	LiI
Sum of radii	1·948	2·413	2·558	2·775
Observed distance	2·009	2·566	2·747	3·022
Calculated allowing for radius ratio effect .	2·009	2·566	2·747	3·025

Pauling has also used this radius ratio concept to account for the irregularities in melting-points and boiling-points of the alkali halides. The observed melting-points of these compounds are shown in Fig. 16 (*a*), and at (*b*) are given the estimated melting-points of the hypothetical crystals having the same radius sums but radius ratio 0·75, i.e. crystals from which the radius ratio effect has been eliminated. The calculation of the 'corrected' melting-points involves a number of assumptions which we shall not discuss here, as we are not greatly concerned with the detailed crystal chemistry of ionic compounds. This explanation of the abnormal physical properties of these compounds, particularly of the lithium salts, has been mentioned here because alternative explanations have been given in terms of the polarization of the ions. From the electronegativity values given on p. 72 it is seen that of the alkali metal-halogen bonds the Li—I bond has the most covalent character, some 57 per cent.

Assuming that in a LiI crystal, in which Li^+ is surrounded by six I^-, the Li does not form more than one covalent bond in any of the possible resonating configurations of the LiI_6 system, then each Li—I bond would have at the most about 10 per cent. covalent character. Pauling's explanation therefore appears preferable to one which postulates considerable covalent character of the bonds.

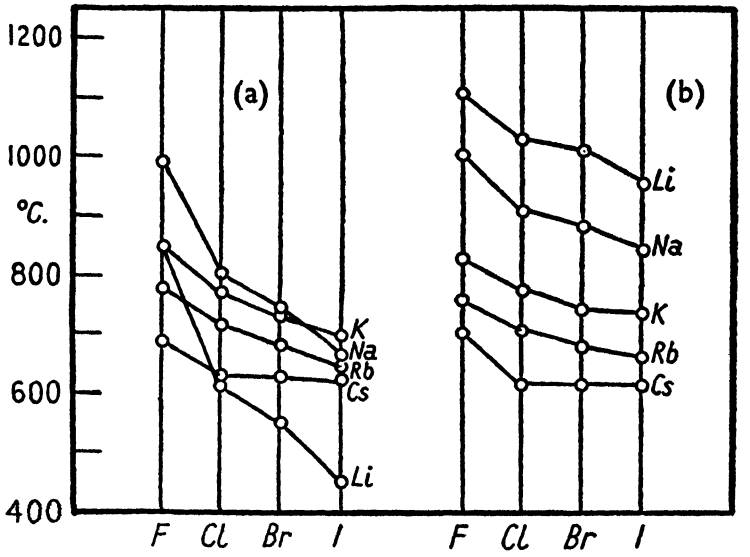


FIG. 16. The melting-points of the alkali halides: (*a*) observed, (*b*) corrected for the radius-ratio effect (after Pauling).

We may summarize our conclusions as follows. The interactions between an ion and its oppositely charged neighbours determine wholly, or to a large extent, the equilibrium interionic distances in ionic crystals. Radii may be assigned to ions such that in general they give by simple addition the distances between the respective pairs of ions. The effective size of an ion is, however, not constant, and these ionic radii vary slightly with the coordination number of the ion. The latter is determined by the ratio of the radii of the ion and of the surrounding ions. The interionic distances in some crystals are not consistent with any set of ionic radii, and in these cases repulsion between ions of similar sign must be taken into account (radius ratio effect). Later we shall see that our picture of an ionic crystal has to be modified in another respect. So far we have been discussing the factors determining the immediate environment of an ion. In NaCl each Na^+ ion is surrounded octahedrally by six Cl^- ions and each Cl^- ion similarly by six Na^+ ions, and we might expect this highly symmetrical arrangement to persist throughout the crystal, from any point in the interior to the boundary. Actually few, if any, real crystals possess such perfect structures, and although for most purposes we may visualize

a crystal of NaCl as having this ideal structure, the small departures from perfect regularity have a profound influence on certain physical properties, and we shall deal briefly with these 'lattice defects' in Chapter V.

We shall now illustrate a few of the simplest ionic crystal structures.

AX. The Sodium Chloride and Caesium Chloride Structures

A unit cell of the rock-salt structure, in which each ion is surrounded octahedrally by six of the other kind, is shown in Fig. 17 (*a*). At ordinary

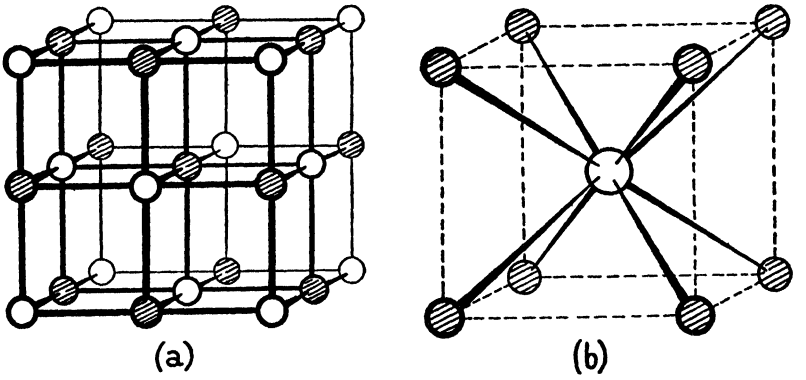


FIG. 17. The rock-salt (NaCl) and caesium chloride (CsCl) structures.

temperature and pressure all the alkali halides except CsCl, CsBr, and CsI crystallize with this structure, as also do the oxides and sulphides of the alkaline-earth metals. (The same structure is found for certain alloys and a few other sulphides and nitrides which are referred to elsewhere.) Caesium chloride crystallizes with the rock-salt structure at temperatures above 460° C. We have said that the correlation of radius ratio with coordination number is in general satisfactory, and this is true for very many ionic crystals—simple and complex—but this impression would not be given by the alkali halides. The radius ratios for these crystals are:

	Li	Na	K	Rb	Cs
F . .	0·44	0·70	0·98	1·09	1·24
Cl . .	0·33	0·52	0·73	0·82	0·93
Br . .	0·31	0·49	0·68	0·76	0·87
I . . .	0·28	0·44	0·62	0·69	0·78

and we should expect only those crystals with a radius ratio between 0·732 and 0·414 to crystallize with the rock-salt structure. These are enclosed by full lines in the above table. We might expect the salts outside this group to have lower or higher coordination numbers. The lithium halides have already been discussed in connexion with the radius ratio effect. Of the salts with radius ratio greater than 0·732 only CsCl,

CsBr, and CsI exhibit a higher coordination number, crystallizing with the CsCl structure—Fig. 17 (*b*)—in which each ion is surrounded by eight of the other kind. (RbCl, RbBr, and RbI adopt this structure under a pressure of about 5000 kg./cm.^{2})

It is reasonable to inquire why salts like RbCl and RbBr do not adopt the CsCl structure and why KF, RbF, and CsF with radius ratios near to or greater than unity do not exhibit even higher coordination numbers. It cannot yet be said that the first question can be answered satisfactorily. Calculations of the lattice energies for the two possible structures (NaCl and CsCl) for such salts show that there is probably little difference in stability between the two, but they do not explain the persistence of the 6-coordinated structure in the radius ratio range above 0·732. The second question is more easily answered. After the cube (C.N. 8) the next highly symmetrical coordination polyhedron is the cubo-octahedron for 12-coordination. When we come to consider the close-packing of equal spheres (p. 109) we shall see that a close-packed arrangement of equal numbers of oppositely charged ions in which each ion is surrounded by twelve of opposite charge is geometrically impossible.

Among other compounds crystallizing with the CsCl structure are CsCN, TlCN, and CsSH (in which the ions CN^- and SH^- attain spherical symmetry by rotating), TlCl, and a number of alloys.

AX_2. The Fluorite and Rutile Structures

Many difluorides and dioxides crystallize with one of these structures, which are illustrated in Fig. 18. In CaF_2 each Ca^{2+} ion is surrounded by eight F^- ions at the corners of a cube, and each F^- ion by four Ca^{2+} ions at the corners of a regular tetrahedron. In rutile the coordination numbers are 6 and 3, there being octahedral and triangular arrangement of nearest neighbours of positive and negative ions respectively. The fluorite structure is to be expected if the radius ratio is greater than 0·73 and the rutile structure for values between 0·73 and 0·414, and this is in general found to be the case. In the few cases where the radius ratio is less than 0·414, structures of lower coordination are found, as in BeF_2 (β-cristobalite structure, p. 464), and the various forms of silica. The application of the radius ratio criterion to SiO_2 is, however, of doubtful validity, as the bonds have about 50 per cent. covalent character (see Chapter XIV for the oxygen chemistry of silicon). GeO_2, with radius ratio close to 0·41, crystallizes with both the 6:3 coordinated rutile structure and also the 4:2 coordinated quartz structure (p. 463).

The oxides, sulphides, selenides, and tellurides of lithium, sodium, and potassium crystallize with the *antifluorite* structure, which is geometrically identical with the fluorite structure with the positions of the positive and negative ions interchanged. Lists of fluorides and oxides with the fluorite and rutile structures will be found on pages 275 and 312.

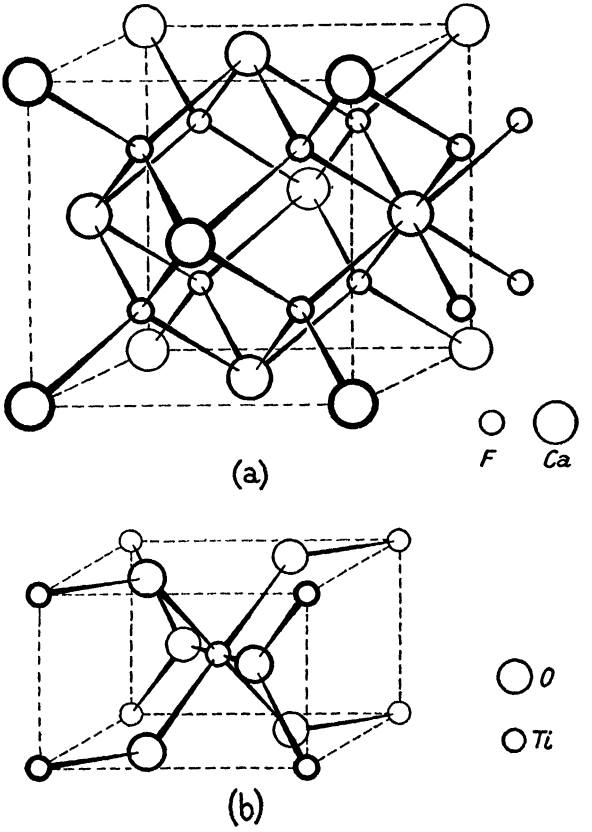


FIG. 18. The fluorite (CaF_2) and rutile (TiO_2) structures.

AX_3 Structures

Very few trioxides or trifluorides have been found to crystallize with simple structures. One simple structure is that of ReO_3, illustrated on p. 331; WO_3 and ScF_3 have closely related structures.

Layer Structures

If reference be made to lists of salts AX_2 and AX_3 crystallizing with the fluorite, rutile, or ReO_3 structures it will be found that, in general, only fluorides and oxides have these typically ionic structures. How then do the corresponding chlorides, bromides, iodides, and sulphides crystallize? Many of these compounds crystallize with structures which are quite different geometrically from those we have just been describing. Let us consider crystals in which every A atom is surrounded octahedrally by six X atoms, and focus our attention on the way in which the AX_6 groups are linked up. In NaCl, for example, every $NaCl_6$ coordination group shares all its corners with other similar groups, giving rise to an infinite 3-dimensional array of Na^+ and Cl^- ions in which every Na^+ is surrounded symmetrically by six Cl^- and every Cl^- by six Na^+. In $CdCl_2$ there is a

similar arrangement of six Cl around every Cd but the $CdCl_6$ groups are linked together—by sharing corners—into infinite sheets. Figure 19 shows a 2-dimensional analogy. In (*a*) we have AX_4 groups sharing all their corners in such a way as to form a planar net in which every X atom

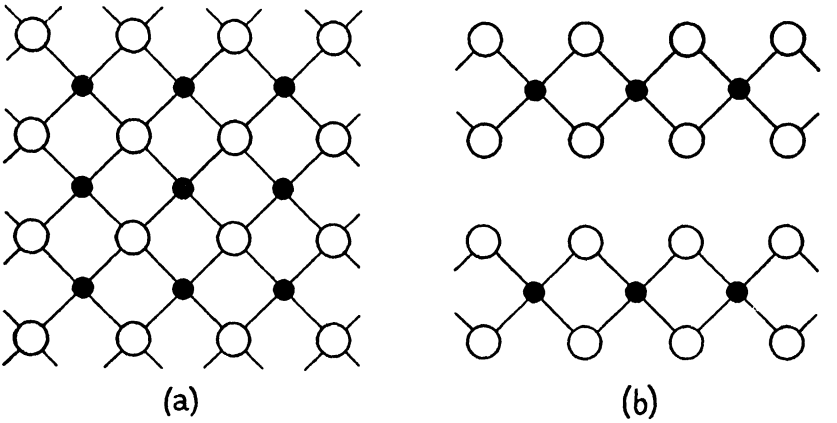


FIG. 19. Atoms forming (*a*) an infinite 2-dimensional network and (*b*) infinite linear chains.

is surrounded symmetrically by 4 A atoms. In (*b*), however, the AX_4 groups share their corners in a different way and we have chains instead of a continuous network. The diagrams (*a*) and (*b*) may be regarded as elevations of or sections through structures of the two types we are considering. We shall describe these layer structures in more detail in later chapters—see particularly pp. 144 and 276. For the present it will suffice to illustrate the CdI_2 structure—Fig. 20. A characteristic feature

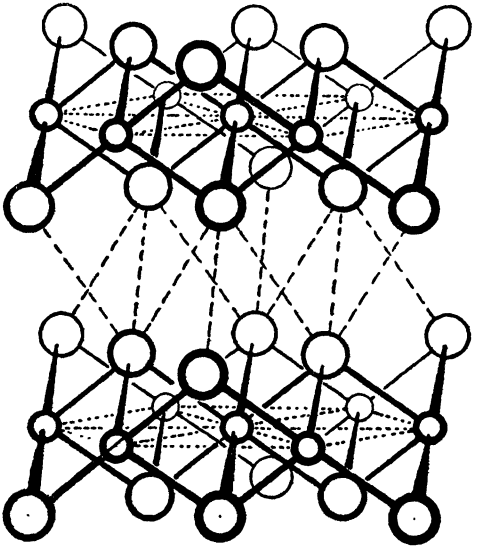


FIG. 20. Portions of two layers of the CdI_2 structure. The small circles represent metal atoms.

of such structures is the unsymmetrical environment of the X atoms, which have their A neighbours all to one side and on the other are in contact only with similar X atoms (cf. Fig. 19 (*b*), above). This is in marked contrast to the symmetrical arrangement of A atoms around X in the rock-salt, fluorite, and other simple ionic structures. The structures of a few halides, oxides, and sulphides are compared in the following table:

Symmetrical structures		*Layer structures*	
Fluorite	*Rutile*	$CdCl_2$*	CdI_2*
CaF_2	—	—	CaI_2
	MgF_2	$MgCl_2$	$MgBr_2$
	ZnF_2	$ZnCl_2$	—
CdF_2	—	$CdCl_2$	CdI_2
	—	$CdBr_2$	—
	CoF_2	$CoCl_2$	$CoBr_2$, CoI_2
	SnO_2	—	SnS_2
	TiO_2	—	TiS_2
ZrO_2	—	—	ZrS_2

The relation between these two structures is described on p. 278.

COMPLEX IONS

We have already mentioned that in some ionic crystals it is convenient to regard as structural units certain compact groups of atoms termed complex ions. The term complex ion is usually restricted in chemistry to any *finite* group of atoms which remain bound together as a group in solution, the complex ion possessing properties characteristic of that particular arrangement of atoms. Common examples are CO_3^{2-}, NO_3^-, SO_4^{2-}, etc. The chemist is primarily interested in ions which are stable in solution because in order to induce salts to interact with one another (i.e. to form a different combination of the ions) it is usually necessary first to separate the ions from one another by the process of dissolution. We are, however, also interested in the structures of solids and shall refer to a group of atoms as a complex ion if the forces holding the atoms together are stronger than those tending to separate them. This criterion may be applied to a group of atoms in a crystal or in solution and has the advantage that it makes no reference to the relative stabilities of the complex ion in these two states. It may appear unnecessary to state what is meant by a complex ion. We know, for example, that a crystal of K_2SO_4 consists of K^+ and SO_4^{2-} ions and that the latter retain their identity in solution. We shall find, however, that we could not restrict the term complex ion to those which, like the SO_4^{2-} ion, are stable at any dilution, for if a complex ion exists in a crystal it does not follow that it will be stable in solution in a particular solvent such as water. Moreover, complex ions may exist in a concentrated solution of a salt but break up when the solution is diluted. In this section we shall confine our attention to

finite complex ions and moreover to mononuclear ions AX_n, where X is either a single atom, as in SO_4^{2-}, or a group of atoms (radical or molecule) as in $[Ni(CN)_4]^{2-}$ or $[Co(NH_3)_6]^{3+}$. Polynuclear finite ions of all degrees of complexity are known from $S_2O_3^{2-}$ and $P_2O_7^{4-}$ to such ions as

$$[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}.$$

Later we shall meet examples of infinite charged aggregates of atoms which are also, of course, complex ions but which, unlike the finite ions, exist only in crystals.

Stability of Complex Ions

It is not possible to discuss here the stability of complex ions towards other chemical reagents. Stability towards acids, for example, ranges from that of SO_4^{2-} on the one hand to that of CO_3^{2-} on the other, the latter being very easily broken up: $CO_3^{2-}+H^+ \rightarrow (HCO_3^-) \rightarrow CO_2+OH^-$. Here we shall merely give one or two examples to show that the stability of a complex ion depends on its environment. The familiar changes in the colour of solutions of halides such as $CoCl_2$ on heating or on acidification in concentrated solution with HCl are due to the formation or breaking up of complex ions such as $[CoCl_4]^{2-}$. In a dilute solution (pink) of $CoCl_2$ there are hydrated Co^{2+} ions, but in the blue solutions $[CoCl_4]^{2-}$ ions. If a hot concentrated solution containing CsCl and $CoCl_2$ in the proportion of two molecules of the former to one of the latter is allowed to crystallize, blue crystals with the composition Cs_2CoCl_4 separate from the deep blue solution. The structure of these crystals has not been analysed, but there is no doubt about the existence of the $[CoCl_4]^{2-}$ ions, for they have been shown to exist in crystals of the closely related salt $Cs_3(CoCl_4)Cl$ which can be grown from a solution containing 3 CsCl : 1 $CoCl_2$. If the concentrated blue solution of either of these salts is diluted it turns pink owing to the dissociation of the $[CoCl_4]^{2-}$ ions. Mercuric iodide dissolves in a concentrated solution of KI owing to the formation of $[HgI_4]^{2-}$ ions, but these break down on dilution of the solution with precipitation of HgI_2. Many other similar cases could be quoted. Shortly we shall see that the tightness of binding within a complex ion in a crystal is affected by temperature, as evidenced by the polymorphism of certain oxy-salts.

The Shape of Complex Ions

It is useful to have some idea of the general shape and size of the common complex ions. In an ion AX_n the positions of the atoms relative to one another are determined by the length of the bonds A—X and by the angles between these bonds. We have discussed briefly some of the factors governing bond lengths and interbond angles—the character of the bond, the orbitals of the atom A used in forming the bonds—and the same considerations apply to bonds in complex ions as in molecules. The configuration of the bonds in a few complex ions has already been mentioned in the first part of this chapter, and many other complex ions

will be described under the stereochemistry of the appropriate elements. The general shapes of many complex ions are summarized in Table 12,

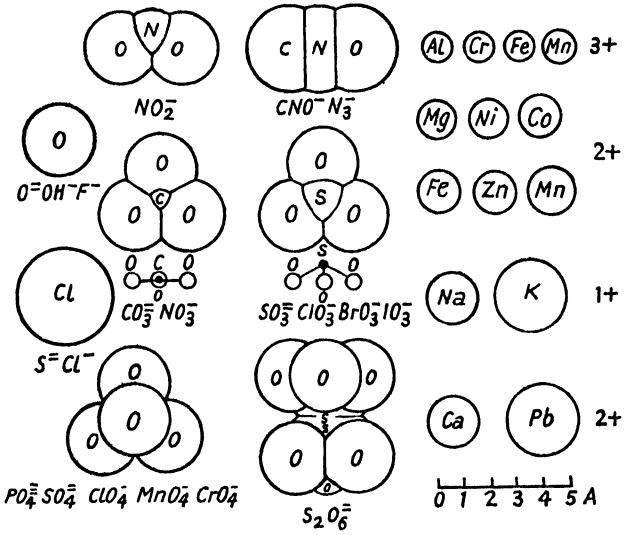


FIG. 21. The relative sizes of some ions (after Bragg).

and Fig. 21 shows scale drawings of a few simple ions to indicate their relative effective sizes in crystals.

TABLE 12

The Shapes of some Complex Ions

A_2, AX	—	O_2^{2-} C_2^{2-} CN^-
A_3, AX_2, AXY	Linear	N_3^- CNO^- CNS^- I_3^- $Ag(CN)_2^-$ ICl_2^-
	Angular	ClO_2^- NO_2^-
AX_3	Planar	CO_3^{2-} NO_3^-
	Trigonal pyramidal	PO_3^{3-} AsO_3^{3-} SbO_3^{3-} SO_3^{2-} SeO_3^{2-} ClO_3^- BrO_3^-
AX_4	Tetrahedral	BF_4^- PO_4^{3-} SO_4^{2-} ClO_4^- $CoCl_4^{2-}$
	Planar	$Ni(CN)_4^{2-}$ $PdCl_4^{2-}$ $PtCl_4^{2-}$
AX_6	Octahedral	SiF_6^{2-} $SnCl_6^{2-}$ $PtCl_6^{2-}$, etc.

(Some of these ions (e.g. CN^-, NO_3^-) become effectively spherical by rotation.)

Crystals containing Complex Ions

The study of crystals containing complex ions has shown that in general the size of a complex ion is remarkably constant in crystals of different salts. Moreover, the way in which the ions, complex or otherwise, pack together in a crystal is determined by geometrical considerations, i.e. by their relative overall sizes and, of course, by the relative numbers of the different kinds of ions. For these reasons we shall not be much interested in the crystal structures of salts containing complex ions except where these structures are closely related to those of other simple

ionic crystals. We are more concerned with the internal structure of, say, the SO_4^{2-} ion than in the fact that there are various structures adopted by sulphates MSO_4 or M_2SO_4. The chemically similar compounds $CaSO_4$ and $SrSO_4$ crystallize with different structures because the Ca^{2+} and Sr^{2+} ions are of different sizes and a mode of packing which is satisfactory for Ca^{2+} and SO_4^{2-} ions is not so for Sr^{2+} and SO_4^{2-} ions. On the other hand, $NaClO_4$, which has little in common with $CaSO_4$ from the chemical point of view, adopts the same crystal structure as that compound, while $KClO_4$ has the same structure as $SrSO_4$. Similarly the closely related $NaNO_3$ and KNO_3 crystallize with quite different structures, while $NaNO_3$ is isomorphous with $CaCO_3$.

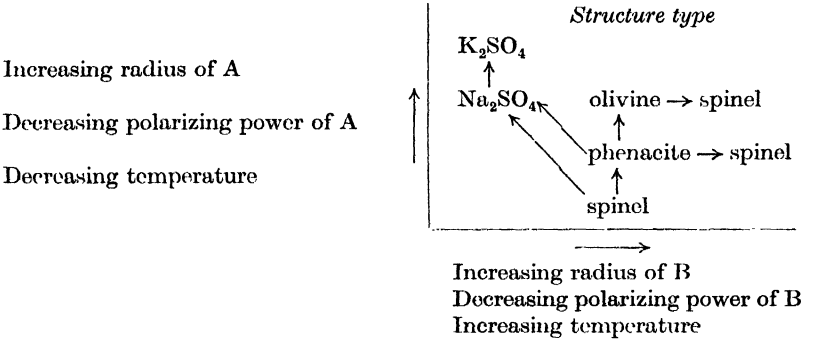
In the case of salts containing complex ions, as in the case of simple ionic crystals, the radius ratio criterion is applicable to determine which of a number of possible structures a particular compound will adopt. Many compounds ABO_3 crystallize with either the calcite or aragonite structures. In the former each A ion is surrounded by six oxygen atoms (of CO_3^{2-} ions) and in the latter by nine. Salts containing the smaller A ions therefore crystallize with the calcite structure while those containing larger A ions adopt the aragonite structure. For salts like $RbNO_3$ and $CsNO_3$ with still larger cations neither of these structures is possible. The following data (after Pauling) show that the change from the calcite to the aragonite structure corresponds to a value of the radius ratio (ρ) around 0·67, using Pauling's 'univalent radii'. His crystal radii and also the ionic radii of Goldschmidt give the value 0·71. A value of 0·73 is to be expected from purely geometrical considerations.

		ρ		ρ		ρ
Calcite structure	$LiNO_3$	0·34	$MgCO_3$	0·47	$ScBO_3$	0·60
(AO_6)	$NaNO_3$	0·54	$ZnCO_3$	0·50	$InBO_3$	0·59
			$CdCO_3$	0·65	YBO_3	0·68
			$CaCO_3$	0·67		
Aragonite structure	KNO_3	0·76	$CaCO_3$	0·67	$LaBO_3$	0·79
(AO_9)			$SrCO_3$	0·75		
			$BaCO_3$	0·87		
	$RbNO_3$	0·84				
(AO_{12})?	$CsNO_3$	0·96				

In our remarks on the stability of complex ions we referred to the polymorphism of certain oxy-salts. Let us consider the structures of some oxy-compounds of general formula A_2BO_4. These compounds adopt many different structures according to the nature of the atoms A and B. In some of these there are well-defined BO_4 groups (the criterion being the lengths of the B—O bonds, see p. 317) and essentially ionic bonds between the A ions and the oxygen atoms of these groups. The structure of Na_2SO_4 is of this type. The sulphates of all the larger alkali metals, K, Rb, and Cs, crystallize with another structure in which the packing of the A and BO_4 ions is different owing to the larger size of the former. The sulphate of the smallest alkali metal, Li, crystallizes with yet another structure, the

phenacite structure named after the mineral Be_2SiO_4 of that name. Whereas in the K_2SO_4 structure the large K^+ ions are surrounded by either nine or ten oxygen atoms belonging to SO_4^{2-} ions, in the phenacite structure the A atom has, like the B atom, only four oxygen neighbours, arranged tetrahedrally. We have seen that the Si—O bonds have only some 50 per cent. ionic character, and it is probable that the Be—O bonds are considerably less ionic in character than, for example, the K—O bonds in K_2SO_4. For this reason the Be_2SiO_4 structure is sometimes regarded as an infinite array of BeO_4 and SiO_4 tetrahedra sharing corners, with bonds of similar type extending throughout the crystal, rather than as an arrangement of SiO_4^{4-} ions held together by Be^{2+} ions.

Another structure common to a number of A_2BO_4 crystals is the spinel structure (p. 332), in which there is no reason for distinguishing the BO_4 coordination groups as complex ions. Now Li_2SO_4 has, at ordinary temperatures, the phenacite structure, but it also has a high-temperature form with the spinel structure, and the same is true of Li_2MoO_4. Also, whereas Zn_2SiO_4 has the phenacite structure, Zn_2TiO_4 (containing the more electropositive Ti) crystallizes with the spinel structure. Facts such as these have been taken to indicate that the individuality of, for example, an SO_4^{2-} ion is affected by the nature of the surrounding ions and by the temperature. Goldschmidt has made extended studies of the relations between the various structures adopted by crystals of a given formula type. He treated the crystals as systems of ions polarized to various extents and introduced the term 'contrapolarization' to describe the effect of a small highly polarizing ion A in weakening the binding within, say, a BO_4 group. The accompanying diagram is typical of the results of Goldschmidt's systematic investigations.



With regard to the detailed structures of crystals containing complex ions we have said that in general the internal structure of the complex ion will interest us more than the way in which the various ions are packed together. Without attempting to classify such crystals we may note three groups in which the structural principles are easily seen.

(1) Structures in which either or both the ionic species of a simple A_mX_n structure are replaced by complex ions, the spatial arrangement of

the ions relative to one another being the same as in the A_mX_n structure. Two cases may be distinguished:

(*a*) The complex ions are approximately spherical. Many compounds of the type $A_2[BX_6]$ crystallize with the anti-fluorite structure, e.g. K_2PtCl_6, K_2SnCl_6, while $[Co(NH_3)_6]I_2$ and $[Mg(NH_3)_6]I_2$ adopt the fluorite structure. As an example of a compound in which both cation and anion are complex we may give $[Ni(H_2O)_6]$ $[SnCl_6]$, the structure of which is a slightly deformed version of that of CsCl.

(*b*) The complex ions attain effective spherical symmetry by free rotation. Non-spherical ions which behave in this way include NH_4^+, NO_3^-, CN^-, SH^-, and we find CsCN and CsSH with the same structure as CsCl. We shall return to this question of rotating groups in Chapter V.

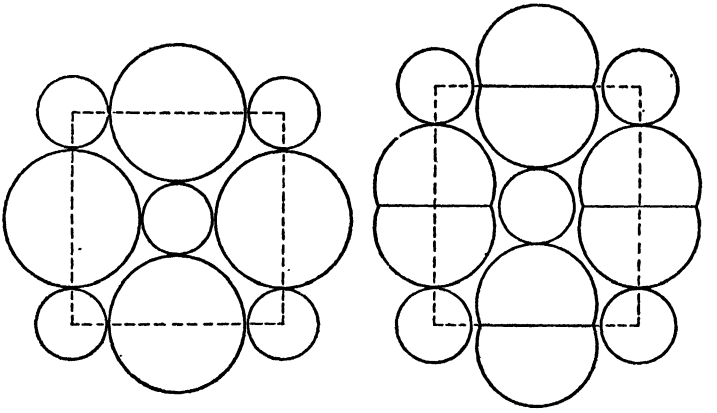


FIG. 22. Sections through the structures of NaCl and CaC_2 to show the packing of the ions.

(2) Structures similar to those of A_mX_n compounds but of lower symmetry owing to the shape of the complex ion. The structure of CaC_2 is related to that of NaCl in this way. In a crystal of calcium carbide all the C_2^{2-} ions are arranged parallel, with the result that the structure is distended in one direction, as may be seen from Fig. 22. The CaC_2 structure should be compared with that of iron pyrites, FeS_2. The latter is not an ionic compound but contains S_2 groups oriented in quite a different way, parallel to the body-diagonals of the cubic unit cell, so that cubic symmetry is retained. In the calcite structure we find Ca^{2+} and planar CO_3^{2-} ions packed together in much the same way as the ions in NaCl, but owing to the far from spherical shape of the complex ions the symmetry of the structure is much lower. The structure of the other form of calcium carbonate, aragonite, is related in this geometrical sense to that of the homopolar crystal NiAs (see p. 387).

(3) In other cases, particularly when the complex ion is large and far from spherical, the structure is determined by the packing of the complex ions—the other ions fitting in the interstices. Fig. 143 (p. 473), showing

the plans of the structures of beryl and benitoite, illustrates this point well. At the end of Chapter IV (p. 148) we give a few examples of the normal modes of packing of ions and molecules with characteristic shapes.

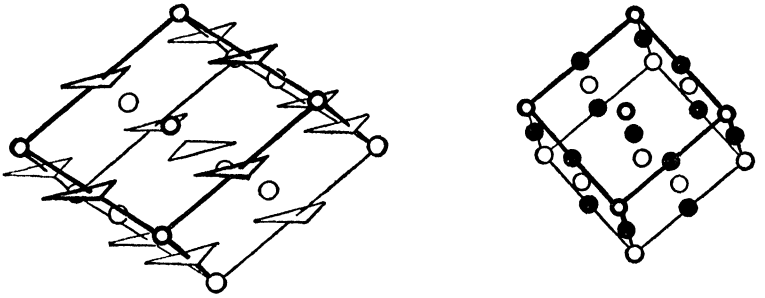


FIG. 23. The calcite and rock-salt structures similarly oriented.

THE STRUCTURES OF COMPLEX IONIC CRYSTALS

We have now examined some of the factors which decide the type of structure adopted by ionic crystals of fairly simple kinds. Suppose now that we are confronted with crystals of much greater complexity, for example, $Mg_5Al_2Si_3O_{10}(OH)_8$ or $Ca_2Al_4Si_{14}O_{36}.12H_2O$. In many cases it has been possible to determine the atomic structures of such crystals, and it is interesting to see whether there are any general principles underlying such structures. The understanding of the rules to which structures must conform assists us in unravelling the structures of yet more complex crystals. In most complex ionic crystals the anions are oxygen ions (and/or OH^-) and less frequently fluorine ions. From a table of ionic radii it will be seen that these ions are considerably larger than the majority of metal ions, particularly those carrying multiple charges. Therefore most of the space is occupied by these anions. The spaces between these O^{2-} or F^- ions are large enough to accommodate most of the metal ions. Accordingly we could describe these complex structures by describing first the way in which the anions are packed and then specifying which interstices are occupied by the smaller positive ions. We find that in many cases the oxygen atoms in complex oxy-salts are packed together as closely as possible. We must therefore consider shortly how equal spheres can be packed together.

There is, however, another way of regarding the structures of complex ionic crystals. In any simple ionic crystal, such as NaCl or CaF_2, each ion is surrounded by a certain number of the other kind. The number of negative ions around a positive ion is determined by the ratio of the radii of the two ions; the coordination number of the negative ion by positive ions is then fixed by the condition that the crystal must be electrically neutral. The crystal may, then, be regarded as built up of AX_n groups linked together by sharing corners, edges, or faces. In the case of a crystal as simple as NaCl this concept is not particularly valuable, but it proves very helpful for complex crystals containing several different kinds of

positive ions with different coordination numbers. This viewpoint also has a great practical advantage. It will be appreciated that in models or illustrations designed to show the packing of the large negative ions it is difficult to see the smaller metal ions situated between them, whereas very complex structures can be depicted if we merely outline the coordination groups (by joining up their corners to form polyhedra) and show how these are linked together.

The Closest Packing of Spheres

If spheres of equal size are packed together in a plane they arrange themselves as shown in Fig. 24 (*a*), with their centres at the corners of

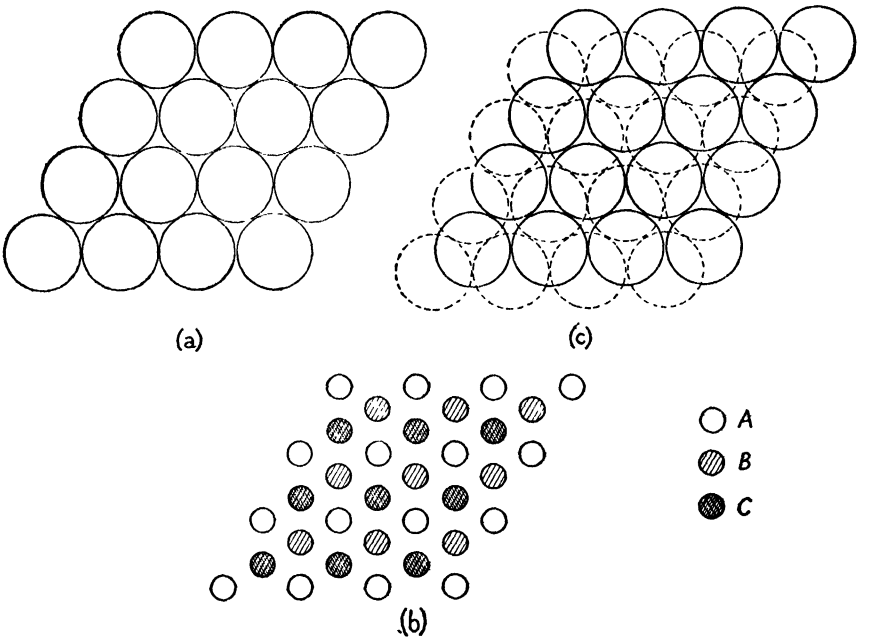


FIG. 24. The closest packing of equal spheres: (*a*) single layer of close-packed atoms, (*b*) positions of atoms in successive layers in cubic close packing, and (*c*) two adjacent layers in hexagonal close packing.

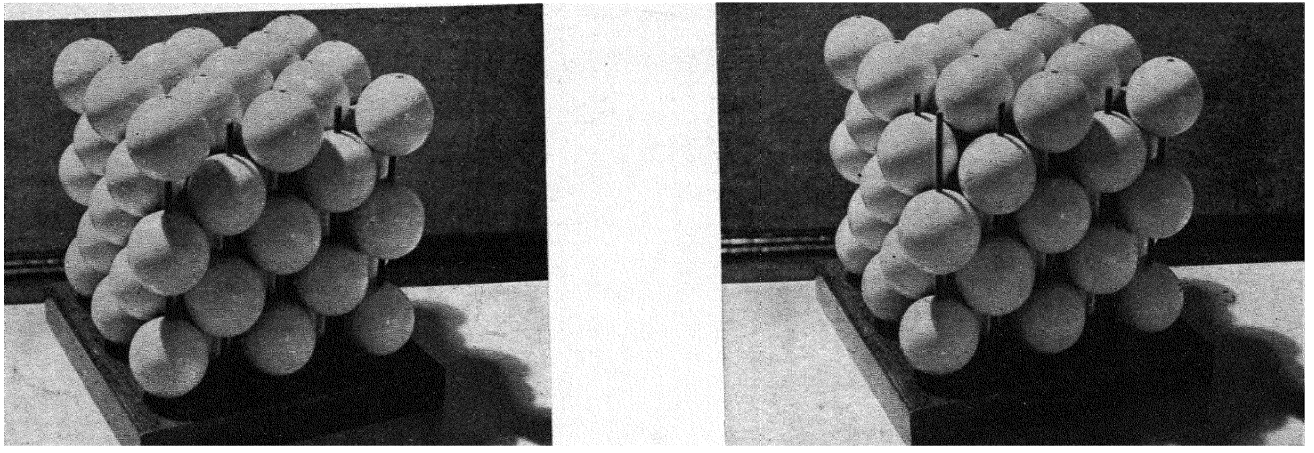
equilateral triangles. Each sphere is in contact with six others. The most closely packed arrangements of equal spheres in three dimensions are built up of layers of this sort. The conditions to be satisfied are that (1) the space occupied per sphere is a minimum; it is actually $5{\cdot}66a^3$ for spheres of radius a in closest packing, and (2) the spheres are all equivalent, i.e. they all have the same environment. The relative orientation of the spheres is disregarded—we assume them to possess full spherical symmetry and that there is no way of determining their orientations. Barlow showed (in 1883) that there are two different ways of packing together equivalent spheres. They arise in the following way (see Fig. 24). If we

label the positions of the atoms in a layer as A, then an exactly similar layer can be superimposed on the first so that the centres of the atoms in the upper layer are vertically above the positions B. (It is obviously immaterial whether we choose the positions B or the equivalent positions C, as may be seen by inverting the diagram.) When we come to place the third layer above the second (B) layer there are clearly two alternatives. The centres of the atoms may lie above either the C or A positions. In the latter case we have the sequence of layers ABABAB..., etc., the simplest form of close packing—hexagonal close packing. In the former the sequence of layers is ABCABC...—cubic close packing. The terms hexagonal and cubic refer to the symmetry of the resulting aggregate. The highest axial symmetry of hexagonal close packing consists of 6-fold axes perpendicular to the layers, but in cubic close packing there are 3-fold axes of symmetry in four directions, inclined to one another as are the body-diagonals of a cube. Since this is not easily seen from Fig. 24, we show in Fig. 25 cubic close-packed spheres viewed from a different angle. It will be seen that the close-packed layers seen in plan in the previous figures are perpendicular to any body-diagonal of the cube. The repeat-unit (unit cell) of cubic close packing is a group of atoms situated at the corners and mid-points of the faces of a cube, hence the alternative name 'face-centred cubic' for a cubic close-packed structure.

In each of these close-packed arrangements, cubic and hexagonal, each atom has twelve equidistant nearest neighbours, six in its own plane and three in each adjacent layer. The next nearest neighbours are, however, differently arranged in the two cases. It will be apparent that any sequence of close-packed layers must lead to a close-packed structure, for any atom will always have twelve equidistant nearest neighbours. Any other sequences of layers, however, differ from the sequences ABABAB... and ABCABC... in that the environment of all the atoms is not the same. Although the arrangement of the nearest neighbours is identical, as regards the arrangement of the next nearest neighbours the atoms fall into two or more sets. For example, in the sequence ABACABAC...('double' hexagonal close packing) there are two types of non-equivalent spheres. This form of close packing has been found for the oxygen atoms in brookite, TiO_2, for the oxygen and fluorine atoms in topaz for the halogen atoms in a number of halides such as $HgBr_2$ and for Cl and OH in Cd(OH)Cl. Among the numerous examples of cubic and hexagonal close packing we may note the following:

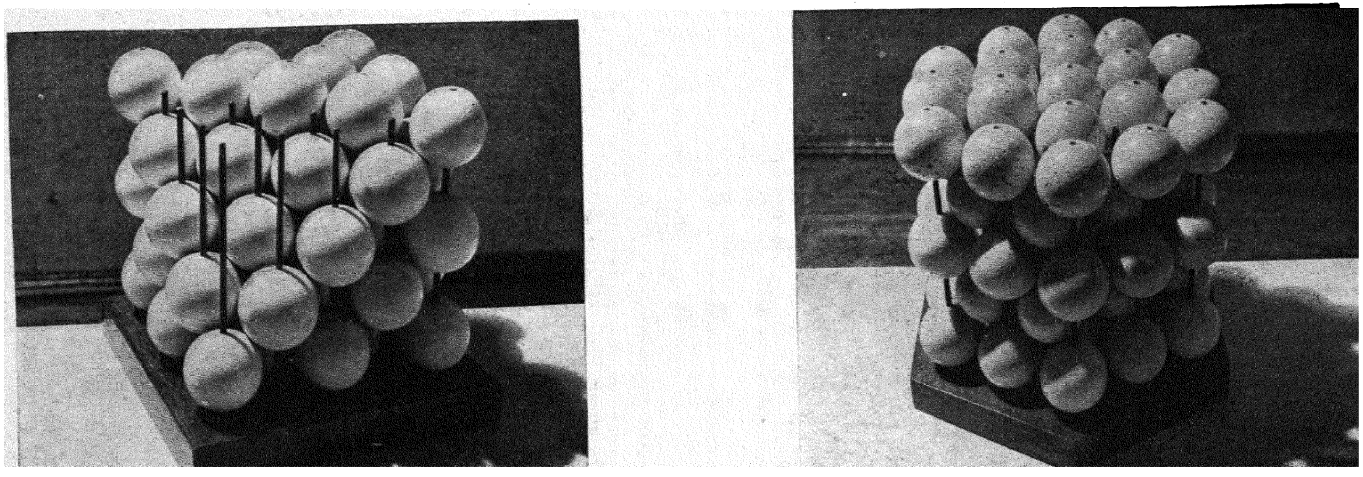
(*a*) Metals (cubic and hexagonal).
The inert gases (cubic) and hydrogen (hexagonal).
Many simple rotating molecules—HCl, H_2S, CH_4, etc. (cubic).

(*b*) In many halides the halogen atoms are close packed (see the discussion of halide structures, p. 276) and in many oxy-compounds —notably silicates—the oxygen atoms are similarly packed. The fluorine ion is very nearly the same size as the oxygen ion so that these two ions together may build up a close-packed structure.



(*a*) (*b*)

FIG. 25. (*a*) Cubic close-packing, (*b*) the same with the corner atom removed.



(*c*) (*d*)

FIG. 25. (*c*) Cubic close-packing with more atoms removed to show a layer of close-packed atoms.
(*d*) Hexagonal close-packing.

(c) Close packing of large cations (K^+, Rb^+, Cs^+, Ba^{2+}, NH_4^+) with anions. Certain positive ions are very similar in size to the large halogen ions—compare F^-, 1·36, and K^+, 1·33 A., or Cl^-, 1·81, and Cs^+, 1·69 A.—and it is therefore possible for such pairs together to form a close-packed assemblage.

In discussing the structure of KF (p. 99) we inquired why a 12-coordinated structure was not found, as a coordination number of 12 would be

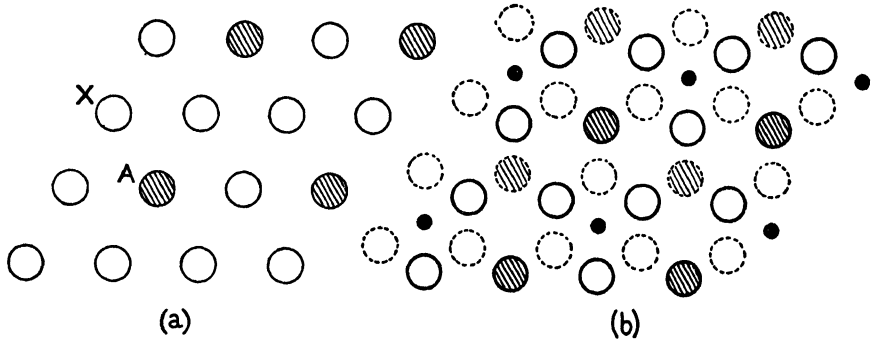


FIG. 26. The closest packing of atoms of two kinds: (*a*) single layer, (*b*) two adjacent layers (full and dotted circles) showing the positions, midway between the layers, for metal atoms (small black circles) within octahedra of X atoms.

expected from the radius ratio. If, however, we attempt to form a close-packed layer in which each ion is surrounded entirely by ions of the other kind, we find that this is impossible. As soon as we have placed six X ions around A (Fig. 26 (*a*)) we see that each X ion has already two X ions as nearest neighbours. The simplest structure built from such layers is shown in Fig. 26 (*b*). Each A^+ ion is surrounded by six X^- ions, but an X^- ion by two A^+ and four X^-. The layer contains three X to every A ion. For singly charged ions (e.g. K^+ and F^-) there is therefore an excess of negative charge to be neutralized. Now when such layers are packed together in closest packing there are, between the layers, holes between six X^- ions, as indicated by the small black circles in Fig. 26 (*b*). These positions—either all of them or a proportion of them—may be occupied by positive ions, resulting in an electrically neutral crystal of general formula $A_xB_yX_{3x}$, where A may be, for example, an alkali and X a halogen.

Although there is no obvious relation between the formulae of compounds such as $KMgF_3$, $Cs_3Tl_2Cl_9$, and K_2SiF_6, the structures of all are based on close-packed layers of the type shown in Fig. 26 (*b*). First we see that the ratio of halogen to alkali atoms is three in each case, as required for this layer, and if we write their formulae $K_3Mg_3F_9$, $Cs_3Tl_2Cl_9$, and $K_3Si_{3/2}F_9$ we see that, from the geometrical point of view, the structures differ only in the proportions of the available octahedral holes which are occupied by Mg, Tl, or Si. Whether or not discrete complex ions B_mX_n can be distinguished in these structures depends on the arrangement of

the B atoms in these octahedral holes. In the structure of $KMgF_3$, which is illustrated in Fig. 27 to show the close-packed layer and the Mg^{2+} ion surrounded octahedrally by six F^- ions, every available octahedral hole between six F^- ions is filled by a Mg^{2+} ion, and there are no discrete MgF_6

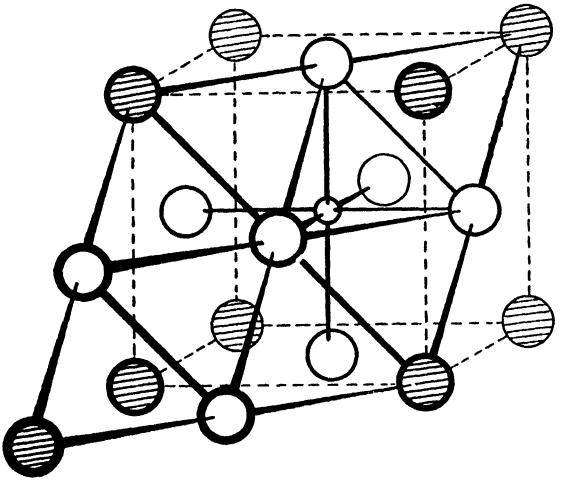


FIG. 27. The perovskite structure of $KMgF_3$ showing a Mg^{2+} ion (small circle) surrounded by six F^- ions and a layer of close-packed K^+ and F^- ions (large shaded and open circles respectively).

groups. In $Cs_3Tl_2Cl_9$, however, only two-thirds of the available octahedral holes are occupied by Tl atoms and they are occupied in pairs, giving rise to $(Tl_2Cl_9)^{3-}$ complex ions. Lastly, in K_2SiF_6 only one-half of the octahedral holes are occupied, and discrete SiF_6^{2-} ions exist in the crystal.

The Linking of Coordination Polyhedra: Pauling's Rules

We now come to the description of the structures of complex ionic crystals in terms of the coordination polyhedra around the positive ions. We have to consider first the nature of these coordination groups and secondly the way in which they are linked together. Pauling has summarized the principles determining the structures of complex ionic crystals in a set of 'rules'. These rules are semi-empirical and are borne out by the structures of many crystals, but they are not obeyed in detail in every case. Since the crystals are treated as aggregates of ions, the rules should be applied only to crystals in which the bonds are essentially ionic, i.e. to oxides and fluorides, the structures of which are determined largely by the packing of the large O^{2-} and F^- ions.

Each positive ion is surrounded by a number of negative ions (its coordination polyhedron), this number being determined by the ratio of the radii of the two ions (Pauling's First Rule). We have already given the minimum values of the radius ratio for some of the more symmetrical coordination polyhedra (p. 89) and considered the application of the

radius ratio criterion to certain structures. The less symmetrical coordination polyhedra AX_n, particularly those where n is odd, are of some interest in this connexion.

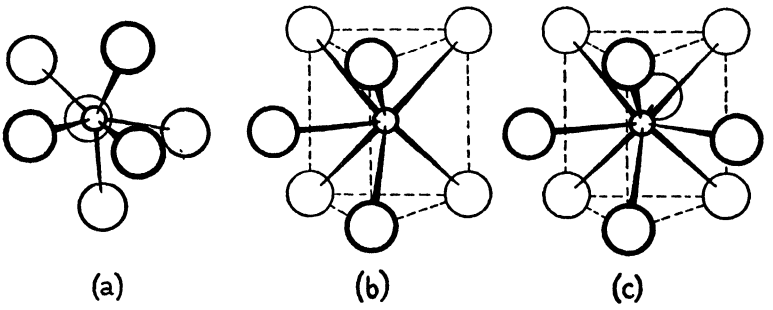


FIG. 28. Arrangement of neighbours for 7- and 9-coordination: (*a*) $[ZrF_7]^{3-}$, (*b*) $[NbF_7]^{2-}$, (*c*) $[Nd(H_2O)_9]^{3-}$.

The coordination number 5 is rarely found but occurs in a few structures (see, for example, p. 324). The most symmetrical non-planar arrangement of five neighbours is the trigonal bipyramidal, but for this the limiting radius ratio is the same as for triangular coordination, so that it is difficult to apply the radius ratio criterion. Coordination groups of 7 and 9 occur in a few crystals. In the former case two arrangements have been found. (*a*) The odd atom is added above the centre of one face of an octahedron, which is distorted chiefly by separating the atoms at the corners of this face. This type of coordination is found in the MO_7 groups in the A-modification of the rare-earth oxides, M_2O_3 (see p. 314), and for the ZrF_7 groups in $(NH_4)_3ZrF_7$. (*b*) The seventh atom is added beyond the centre of one of the rectangular faces of a trigonal prism, with some subsequent distortion. This arrangement is found in K_2NbF_7 and K_2TaF_7. An interesting configuration for nine neighbours is found in $Nd(BrO_3)_3.9H_2O$ in which each Nd atom is surrounded by nine water molecules. This coordination group is illustrated in Fig. 28 (*c*); it arises by adding atoms beyond the centres of each of the vertical faces of a right triangular prism. The same arrangement is found for the nine Cl neighbours of an NH_4^+ ion in NH_4CdCl_3 (see p. 288). We return to the discussion of radius ratios in Chap. IX in connexion with the structures of oxy-salts.

The other rules relate to the sharing of atoms between coordination polyhedra. A crystal of Mg_2SiO_4 may be regarded as built up of SiO_4^{4-} ions and Mg^{2+} ions or alternatively of close-packed oxygen atoms with Si atoms in tetrahedral and Mg in octahedral holes. The oxygen atoms of the MgO_6 coordination polyhedra are all attached to Si atoms, and in fact every oxygen atom in the structure is bound to three Mg and to one Si atom. For such an anion shared between several coordination polyhedra Pauling's Second Rule equates its charge (in this case -2) to the sum of the strengths of the bonds reaching it from the cations to which it is linked. The electrostatic strength of a bond is defined as follows.

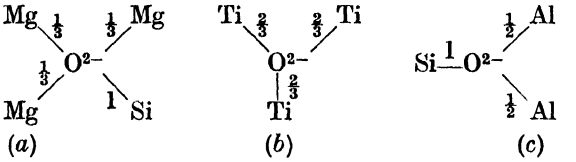
If a positive ion with charge $+ze$ is surrounded by n negative ions, then the strength of the bonds from the positive ion to its negatively charged neighbours is z/n. For the Mg—O bond in a MgO_6 group z/n is clearly 2/6 or $\frac{1}{3}$. The strengths of other bonds in oxy-salts are:

B—O	in	BO_3,	1	Al—O	in	AlO_6,	$\frac{1}{2}$
		BO_4,	$\frac{3}{4}$				
Be—O		BeO_4,	$\frac{1}{2}$	Mg—O		MgO_6,	$\frac{1}{3}$
Si—O		SiO_4,	1	Ti—O		TiO_6,	$\frac{2}{3}$

For the oxygen atom forming part of several coordination polyhedra we have a number of bonds with different values of z/n and the sum of these must equal -2, the charge on the oxygen ion, i.e.

$$-2 = z_1/n_1 + z_2/n_2 + z_3/n_3, \text{ etc.}$$

This rule implies that in ionic crystals charges are neutralized locally. We may illustrate this rule for Mg_2SiO_4 as at (*a*). From the above list of electrostatic bond strengths we see that an oxygen ion, charge -2, can



be satisfied by two bonds to Si atoms (as in the $Si_2O_7^{6-}$ ion) or by bonds to various other combinations of atoms, e.g. to 4 Al, 3 Ti (see the structure of rutile, p. 100), Si+2 Al, or Si+3 Mg (in olivine, Mg_2SiO_4, p. 469). Some of these are set out diagrammatically above. This rule limits the number and types of coordination polyhedra which may meet at any point in a structure.

We might expect to find coordination polyhedra with corners, edges, or faces in common with one another. The sharing of edges or faces, however, obviously brings closer together the positive ions at the centres of the polyhedra than does the sharing of corners. If for tetrahedra AX_4 sharing corners the distance between A atoms (i.e. A—X—A) is unity, then if edges are shared this distance is reduced to 0·58 and if faces are shared to 0·33. The corresponding values for octahedra are 0·71 and 0·58. Pauling's Third Rule states that the presence of shared edges and especially of shared faces of coordination polyhedra decreases the stability of the structure since the positive ions are thereby brought closer together, and this effect is large for positive ions of high charge and small coordination number. Actually, of course, we do find coordination polyhedra sharing edges in many structures, e.g. TiO_6 octahedra in rutile, AlO_6 octahedra in corundum, etc., but in general considerable distortion of the groups is found. We find the shared edges are shortened owing to repulsion of the positive ions, the distance between which is thereby somewhat increased as shown in Fig. 29, in which the effect is deliberately exaggerated. This shortening of the shared edges of coordination polyhedra is characteristic

of ionic structures. In fact the relative lengths of shared and unshared edges of coordination groups and also the way in which the latter are joined up often illustrates differences in bond type in different structures. For example, the shared edges of FeS_6 octahedra in FeS_2 (marcasite)

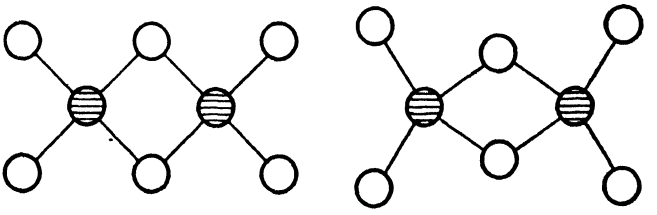


FIG. 29. Distortion of AX_4 groups sharing an edge.

which share faces are *longer* than the unshared edges. Also, whereas SiO_4 tetrahedra share only corners, the SiS_4 tetrahedra in SiS_2 share edges, an indication that the sulphide is an essentially covalent crystal.

Pauling's Fourth Rule states that in a crystal containing different kinds of positive ions those with large charge and small coordination number tend not to share polyhedron elements with one another, i.e. they tend to be as far apart as possible in the structure. This is simply a corollary to the Third Rule. We shall not discuss the structures of complex ionic crystals any further at this stage. The principles determining their structures will be better appreciated when those structures are described in later chapters.

CHAPTER IV

THE STATES OF AGGREGATION

If we reflect on the nature of the reactions commonly carried out by the chemist, we find that only in a very few cases are the reactants both solids, both liquids, or both gases. In particular we are rarely concerned with reactions between solids. Some at least of the reactions of this kind which have been described involve either liquid or vapour phases. We have already described the structures of some solids, and in subsequent chapters we shall describe the atomic arrangement in many more. The chemist has long utilized the process of crystallization as a means of purifying compounds, and in the preparation of many substances he relies on differences in solubility to separate one component of a system from the others. However, in order to promote a chemical reaction between two substances which are both solids at ordinary temperatures it is usual first to break down the solids by dissolution in suitable solvents or by vaporization. It is therefore not sufficient merely to know how the atoms are arranged in a crystalline compound: we also need to know what regrouping of the atoms takes place when the crystal is dissolved or vaporized. In this chapter therefore we shall have to consider the relation between the structures of a substance in the various states of aggregation, but we shall first remind the reader of a few of the characteristic properties of solids, liquids, and gases, of solutions, and of the 'vitreous' and 'liquid crystalline' states.

SOLIDS, LIQUIDS, AND GASES

We are familiar with the fact that at ordinary temperatures and pressures some elements and compounds exist as solids, others as liquids or gases. In general the effect of heating a solid is first to melt it to a liquid and finally to vaporize it, and conversely if a vapour is cooled it passes through the liquid to the solid state. We shall see, however, that both these statements need qualifying. The different states of a given substance differ in energy content. In a solid the atoms or molecules have only sufficient thermal energy to vibrate about their mean positions,* and the mean positions of different atoms (molecules) are fixed in relation to one another. The fact that solids have measurable, though usually small, vapour pressures shows that the liquid state is not a necessary intermediate stage between the solid and vapour phases, i.e. solids may slowly vaporize at constant temperature. Moreover, if a solid with a high vapour pressure is heated rapidly it may pass from the solid to the vapour

* In the next chapter, where we deal in more detail with solids, we shall see that this statement also is not always true.

state without melting (sublimation), as in the case of iodine. Conversely, if a vapour is rapidly cooled the substance may deposit as the solid. There is also an exception to the general rule that if a liquid is cooled sufficiently it will solidify under atmospheric pressure. A solid is stable only if the amplitude of the oscillations of the constituent atoms is small compared with the interatomic distances. Helium forms a true solid only under pressures greater than 25 atmospheres; at lower pressures two liquid phases are formed which possess many abnormal properties. The following points about change of phase may be noted. A solid cannot be superheated, but a liquid may be supercooled. As soon as the energy content of a solid reaches a certain critical value the whole structure collapses. Supercooled liquids are unstable relative to the crystalline solid, and in general the introduction of a nucleus of the solid leads to immediate crystallization of the whole mass of liquid. In a few cases, however, the supercooled liquid reverts with extreme slowness to the crystalline state. This is so with glasses, which are highly supercooled melts and can be remelted and cooled many times without devitrification taking place. Gases differ from liquids not only in the greater kinetic energy but also in the greater mean separation of the molecules. As an alternative to reducing the temperature of the gas, increasing the pressure (at constant temperature) may be used to condense a gas to a liquid. In this way the molecules are brought nearer together until within the range of one another's attractive forces. Increase of pressure, however, results in liquefaction only if the temperature is below a certain value (the critical temperature); above this temperature a gas cannot be liquefied whatever the pressure.

Whereas in a solid the atoms have only sufficient thermal energy to vibrate about their mean positions, in a liquid they are free to move relative to one another. One of the characteristics of solids is that they possess rigidity, shape, and size, and offer considerable resistance to mechanical deformation. A liquid, however, accommodates itself, like a gas, to the shape of the containing vessel, but unlike a gas does not expand to fill all the available space. On account of the fluidity of liquids it was at first thought that their properties could be treated theoretically by methods analogous to those used for gases (kinetic theory). However, in a liquid the molecules are in contact with neighbouring molecules, as is the case in solids, whereas in a gas the mean separation is far greater than the molecular diameter (cf. mean free path of $6{\cdot}25\times10^{-6}$ cm. with the molecular diameter $3{\cdot}66\times10^{-8}$ cm. for O_2 at N.T.P.). From the geometrical viewpoint the essential differences between a solid and a liquid are that

(1) in the former the nearest neighbours of a given molecule are always the same molecules arranged in the same way, but whereas in a liquid there may be the same average number of nearest neighbours, the molecules are constantly changing places so that a molecule has not always the same neighbours;

(2) in a solid the arrangement of molecules is periodic in space, i.e. there is 'long-distance' order. In a liquid this is absent and the number and arrangement of second nearest neighbours, for example, will vary from one molecule to another.

Accordingly when we compare such properties as density, thermal expansion, and compressibility for solids and liquids on the one hand with those of gases we find that they are of the same order of magnitude for the two former states of aggregation but very different for the latter. The densities of gases range from about 10^{-4} to 10^{-2} gram/c.c. and are related in a simple way to the masses of the atoms (or molecules) since a gram molecular weight of any gas at N.T.P. occupies 22·4 litres. The densities of most liquids and solids lie between 1 and 5, though solid hydrogen lies well outside this range and metals vary from 0·5 (lithium) to 22·5 (osmium).

Density of hydrogen		*Density of radon*		
Solid	0·0763 g./c.c.	Solid	4·0 g./c.c.	approx.
Liquid	0·07 (−252° C.)	Liquid	4·4 (−62° C.)	
Gas	0·00009 (N.T.P.)	Gas	0·01 (N.T.P.)	

We should note that the densities of solids are not related in such a simple way to the masses of the component atoms as is the case with gases. The density of a solid is a function of the mass of the atoms and of their concentration in space, and the latter depends both on the arrangement of the atoms relative to one another (i.e. the pattern of their centres) and on their distance apart. Thus although the atomic weights of osmium and lead are very similar (190·3 and 207·2 respectively) and the atoms are arranged in the same way in the crystalline solids (both are cubic close-packed) yet their densities are 22·5 (Os) and 11·7 (Pb). In osmium the distance between an atom and its nearest neighbours is 2·98 A., but in lead 3·86 A.

In general the density of a substance in the liquid state is less than that of the solid, the motion of the atoms or molecules in the liquid resulting in a less efficient packing. Certain metals such as bismuth are exceptional in this respect. The most compact arrangements for atoms are the various types of close-packing which we described in the last chapter, and the majority of metals crystallize with close-packed structures. We should also expect the atoms in a liquid metal, at any rate at temperatures just above the melting-point, to be practically close-packed. Solid bismuth has a rather more 'open' structure than most metals, so that the atoms in the liquid are actually more closely packed than in the solid. Compare:

	Bi (271° C.)	Hg (−38·8° C.)
Density of solid .	9·67	14·193 g./c.c.
Density of liquid .	10·00	13·690

The coefficient of thermal expansion (cubical) at constant pressure is of the same order of magnitude for solids and liquids but very different from that of gases. For the solid elements it ranges from 1 to 30×10^{-5}, and

liquid mercury has about the same value ($18{\cdot}2 \times 10^{-5}$) as rhombic sulphur or solid lithium. For a gas, on the other hand, the value varies directly as the absolute temperature (at constant pressure), i.e. the volume increases by 1/273 (approx. 4×10^{-3}) of its value at 0° C. for every degree rise in temperature. In Fig. 30 we show the variation with temperature of the coefficient of thermal expansion and of the specific heat at constant

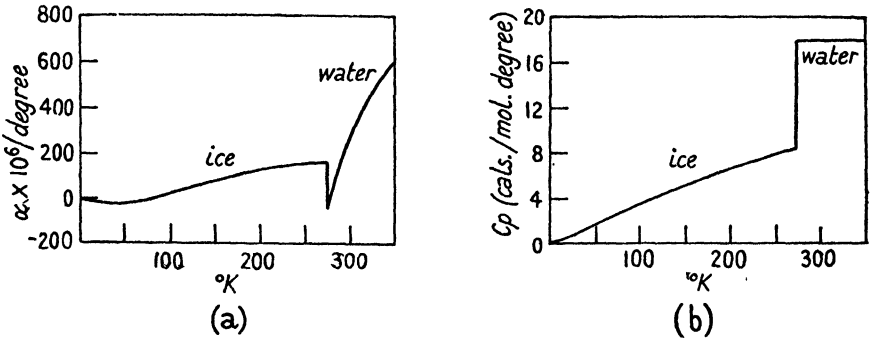


FIG. 30. (*a*) Variation with temperature of the coefficient of volume expansion (α) of water at atmospheric pressure. (*b*) Variation with temperature of the specific heat of water at constant pressure.

pressure of water in the solid and liquid forms. In both cases those quantities are of the same order of magnitude in these two states of aggregation.

So much for the resemblance between solids and liquids in contrast to gases. This resemblance raises the question, How are the properties of a substance affected by the process of melting? The extent to which a particular physical property is altered when the substance passes from the solid to the liquid state not only varies for different properties but also depends on the type of crystal structure (metallic, ionic, etc.) which the substance adopts. Some properties are, of course, characteristic of the solid state and have no meaning when applied to liquids, i.e. hardness, cleavage, and other mechanical properties. Birefringence is also a property almost entirely confined to solids. All crystals other than those with cubic symmetry (see Chap. V) exhibit birefringence. The isotropy of cubic crystals is due to the very high symmetry of their internal atomic arrangement; that of gases, liquids, solutions, and glasses results from the random (or at least highly irregular) arrangement of the constituent atoms or molecules. Any influence which tends to produce orientation in the latter cases may lead to the development of birefringence. Thus certain liquids become birefringent in strong magnetic or electric fields and solutions of substances with very long molecules may show 'flow birefringence' when flowing through a fine capillary tube (e.g. solutions of tobacco mosaic virus). Glass subjected to strain and 'liquid crystals' are also doubly refracting.

The magnitude of the electrical conductivity of ionic crystals is very

different for the solid and the melt, since the conductivity is due to the movement of ions, i.e. is electrolytic as opposed to the electronic conduction in metals. The conductivity of ionic crystals is appreciable only at temperatures approaching the melting-point, having values around 10^{-4} ohm^{-1} cm. and decreasing rapidly with temperature. For fused halides typical values range from 0·1 to 10 ohm^{-1} cm., just above the melting-point. On the other hand, the electrical and optical properties of metals (conductivity, opacity, reflecting power) which are due to the mobility of the free electrons are of the same order of magnitude for the solid and liquid. In a similar way those properties of molecular crystals which are determined by the electronic configuration within the molecule are much the same for the liquid as for the solid.

If applied to an atom or molecule of a gas the term environment would have no useful meaning; there is random arrangement of the particles, and these are in contact only when collisions occur. In a liquid the environment of an atom or molecule is continually changing both as regards number and orientation of neighbours but only within certain limits, so that we are justified in talking of its mean environment. When considering the environments of atoms in liquids it is convenient to distinguish between atomic and molecular liquids. The former are composed of discrete atoms no one of which is attached permanently to any other; in the latter the structural units are molecules, groups of atoms bound much more tightly within the group than to atoms in other molecules. In an atomic liquid an atom has usually a large number of nearest neighbours (ideally twelve for a perfect close-packed liquid) at approximately the same distance. In a molecular liquid, however, the environment of an atom is a function of (1) the actual internal structure of a molecule, which remains sensibly constant, and (2) the way in which the molecules are packed together. This point is easily illustrated by means of a 2-dimensional analogy. In Fig. 31 (*a*) we show a group of close-packed atoms, each having six nearest neighbours. Fig. 31 (*b*) shows a group of close-packed molecules, each of which consists of three atoms. The packing of the molecules in (*b*) is the same as that of the *atoms* in (*a*), but the nearest neighbours of an *atom* in (*b*) are the two other atoms of its own molecule. The next nearest neighbours are much farther away and consist of some four or five atoms of adjacent molecules. The way in which the molecules pack together will be determined by two factors, apart, of course, from temperature. These factors are (1) the shape of the molecule (2) the presence of polar groups in the molecule. (We include under (2) any strong interaction between particular atoms of different molecules.) Increase in the thermal energy of the molecules tends naturally to decrease the importance of both of these factors, but at temperatures not much above the melting-point we should expect them to play nearly as large a part in determining the structure of the liquid as that of the solid at lower temperatures. Since we shall be considering the packing of molecules in solids in a later section, we can postpone further discussion of this subject.

In favourable cases a considerable insight into the structure of simple liquids can be obtained by studying the way in which the intensity of X-rays diffracted by a liquid varies with the angle of diffraction. In general liquids give poor X-ray diffraction patterns compared with those of solids, and the exposure times required are very large. As examples of liquids of three different kinds which have been studied in this way we

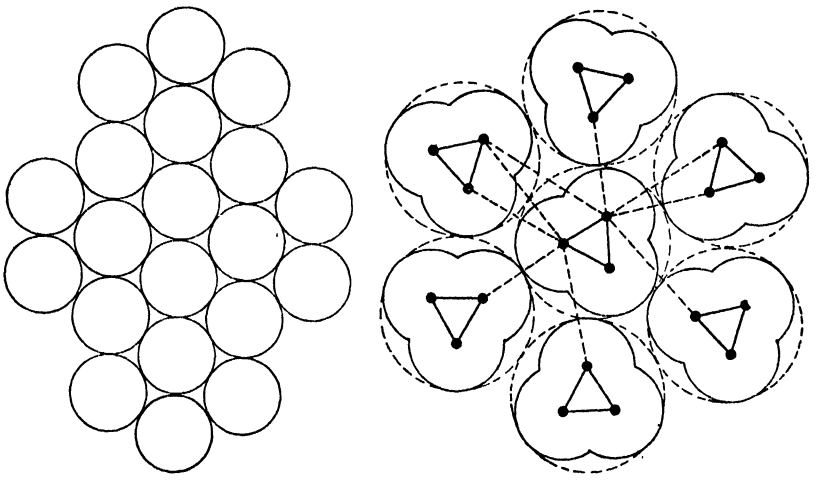


FIG. 31. Close packing of (*a*) single atoms, (*b*) triatomic molecules.

may mention mercury, yellow phosphorus, and water. (We shall discuss the structure of water in more detail in Chap. XI.) In the case of mercury the experimental scattering curve agrees closely with that calculated for a close-packed liquid. Liquid yellow phosphorus is a liquid of quite a different type. It consists of tetrahedral P_4 molecules, so that the nearest neighbours of any atom are the three other atoms of its own molecule. All other neighbours are at a much greater distance as explained above (Fig. 31). The intramolecular P—P distance is 2·25 A., but the distance to the next nearest neighbours (some 6 to 8 in number) is about 3·9 A. Water is a very abnormal liquid in many respects. Instead of being, like H_2S, a simple close-packed molecular liquid it has a very open structure derived from that of ice, in which every molecule is surrounded tetrahedrally by four others. Owing to their very small scattering-power for X-rays, hydrogen atoms cannot be directly located, but their positions can be deduced because they are largely responsible for the directed attractive forces between neighbouring oxygen atoms (see 'Hydrogen Bond', Chap. VII, and 'Hydroxyl Bond', Chap X). From the X-ray diffraction pattern given by water at 1·5° C. it is deduced that every oxygen atom is surrounded on the average by 4·4 nearest neighbours at 2·9 A. and by a group of 'next nearest' neighbours at about 4·5 A. These figures show the close relation between the structures of water and of ice, in

which the distances from a given oxygen atom to its nearest and next nearest neighbours are 2·71 A. and 4·47 A.

LIQUID CRYSTALS

We have observed that if a crystalline solid is heated it melts sharply at a definite temperature which is characteristic of the particular element or compound, i.e. there is a sudden change from the ordered structure of the crystal to the liquid with its random arrangement of atoms or mole-

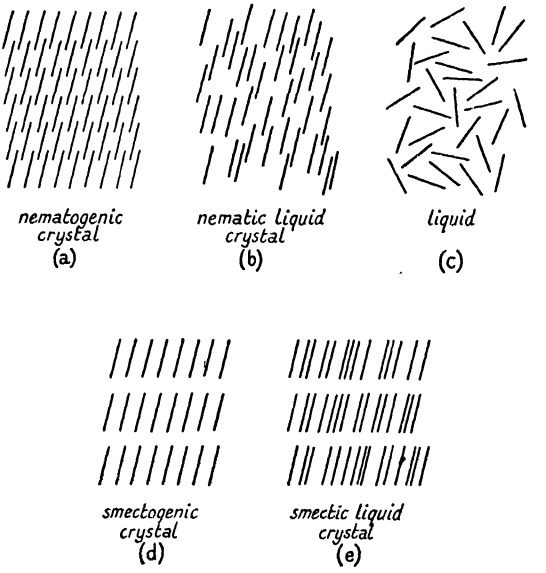


FIG. 32. Possible types of arrangement of long rod-shaped molecules (2-dimensional).

cules. There are a few exceptions to this rule, but since they are all organic compounds we shall give them only a brief mention. The molecules of these compounds are very unsymmetrical in shape, being rod- or lath-shaped, and they form phases called liquid crystals in which the relative orientation of the molecules in the crystal is to some extent preserved. We remarked that the packing of the molecules in a molecular liquid must be governed by factors similar to those which determine the structure of the solid. For example, molecules of approximately spherical shape (such as CCl_4) are likely to be more or less close-packed in both the solid and liquid states. For molecules of extreme shape, however, some interesting possibilities arise. We may again use a 2-dimensional analogy to illustrate this point. Let us suppose that the molecules are arranged in the crystal as shown in Fig. 32 (*a*). The completely disordered state, corresponding to the true liquid, would be represented by (*c*). The change from (*a*) to (*c*) requires a considerable increase in the thermal energy of the molecules, and it is easy to imagine that as the crystal is heated an

intermediate state (*b*) could arise in which the parallel orientation of the molecules is retained but the periodicity characteristic of the crystal is lost. This intermediate state is described as a nematic liquid crystal. For a crystal in which the molecules are arranged (with their axes parallel) in parallel layers instead of interleaved as above, the corresponding liquid crystalline state (smectic) is that shown in Fig. 32 (*e*). In this case there is no longer regular spacing of the molecules within each layer but the molecules are still arranged in parallel layers. It will be obvious that there are many theoretically possible states intermediate, from the geometrical point of view, between solid and liquid, but for discussions of these and of the striking optical properties of liquid crystals we must refer the reader to other works. The types of molecular arrangement in the crystal which are likely to give rise to nematic or smectic liquid crystals are those shown in Fig. 32 (*a*) and (*d*).

GLASSES

We remarked previously that whereas solids cannot be superheated (i.e. heated to temperatures above their melting-points without melting) liquids may be supercooled, and certain supercooled melts show little tendency to crystallize. The technically important glasses are the best-known examples of such supercooled melts, but the term glass may be applied to any material with the following characteristic properties. A glass resembles in some respects a normal solid and in others a liquid. At a sufficiently low temperature (e.g. at room temperature in most cases) a glass forms a rigid mass, sometimes possessing considerable mechanical strength, with a definite hardness, small thermal expansion, and a characteristic conchoidal fracture. Glasses when free from strain are isotropic and, unlike true crystalline solids, do not melt sharply but begin to soften at temperatures well below those at which they flow freely. Like liquids they give X-ray diffraction patterns consisting of a few rather diffuse rings, in contrast to the numerous well-defined reflections from crystals. On account of our familiarity with glass-ware we are apt to overlook the fact that the vitreous state is a rare physical state. Of the elements, only one, selenium, forms a glass, though plastic sulphur has some of the properties of a vitreous solid. Among compounds, the only ones which form glasses are a few oxides and oxy-salts, and BeF_2.

The oxides are B_2O_3, SiO_2, GeO_2, and a number of trioxides and pentoxides of elements of the fifth Periodic Group. The important vitreous oxy-salts are mostly borates, silicates, or phosphates, of which the following are typical: $Na_2B_4O_7$, $Li_2B_2O_4$, $CaSiO_3$, $PbSiO_3$, $Cd_2P_2O_7$. The numerous varieties of glass used for glass vessels, windows, lenses, and so on consist of mixtures of silicates (or sometimes boro-silicates) of alkali or alkaline-earth metals, lead, and sometimes also aluminium.

X-ray studies of vitreous materials show that the immediate environment of the atoms is similar to that in the crystalline state, but that the arrangement of the more distant neighbours is less regular and varies from

atom to atom. Thus in vitreous silica or BeF_2 there are tetrahedral SiO_4 and BeF_4 groups respectively, but these are linked together at random instead of with perfect 3-dimensional periodicity. The gradual softening of glasses as opposed to the sudden melting of a crystalline solid results

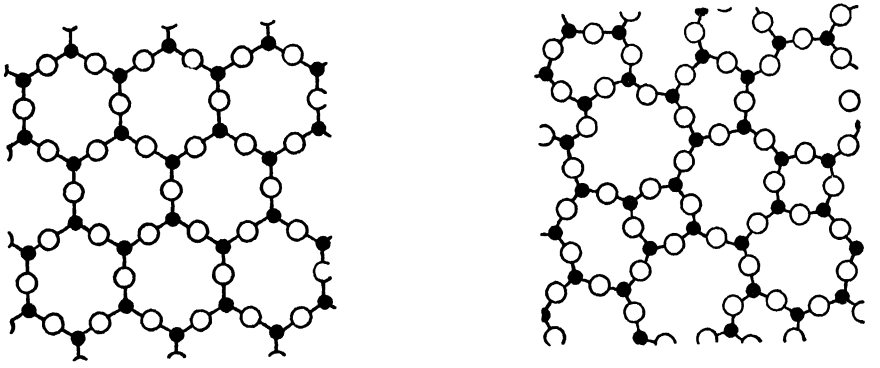


FIG. 33. Diagrammatic representation of the crystalline and vitreous forms of a compound A_2X_3 (after Zachariasen).

from this structural non-equivalence of the atoms. The sort of difference which exists between a crystal and a glass may be illustrated diagrammatically as in Fig. 33. We cannot discuss here the various attempts which have been made to account quantitatively for the X-ray diffraction patterns of glasses, but the following general considerations are relevant. For a glass the energy content must not be very much greater than that of the normal crystalline phase. A glass is usually formed by rapid cooling of the liquid, whereby the final ordering of the atoms into the regular array characteristic of a crystal is rendered difficult. It is probable that any glass will revert to the more stable crystalline state if given sufficient time even at ordinary temperatures, but the transition is facilitated by a rise of temperature. The devitrification of vitreous silica after repeated heating and even of ordinary soda-silica glasses is a well-known phenomenon, but 'vitreous ice' provides a more striking example. Water vapour can be condensed below $-110°$ C. to a glass, but if this is warmed even to $-80°$ C. it crystallizes.

It is tempting to speculate on the reasons why such a limited number of elements and compounds form glasses. In crystalline selenium the atoms are linked together by strong bonds into spiral chains which extend throughout the crystal and are packed together with their axes parallel (see p. 538). The forces between atoms of different chains are much weaker than those between adjacent atoms of a given chain, as shown by the respective interatomic distances. Liquid selenium probably consists of Se_2 molecules, so that when this liquid is slowly cooled these molecules first link up to form chains and the chains arrange themselves in an orderly way, i.e. crystalline selenium is formed. If, however, the liquid is cooled very rapidly it is impossible for the second process, viz. the

joining up and aligning of the fragmentary chains, to go to completion, and a glass results. Sulphur does not form a glass, but if the liquid is rapidly cooled, plastic sulphur is formed. In the stretched material we now know that there are chains of sulphur atoms which have been oriented by the process of stretching. In ordinary plastic sulphur these chains will be twisted and intertwined. In the transition from liquid to rhombic sulphur the diatomic molecules present in the liquid link up to form S_8 molecules consisting of closed eight-membered rings which then pack together in the crystal. In the formation of plastic sulphur this linking up into rings all of one size does not take place and we are left with portions of sulphur chains. It is seen that in the case of both sulphur and selenium the chief consideration is the formation of two strong bonds; once these are formed other details of atomic arrangement are only of secondary importance. Only in the crystalline elements does every atom form two such bonds (neglecting the Se atoms at the surfaces of a crystal), but in vitreous Se and plastic S the majority of atoms are satisfied in this way so that these non-crystalline states are tolerably stable.

Now the glass-forming oxides and oxy-salts would at first sight appear to have little in common with selenium or sulphur. However, in most if not all of these compounds we may regard as the primary structural units closely knit groups such as BO_3, SiO_4, or PO_4 which will be present in the melts. These units join up by sharing corners, but the precise way in which they link up is of secondary importance so long as they join up. (As proof of this we may quote the extraordinary variety of silicate structures; when complex borates and phosphates have received more attention it may be found that they rival silicates in this respect.) In glasses of different sorts the average number of corners of, e.g., SiO_4 tetrahedra which are shared with others will vary with the Si:O ratio just as in crystalline silicates. For example, in vitreous silica each SiO_4 group is linked through its oxygen atoms to four others, the regular spatial arrangement of the silicon and oxygen atoms which is characteristic of the crystalline forms of silica being absent. In vitreous $CaSiO_3$, on the other hand, only two corners of each SiO_4 tetrahedron are shared, leading to rings or chains just as in the case of sulphur and selenium. The reader will have a better appreciation of the great variety of ways in which SiO_4 tetrahedra can be linked together after a study of the structures of crystalline silicates has been made (Chap. XIV). It is perhaps worth mentioning that glasses are not formed by simple ionic crystals or by compounds which form homopolar crystals.

SOLUTIONS

There are six kinds of solutions:

	Gas	*Liquid*	*Solid*
Gas . . .	*a*	*b*	*c*
Liquid . .	—	*d*	*e*
Solid . . .	—	—	*f*

We shall have very little to say about the first four, *a–d*. Solutions of gases in other gases, usually called mixtures of gases, have two characteristics. Firstly, there is very little interaction, except, of course, in cases where chemical reaction occurs, between the atoms or molecules of one gas and those of the other. In general the properties of the mixture are the sum of those of the constituent gases. Secondly, gases mix in all proportions. This is in marked contrast to the other combinations, *b–f*, where generally the miscibility is limited. Solutions of gases in liquids will interest us only when the structure of a gaseous molecule is different from that of the dissolved gas. This point will be discussed in the next section.

Solutions of Gases in Solids

The absorption of gases by certain solids is a matter of considerable importance to the chemist and also to the physicist. We may mention the use of charcoal to absorb gases, to separate gases by utilizing the selective absorption of one gas rather than another, and to remove the last traces of gas in vacuum systems. By bringing together the molecules of different gases, such solids can act as catalysts for some reactions between gases. The subject of the absorption of gases by solids is a large and complicated one which is largely concerned with the nature of surfaces and with their interaction with gas molecules. When we described the structure of a crystal of sodium chloride we said that every sodium ion in the crystal is surrounded by six chlorine ions and conversely every chlorine ion by six sodium ions. This is true for ions inside the crystal but not, of course, for those at the bounding surfaces. The environments of these ions will be unsymmetrical, so that at the surfaces of solids there may be very strong fields. The result is that atoms or molecules of a gas are attracted by and held firmly on to the surfaces of many solids. The difficulty of removing the last traces of gas from glass surfaces, a process which necessitates baking the surface *in vacuo* at a temperature not far from the softening-point of the glass, is familiar to those whose work requires high vacua. Certain solids, notably charcoal, possess very extensive internal surfaces to which the apparent volume of the solid bears no simple relation. Thus charcoal which has been 'activated' by heating *in vacuo* to remove all absorbed gases will take up as much as 170 times its volume of ammonia at room temperature and this volume is greatly increased at lower temperatures. For oxygen the volumes absorbed (all reduced to volumes at N.T.P.) are—18 volumes at 0° C. compared with 230 volumes at −185° C. Charcoal may be regarded as built up of minute portions of the graphite structure (see page 436) linked together in an irregular way so that many of the valencies of the carbon atoms are unsatisfied. The result is a porous material into which gases (and also liquids) can penetrate to be absorbed on the extensive surfaces of the crystallites. We may contrast with graphite two other types of solid which also absorb considerable quantities of certain gases.

The arrangement of the atoms in certain crystals is such as to leave open tunnels throughout the crystal, tunnels large enough to accommodate the molecules of some gases and liquids. We shall describe the structures of typical crystals of this kind in later chapters. The mineral beryl, $Be_3Al_2Si_6O_{18}$, often contains occluded helium which is presumably accommodated in this way, and a group of minerals called zeolites are notable for adsorbing gases such as ammonia, carbon dioxide, and also foreign ions (see p. 482).

As an example of a third type of penetration of gases into solids we may take the absorption of hydrogen by palladium. (One or two other metals also possess this property, but to a much smaller extent.) If metallic palladium is first heated to about 400° *in vacuo* and then cooled (still *in vacuo*) it will then take up some 600 times its own volume of hydrogen. This is a property of the massive metal—if the metal is very finely divided, as for example is the case with colloidal palladium, it will then absorb up to 3,000 times its own volume of the gas, but this large increase is due to the increased surface area. The porosity of palladium to hydrogen has been studied by many workers, and some idea of the ease with which the gas passes through the metal can be gained from the fact that at 476° C. 5,570 c.c. of hydrogen (at atmospheric pressure) pass per minute through palladium foil 0·3 mm. thick and 1 square metre in area into a vacuum. We stated that activated palladium absorbs 600 times its own volume of hydrogen (reduced to N.T.P.). This corresponds to about $\frac{1}{2}$ atom of hydrogen per atom of palladium. If more hydrogen than this is introduced the excess is easily pumped off, and the dissociation pressure of the Pd—H then remains constant until practically all the gas is removed. There has been much speculation as to constitution of this Pd—H system. The hydrogen is presumably accommodated in the interstices of the structure, which consists of a cubic close-packing of palladium atoms, as in other interstitial compounds of metals with the small elements H, B, C, and N. The idea that the hydrogen is ionized, as suggested by the large value of the heat of 'solution' (20 k.cals. greater than the heat of dissociation of molecular hydrogen), is supported by the variation of the paramagnetic susceptibility of the metal with hydrogen content. The susceptibility decreases as hydrogen is introduced, becoming zero at a H:Pd ratio of about 0·5 to 0·6, facts which are interpreted as showing that the hydrogen is completely ionized in the lattice.

We shall have something to say about solid solutions (*f*) in the next chapter. The interaction of solids and liquids (*e*) is of particular interest in chemistry.

Interaction of Solids with Liquids

When a solid is brought into contact with a liquid one or more of a number of phenomena may be observed.

(1) There is apparently no interaction, i.e. the solid is insoluble in the liquid. It is probable that this is never strictly true, but the solubility is in

some cases so small (as of mercury in water) that the solid is regarded as insoluble in the particular solvent.

(2) The solid phase disappears, i.e. becomes dispersed throughout the liquid. The term solution is applied to a homogeneous mixture in which the solute is dispersed throughout the solvent on an atomic (or molecular) scale. Suspensions consist of coarse particles of solid in a liquid, but unlike true solutions these are not stable, the particles settling out under the influence of gravity. Intermediate between true solutions and suspensions are the 'suspensoid' sols, one of the two main types of colloidal 'solution'. (In the other type the dispersed phase is a liquid, and on account of their position between solution and emulsion these are called emulsoids.)

In suspensoid colloidal solutions, or sols, the particle size is commonly of the order of 10^{-4}–10^{-5} cm., as compared with 10^{-8} cm. for atoms and ions. Such particles are sufficiently small to be kept in rapid motion (the Brownian movement) by the thermal energy of the molecules of the liquid medium. The particles are charged, as shown by the following facts. They move under the influence of an electric field, being coagulated at the electrode. The weight of material discharged is not, however, consistent with Faraday's first law of electrolysis. One Faraday (96,500 coulombs) discharges far more than a gram-equivalent of the solid, because the particles are not simple ions. For example, in a gold sol they may consist of 300–400 atoms. Secondly the sols are very sensitive to the addition of electrolytes. Ions carrying multiple charges are more effective in precipitating colloids than singly charged ions. For example, the particles in an As_2S_3 sol are negatively charged and the same weight of As_2S_3 is precipitated by the following relative numbers of Na^+, Ca^{2+}, and Al^{3+} ions:

Na^+	Ca^{2+}	Al^{3+}
566	7·2	1

There are no simple relations between these numbers and the charges on the respective ions because of the selective adsorption of different ions by the particles of the sol.

Owing to the fact that the particles of a sol are so much larger than ions a sol may be freed from excess electrolytes by allowing the latter to diffuse out through a suitable membrane, the pores of which are large enough to allow the free passage of ions but smaller than the sol particles. This process is termed *dialysis*. (One way of effecting such a separation is to place the mixture of sol and salt solution inside a porous pot within the walls of which a membrane of copper ferrocyanide has been deposited, the pot being placed in a vessel containing water.)

Sols of elements and inorganic compounds may be prepared in various ways. For metals the simplest is the reduction of a salt solution by a reducing agent like formaldehyde. Alternatively the metal may be dispersed by forming an alternating arc between electrodes of the metal in water or other suitable liquid. Of the metal sols those of silver and

platinum are the most permanent—if carefully prepared they show no signs of coagulating even after a period of years. If such a sol is evaporated to dryness the colloidal metal will not again 'dissolve' (irreversible colloid), but if certain organic colloids are added to the solution of the metallic salt before it is reduced to metal, the so-called 'protected' colloids are produced and these re-form sols after evaporation and subsequent treatment with water. The formation of sols by compounds such as the hydroxides of tri- and tetravalent metals (Al, Cr, Fe, Sn, Th) is a matter which concerns the chemist in a number of ways. For stability these sols require the presence of small but fairly critical concentrations of other electrolytes, and when the sol is coagulated some of these ions remain adsorbed on the precipitated hydroxide. Thus $Al(OH)_3$ precipitated from a solution of an aluminium salt by sodium hydroxide is never free from sodium salts. Continued washing eventually results in re-formation of the sol. Points like this are of importance in analytical chemistry. The formation of these sols also interests us from the structural point of view. The 'solubility' of many hydroxides in excess alkali was formerly interpreted as evidence for the formation of complex ions (see aluminates, stannites, etc., Chap. IX). In some cases at least the function of the excess alkali hydroxide is to act as a 'peptizing' agent. Peptization is the term applied to the action of a solution containing the appropriate ions in causing a solid to form a sol. In such cases the amount of alkali required is very much less than that which would be required if the process were the neutralization of an acid to form a salt. For example, 1 gram-equivalent of potassium hydroxide peptizes some 200 gram-equivalents of $Sn(OH)_4$ (or $SnO_2.nH_2O$).

(3) The solid takes up a limited amount of the solvent without the formation of a liquid phase. Examples of this behaviour are

(*a*) The formation of a salt hydrate, or of a higher hydrate from one containing less water of crystallization.

(*b*) The adsorption of a liquid by a zeolitic crystal.

From the structural standpoint the processes involved are very different. The crystal structure of a true hydrate (or other crystal containing solvent of crystallization) generally bears no relation to that of the anhydrous compound, so that until the hydration is completed there are two solids present with completely different structures. (The structures of some hydrates are described in Chap. XI.) When a liquid is adsorbed by a zeolite, on the other hand, there is no breakdown of its lattice, which consists of a rigid framework in the interstices of which the solvent molecules are accommodated (see Chap. XIV). In (*a*) the addition of excess solvent simply results in the dissolution of the hydrate (accompanied in some cases by hydrolysis), and in (*b*) the zeolitic crystal may or may not be soluble in the solvent. The zeolites themselves are silicates which are quite insoluble in such solvents as water and alcohol which they adsorb, but crystals such as those of $Pd_2Br_4[As(CH_3)_3]_2$ which retain dioxane zeolitically are soluble in excess of the solvent.

(4) Finally, there may be a chemical reaction between the solid and liquid. It is instructive to try to discover what is the fundamental change taking place in such cases. Consider, for example, some instances of the decomposition of simple inorganic solids by water. How well do the chemical 'equations' written for such reactions indicate the changes which really occur? The following examples will serve as illustrations.

(*a*) $2Na+2H_2O \longrightarrow 2NaOH+H_2\uparrow$
(*b*) $NaH+H_2O \longrightarrow NaOH+H_2\uparrow$
(*c*) $BiCl_3+H_2O \longrightarrow BiOCl+2HCl$
(*d*) $PCl_5+4H_2O \longrightarrow H_3PO_4+5HCl.$

In (*a*) the fundamental process is the ionization of sodium atoms, i.e. the loss of electrons to form Na^+ ions. These electrons are acquired by H^+ ions which are thereby discharged and unite to form H_2 molecules. For every H^+ discharged an OH^- ion remains, leaving a solution containing equivalent amounts of Na^+ and OH^- ions. A crystal of sodium hydride consists of Na^+ and H^- ions. The former are stable in water, but the latter are immediately discharged by H^+ ions, so that the essential reaction is

$$H^-+H^+ \rightarrow H_2.$$

There is no change in the Na^+ ion which previously existed in the NaH crystal and now exists in solution. Of course, as in (*a*) for every H^+ used an OH^- is left. Similarly in the decomposition by water of sodamide ($NaNH_2$) we have

$$NH_2^-+H^+ \rightarrow NH_3.$$

We may say then that reactions of this type result because some ions which are stable in crystals cannot exist in aqueous solution. This is the case not only with some negative ions (H^-, NH_2^-, C_2^{2-}, etc.)* but also with certain positive ions. Thus ions like Cu^+, Mn^{4+}, and Au^{3+} are unstable in aqueous solution and reactions in which they might be expected to be formed are therefore complicated by secondary reactions. Manganese dioxide dissolves in cold concentrated hydrochloric acid, the solution apparently containing trivalent manganese in some form, as evidenced by the formation of complex salts like K_2MnCl_5 when KCl is added. The crystal of MnO_2 contained Mn^{4+} ions, but if the solution in hydrochloric acid is warmed chlorine is evolved and a solution containing Mn^{2+} ions results. The net result is therefore

$$Mn^{4+}+2Cl^- \rightarrow Mn^{2+}+Cl_2\nearrow,$$

though this reaction may proceed through intermediate stages. Again, cuprous sulphate is decomposed by water, so that if we assume this to be an ionic crystal we have

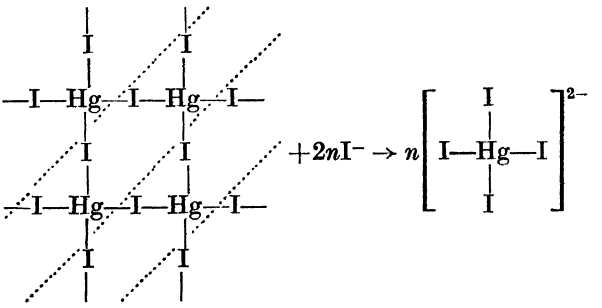
$$2Cu^+ \rightarrow Cu^{2+}+Cu\downarrow.$$

Similarly from AuCl we obtain $AuCl_3$ and Au.

* Not only the carbides of the more electropositive elements such as calcium and aluminium but also the borides, nitrides, and phosphides are probably ionic, so that this list of ions could probably be extended considerably.

In (*c*) and (*d*) we have examples of reactions of quite different types from the above. The compound BiOCl exists only in the solid state so that we cannot simplify the equation. In (*d*) we start with a solid in which every phosphorus atom is bound to chlorine atoms (for the structure of PCl_5 see p. 411) and finish with the phosphorus in the form of PO_4^{3-} ions. In both (*c*) and (*d*), therefore, M—Cl bonds have been broken and M—O bonds formed, so that these reactions differ in this important respect from the previous examples.

It may not be out of place to make a few remarks here on the use of the term *soluble*. This word is used in a number of rather different senses in chemistry. We say that a salt like NaCl is soluble in water, that HgI_2 is soluble in excess of potassium iodide solution, and that a metal such as iron dissolves in, say, dilute hydrochloric acid. In a sufficiently dilute solution of NaCl each Na^+ and each Cl^- ion is surrounded entirely by water molecules, so that the process of dissolution of the crystal has simply involved separation of ions already in existence in the crystal. If we regard a metal as consisting of positive ions held together by free electrons, then the dissolution of the metal in acid is quite similar except that the electrons must be removed by the discharge of H^+ ions (hence the need for an acid). When HgI_2 dissolves in potassium iodide solution, however, there are formed discrete $[HgI_4]^{2-}$ ions which did not exist in the crystal. In a crystal of HgI_2 each Hg atom is linked to four iodine atoms, but each of the latter is shared between two metal atoms to give the Hg:I ratio 1:2. We may represent the reaction diagrammatically:



Structure in Solutions of Electrolytes

In considering the dissolution of NaCl we specified the formation of a solution so dilute that the Na^+ and Cl^- ions were completely surrounded by water molecules. Now if we make a concentrated solution of cobalt chloride in water the solution has a deep rose colour, but if the solution is heated it becomes deep blue, a change which is attributed to the formation of $[CoCl_4]^{2-}$ ions. In other cases, e.g. NaCl, there is no such obvious suggestion of the formation of complex $NaCl_x$ ions in concentrated solutions. When, however, any salt solution is concentrated the growth of the crystalline salt begins when the solution has reached a certain strength and we are naturally led to inquire what is the 'structure' of such a solution or indeed

of any salt solution. This subject forms part of our wider study of the structure of matter in the various states of aggregation, but the elucidation of the structure of solutions is far more difficult than is the case with solids. For our purposes we may put the problem in the form of two questions: What are the structural units in a solution of, say, a salt in a solvent, and how are these units arranged relative to one another and to the solvent molecules? In the case of electrolytes, the study of the electrical conductivity of their solutions has thrown considerable light on these points.

Faraday was responsible for the idea that when a current of electricity passes through a solution it is carried by charged particles, or ions. It was assumed that some of the molecules of the solute broke up into ions when a potential difference was applied to the solution, the degree of dissociation being greater for the more strongly conducting solutions. On this view, however, we might expect that a certain minimum potential difference would be necessary to disrupt the solute molecules, whereas it was known that in many cases a measurable current flowed even when the applied potential was very small. Accordingly Arrhenius (1883) suggested that in any conducting solution a certain number of ions are always present, a definite fraction of the solute having been dissociated at the moment of dissolution of the solute in the solvent. By assuming that the degree of dissociation was greater for 'strong' electrolytes it was unnecessary to postulate that any further dissociation occurred when the potential difference was applied. At about the same time van 't Hoff had found that the ordinary gas laws were often applicable to solutes in dilute solutions. For many dissolved substances the osmotic pressure was found to have the same value as the gas pressure the substance would exert if it were a gas at the same temperature and occupying the same volume as the solution. Some solutes, on the other hand, exhibited a greater osmotic pressure. Arrhenius, noticing that these exceptional solutes were all electrolytes, saw that these abnormal osmotic pressures were consistent with his idea of permanent dissociation. The osmotic pressure of a solution may be determined indirectly from the depression of the freezing-point of the solvent, and we may denote by i the ratio (observed depression of freezing-point)/(theoretical depression). High osmotic pressures would be expected if every positive or negative ion contributed to the pressure in the same way as an undissociated molecule. Arrhenius also calculated the factor i independently from conductivity measurements in the following way. If in a solution containing m molecules of solute a fraction α of these have dissociated, and if on dissociation each molecule produces n ions, then instead of m molecules we have $m(1-\alpha)+mn\alpha$ particles (molecules and ions), so that

$$i = \frac{m(1-\alpha)+mn\alpha}{m} = 1-\alpha+n\alpha.$$

If we assume that at infinite dilution all the molecules are dissociated and

that in dilute solutions the mobility of the ions is independent of the concentration, then the ratio of the equivalent conductivity* Λ at any given concentration to that at infinite dilution (Λ_∞) will be a measure of the degree of dissociation α,

$$\frac{\Lambda}{\Lambda_\infty} = \alpha.$$

Hence i can be calculated from conductivity measurements and compared with the values from the depression of freezing-point. The values agree well, as is seen from the following examples:

	i (*f. pt.*)	i (*conductivity*)
KCl	1·82	1·86
$Ba(OH)_2$ . . .	2·69	2·67

In spite of this apparent confirmation, Arrhenius's hypothesis met with serious objections. Firstly, if a partially dissociated electrolyte obeys the gas laws then the relation between degree of dissociation (α) and dilution should be the same as for the dissociation of a gas, viz.:

$$\frac{\alpha^2}{(1-\alpha)V} = \text{constant},$$

or since $\alpha = \dfrac{\Lambda}{\Lambda_\infty}$, $\dfrac{\Lambda^2}{\Lambda_\infty(\Lambda_\infty - \Lambda)V} = \text{constant}.$

The relation is true for dilute solutions of weak electrolytes (e.g. NH_4OH, acetic acid), but breaks down for strong electrolytes (e.g. KCl) and even for concentrated solutions of weak electrolytes. Secondly, when Arrhenius put forward his theory it was generally supposed that in the solid form a strong electrolyte like KCl consisted of molecules, but the study of the crystal structures of such salts showed them to be completely ionized in the solid state. Supposing then that the salt is completely ionized at infinite dilution, the problem now is to explain, not why the factor i is greater than unity but why, in more concentrated solutions, it should ever be less than two. To overcome these difficulties the idea of the 'ionic atmosphere' was introduced. Just as in a crystal a positive ion is surrounded by a number of negative ions, so in solution we must assume that there will be a tendency for an ion to be surrounded by those of opposite sign, though this tendency will be opposed by the thermal motion of the ions and of the solvent molecules. Consequently we should expect any ion to be surrounded, at any given instant, by rather more ions of opposite sign than of its own sign. We are not now talking of nearest neighbours; in a dilute solution these will be all, or nearly all, solvent molecules. (The extent of solvation of ions and the strength of attraction of the ions for the solvent molecules is greater for strongly polar solvents like water, in which many ions are permanently hydrated.) The asymmetry of this ionic atmosphere will depend on a number of

* Equivalent conductivity = specific conductivity (reciprocal of specific resistance) multiplied by the volume in c.c. of solution containing 1 gram-equivalent of solute.

factors—the ionic charges, the dielectric constant of the solvent, the concentration of the solution, and the temperature.

The presence of this ionic atmosphere affects the conductivity of the solution in two ways. A positive ion is surrounded by a slightly negative ionic atmosphere. When the ion moves rapidly there is a slight time-lag between the neutralization of the negative atmosphere behind the ion and the building up of the positive atmosphere ahead of it, resulting in a retarding force on the ion. This retardation increases with the concentration, leading to the reduced conductivity at higher concentrations which Arrhenius assumed was due to a smaller degree of dissociation. The second effect due to the ionic atmosphere arises in the following way. Around a positive ion there is a slight excess of negative ions which are moving in the opposite direction. Since the ions carry solvent with them, there is in the immediate neighbourhood of a given ion a flow of solvent in the opposite direction to its own movement. The magnitude of this *electrophoretic* effect depends on the asymmetry of the ionic atmosphere and hence on the concentration. Together these two effects lead to an equation of the form

$$\Lambda_\infty - \Lambda = (a\Lambda_\infty + b)\sqrt{2c},$$

where c is the concentration in gram-equivalents per litre. The existence of the ionic atmosphere has been confirmed in a rather elegant manner. If we suppose that the central ion could be removed from its ionic atmosphere, the asymmetry of the latter would soon be neutralized by the movement of the neighbouring ions. This process would take a certain time (*the time of relaxation*)—of the order of $10^{-10}/c$ seconds. Therefore if we can make the ion move so fast that it travels a distance many times greater than the diameter of its ionic atmosphere in this time, then the retarding effect due to the asymmetry of the ionic atmosphere will disappear. The electrophoretic effect, which depends on the concentration, will never quite disappear. Accordingly, it is found that in very high fields the equivalent conductivity Λ increases, approaching a limiting value nearly equal to Λ_∞, though on account of the residual electrophoretic effect the field required to attain this limiting value is greater the greater the concentration. The concept of the ionic atmosphere was found to be mainly responsible for the difference between Λ and Λ_∞ of dilute aqueous solutions of strong electrolytes (Debye-Hückel theory, 1923.)

Concentrated solutions present a more complicated problem. The work required to separate charges q_1 and q_2 at a distance d apart in a solvent of dielectric constant K is $q_1 q_2/Kd$. If they are far apart this work is small compared with their thermal energy, $2kT$, and this is the case in the dilute solutions treated in the Debye-Hückel theory. In more concentrated solutions, however, some pairs of ions will approach so close to one another that they remain associated (ion-pair) until they are eventually separated by receiving sufficient energy from solvent molecules. Such ion-pairs will not contribute to the conductivity. The very large increases in conductivity observed in some solutions (e.g. of $CoCl_2$ in acetone) as the

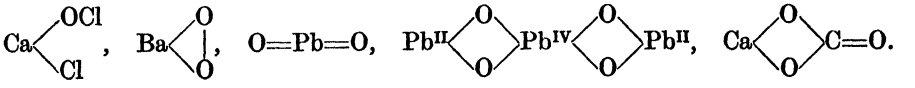
field is increased can only be explained by the dissociation of these ion-pairs. In water, however, such association is less likely to occur because of the large dielectric constant and the hydration of the ions. According to Bernal and Fowler, all positive ions except the largest (K^+, NH_4^+, Rb^+, Cs^+, Tl^+) are permanently hydrated in solution, the univalent ions and Be^{2+} being 4-coordinated and all others 6-coordinated. Of the negative ions probably only OH^- and F^- are hydrated.

These remarks are probably sufficient to show that there is a 'structural chemistry' of solutions as well as of liquids and solids.

THE RELATION BETWEEN THE STRUCTURES OF A SUBSTANCE IN DIFFERENT STATES OF AGGREGATION

The study of the relation between the structures of a substance in the different states of aggregation is important for a number of reasons. Apart from the fact that our knowledge of the stereochemistry of a substance is incomplete if we only know its structure in, say, the solid or vapour state, there are more cogent reasons for studying this aspect of structural chemistry. As soon as a consistent set of (relative) atomic weights had been established, correct empirical formulae could be assigned to compounds showing the relative numbers of atoms of different kinds which were combined together. In the case of vapours it was also possible to find the actual numbers of atoms in a single molecule, i.e. to determine the ratio of the molecular weight to the sum of the weights of the atoms in the empirical formula. For example, a molecule of ethane has the composition C_2H_6 and not CH_3 and the vapour of phosphorus just above its boiling-point consists of P_4 molecules, not single atoms. The molecular weights of substances in solution can also be found, though in this case we cannot discover whether or not solvent is combined with the solute molecules.

The next problem is to find how the atoms are arranged in space relative to one another. Until the application of X-rays to the study of structures of crystals there was no way of determining the degree of molecular complexity in a solid. Only the empirical formula of a solid was known, but quite naturally attempts were made to assign structural formulae to solids, formulae which should now be only of historical interest. Since classical structural chemistry had been concerned only with isolated molecules, in the vapour or dissolved state, it was natural to assume that discrete molecules existed also in solids. Thus we find formulae such as



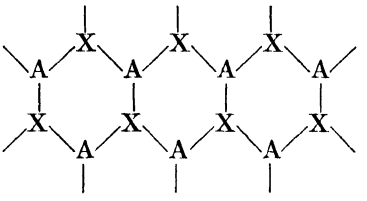
Later it was realized that salts consist of charged atoms or groups of atoms (simple or complex ions), so that $CaCO_3$, for example, is $Ca^{2+}(CO_3)^{2-}$, and the enthusiasm for 'ionic' structural formulae led in some cases to new but still incorrect formulae for solid salts. For example, cupric chloride

crystallizes from water as blue crystals with the composition $CuCl_2.2H_2O$, and a dilute aqueous solution of the salt is blue. A concentrated solution acidified with HCl is, however, brown, and the presence of $[CuCl_4]^{2-}$ ions was demonstrated by the movement of these ions towards the anode when the solution was electrolysed in contact with a solution of a colourless chloride. From this it was suggested that $CuCl_2$ might be $Cu^{2+}[CuCl_4]^{2-}$, i.e. assuming that the ions existing in the solution also exist in the crystal. The structure of anhydrous cupric chloride is not known, but it is certainly not $Cu[CuCl_4]$. Cobalt chloride, which forms analogous $[CoCl_4]^{2-}$ ions, crystallizes with a layer structure described on page 278. The formulation of red lead as lead orthoplumbate, $Pb_2[PbO_4]$, might also be quoted in this connexion. A further result of the ignorance of the structure of solids was the postulation of hypothetical acids from which it was supposed certain metallic compounds were derived. The silicic and boric acids provide a good illustration of this point—the structures of silicates and borates are described in Chapters XIV and XV respectively.

These difficulties all arise from the simple fact that whereas in solution or in the vapour state a compound must exist in the form of finite molecules, in the crystal indefinitely extended molecules or complex ions may occur, which are terminated only at the boundaries of the crystal. Thus a compound with the empirical formula AX must exist in the vapour either as simple molecules AX or as some comparatively simple *finite* polymer, such as A_2X_2, but in the crystal we may find either infinite 1-dimensional molecules,

—A—X—A—X—A—X—

infinite 2-dimensional molecules,



or finally infinite 3-dimensional 'molecules' as in the case of a crystal of ZnS (4-coordination) or NaCl (6-coordination). It will be appreciated that if in a complex silicate, for example, which we may write $M_x^m Si_y O_z$, there is an infinite 1-dimensional complex ion with the empirical composition (Si_yO_z), then to talk of the corresponding acid $H_{mx}Si_yO_z$ is meaningless. Even when the salt contains finite complex ions, there is no simple relation between the structure of the free acid and the salt, nor is there any connexion between the stability of the free acid and its salts.

Let us now compare the structures of a few substances in the vapour and crystalline states. The inert gases and many metals (e.g. Hg, Na, K, Zn, Cd) form monatomic vapours and the single atoms are the structural units in the solids. The atoms are close-packed (or approximately so), and

there is no segregation of the atoms into groups distinguishable as molecules. Many non-metals are diatomic in the vapour state (O_2, N_2, halogens) and the same molecules persist in the liquid and solid states, but a few elements form more complex molecules at temperatures just above their boiling-points, e.g. S_8, P_4, As_4. These three elements are all dimorphous. Rhombic sulphur has been shown to consist of S_8 molecules, but the structure of monoclinic sulphur is not known. The tetratomic molecules P_4 and As_4 almost certainly exist in the white and yellow forms of these elements, but only the 'metallic' varieties, which have quite different structures, have been studied in detail. These complex molecules dissociate at higher temperatures, first into simpler molecules such as S_2, and then finally into atoms. The vapours of compounds necessarily consist of molecules, but not all compounds vaporize without decomposition when heated. Many salts containing complex ions decompose on heating (e.g. $CaCO_3 \longrightarrow CaO+CO_2$) and simple molecules may break up to give molecules of different composition. These processes are not necessarily reversible as is depolymerization, which reverses on cooling. Thus

$$2N_2O_5 \rightarrow 2N_2O_4+O_2$$

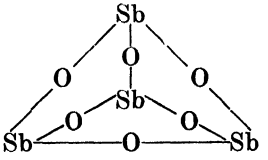
but

$$2NO_2 \rightleftharpoons 2NO+O_2.$$

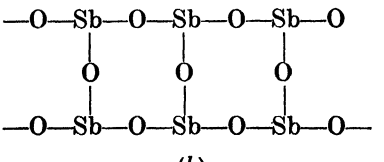
and finally

$$2NO \rightleftharpoons N_2+O_2.$$

Just as many elements do not vaporize directly to atoms so the molecules in the vapour of a compound are not necessarily the simplest possible molecules. For example, P_4O_{10} molecules persist in the vapour of phosphorus pentoxide up to at least 1,400° C. and the trioxides of phosphorus, arsenic, and antimony remain in the form of dimeric molecules up to very high temperatures (e.g. Sb_4O_6 at 1,560° C.) These molecules occur in crystalline As_4O_6 and in one form of Sb_4O_6, which is dimorphous. The idealized form of such a molecule is shown at (*a*), the As or Sb atoms being situated at the apices of a tetrahedron and linked together by the oxygen atoms. Similar molecules presumably occur in crystalline P_4O_6, the structure of which is not known, for its molecular weight in benzene and CS_2 corresponds to the double molecule P_4O_6, and electron diffraction studies have shown that the molecules in the vapour have the tetrahedral configuration shown at (*a*). The second polymorphic form of antimony trioxide contains chains of the type shown at (*b*). The relation between



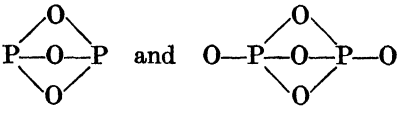
(*a*)



(*b*)

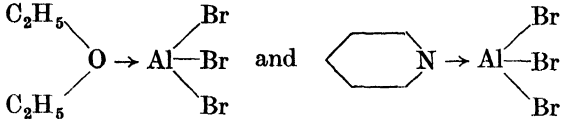
the finite tetrahedral molecule (*a*) and the infinite chain (*b*) is similar to that between the S_8 ring molecule in sulphur vapour and in rhombic sulphur and the infinite chains in plastic sulphur and crystalline selenium

(q.v.). In the vapour of phosphorus pentoxide there are tetrahedral molecules derived from P_4O_6 with the configuration shown at (*a*) by adding an oxygen atom at each corner (P atom). The single molecules M_2O_3 and M_2O_5 which are formed at very high temperatures are presumably of the form

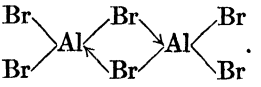


related to one another in exactly the same way as P_4O_6 to P_4O_{10}. See also p. 415.

Most halides vaporize as simple molecules, but a few form more complex molecules. Cuprous chloride, for example, persists as double molecules up to at least 1,690° C. and a number of trihalides first vaporize as M_2X_6 molecules which dissociate to MX_3 at higher temperatures. $AlCl_3$ is entirely dissociated to single molecules at 660° and $FeCl_3$ at 750°. The form of these latter compounds in solution depends on the nature of the solvent. Thus molecular weight measurements show that aluminium bromide apparently exists as $AlBr_3$ molecules in solution in ether and pyridine but as Al_2Br_6 molecules in carbon disulphide. What actually happens is that the aluminium atom forms its fourth tetrahedral bond by attaching itself to the oxygen of $(C_2H_5)_2O$ or N of pyridine, so that the molecules in solution are really



in which the aluminium has the same tetrahedral arrangement of four bonds as in the Al_2Br_6 molecule:

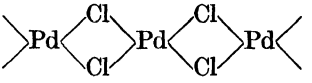


The carbon atom in CS_2 does not utilize its unshared electron pair (assuming single C—S bonds) in this way and accordingly Al_2Br_6 molecules are formed.

Let us now compare the crystal structures of a number of simple halides. The following halides vaporize to molecules of the composition shown below:

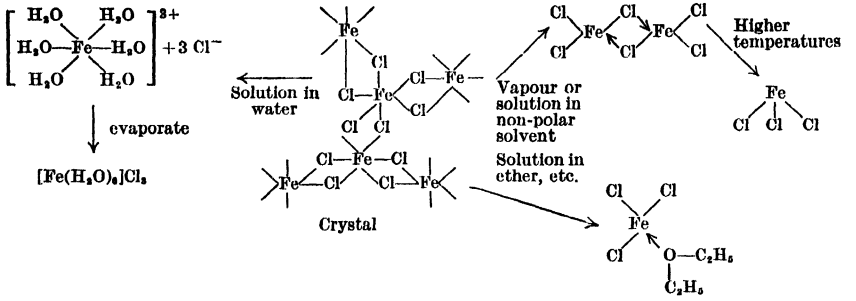
Halide	*Molecule in vapour*	*Type of crystal structure*	*Coordination number of metal*
Potassium iodide	KI	Rock salt	6
Cuprous chloride	Cu_2Cl_2	Zinc-blende	4
Cadmium bromide	$CdBr_2$	Cadmium chloride layer lattice	6
Ferric chloride	Fe_2Cl_6	Layer lattice	6
Palladous chloride	$PdCl_2$	Chain lattice	4
Stannic chloride	$SnCl_4$	Molecular structure	4

Only in one case ($SnCl_4$) is the atomic arrangement in the solid similar to that in the vapour. In all the other crystals the metal atom has a greater number of halogen neighbours than in the vapour molecule. In KI the octahedral and in CuCl the tetrahedral arrangement of neighbours leads to an array of atoms which extends throughout the whole crystal in all directions. We shall refer to such an arrangement as a 3-dimensional complex. In $CdBr_2$ and $FeCl_3$, on the other hand, the metal atoms have six halogen neighbours arranged octahedrally, but these MX_6 groups are linked together by sharing X atoms in such a way that sheets with the composition MX_2 or MX_3 result. The structure of CdI_2, which is of this type, has already been illustrated in Fig. 20. Finally, in crystalline $PdCl_2$ there are chains of atoms extending through the crystal, forming what we



may regard as infinite linear molecules. We shall find it convenient for many purposes to classify crystals according to the type of 'complex' which they contain, the complexes being finite, or infinite in one, two, or three dimensions. We shall return to the structures of these and other halides in Chap. VIII.

Before proceeding to the classification of crystals let us consider briefly a simple compound like ferric chloride in the light of the above remarks. We have seen that in the vapour at low temperatures the compound is in the form of Fe_2Cl_6 molecules. When these condense to form a crystal a radical rearrangement of the atoms takes place and instead of a finite molecule in which every iron atom is attached to four chlorine atoms we have infinite 2-dimensional molecules in which every iron is surrounded by six chlorine atoms. When this crystal dissolves in a solvent like CS_2 the double molecules Fe_2Cl_6 re-form, but in solvents like ether simple tetrahedral molecules $(C_2H_5)_2O \rightarrow FeCl_3$ are formed. We are accustomed to regard a process like the dissolution of a crystal as a simple reversible process, in the sense that removal of the solvent leads to the recovery of the original solute. This will be true for non-polar solvents but not for dissolution in a highly polar solvent like water. When a crystal of ferric chloride dissolves in water separation into Fe^{3+} and Cl^- ions occurs, and many of the properties of an aqueous solution of $FeCl_3$ are the properties of these individual ions rather than of ferric chloride. Thus the solution precipitates AgCl from a solution of $AgNO_3$ (property of Cl^- ion) and it oxidizes $SnCl_2 \rightarrow SnCl_4$ or $TiCl_3 \rightarrow TiCl_4$, these being due to the transformation $Fe^{3+} + e \rightarrow Fe^{2+}$. In aqueous solution the ferric ion is hydrated, probably hexahydrated, and these water molecules are firmly attached to the ion. Evaporation of the solution at ordinary temperatures therefore leads to crystallization of the hexahydrate $[Fe(H_2O)_6]Cl_3$, and the original anhydrous $FeCl_3$ cannot be recovered from the solution in this way. We may set out the structural chemistry of $FeCl_3$ in the following way:



A CLASSIFICATION OF CRYSTALS

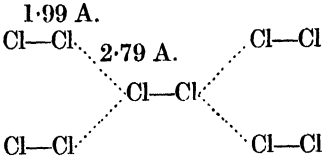
At first sight it might appear that the most obvious way of classifying crystal structures would be to group them according to the types of bonds between the constituent atoms, recognizing the four extreme types, ionic, homopolar, metallic, and van der Waals. A broad division of crystals into ionic, homopolar, metallic, and *molecular* crystals is generally made, but we should notice the following points. Firstly, there are comparatively few crystals in which *all* the interatomic bonds are essentially ionic or essentially homopolar. Secondly, in all crystals which contain complexes (other than 3-dimensional complexes) there are bonds of different types. For example, the C—O bonds in $CaCO_3$ are far less ionic in nature than are the Ca—O bonds, and in all molecular crystals the intra-molecular bonds are of quite a different kind from those acting between one molecule and another. We should therefore immediately have to recognize the following intermediate classes:

(1) All the bonds are similar but are not pure types (e.g. Si—O, 50 per cent. ionic, 50 per cent. homopolar).
(2) The bonds are of two essentially different kinds.
(3) Combinations of (1) and (2). For example, in $CdCl_2$ we may distinguish the Cd—Cl and the inter-layer Cl—Cl bonds as being of different types, but in addition the Cd—Cl bonds are themselves intermediate between ionic and homopolar bonds.

It is found that classifications based purely on bond type become complicated without being comprehensive. They also have the disadvantage that they over-emphasize the importance of 'pure' bond types, bonds of intermediate character being treated as departures from these extremes. For our purpose it is preferable to be able to discuss the nature of the bonds in a particular crystal without having prejudged the issue by classifying the crystal as, for example, an ionic crystal. A further reason for classifying crystals simply according to the extent of the complex(es) in the structure is that the stereochemical requirements of the atoms are satisfied within the complex. In general, therefore, we shall deal only with the internal structure of the complexes; the way in which they pack together in the crystal will be only a matter of secondary interest. The bonds between the complexes are non-directed (except in the case of hydrogen bonds), so that the packing of the complexes is determined by

their shape and by their charges if they are ions. As a matter of interest we shall give later some examples of the characteristic ways in which complexes of certain shapes pack together.

It is appropriate to consider briefly on what grounds we describe a particular group of atoms as a 'complex'. The recognition of finite complexes generally presents no difficulties, the complex being either a neutral molecule or a complex ion. In simple molecular crystals the only forces acting between atoms of different molecules are the relatively weak van der Waals bonds. In certain crystals containing polar molecules (i.e. organic molecules with OH or NH_2 groups), and also in some crystalline hydrated oxy-salts and acid-salts, we find the distances between certain pairs of atoms of different molecules or complex ions to be shorter than usual. The 'hydrogen bond', due to the presence of a hydrogen atom between such pairs of atoms, was discovered in this way in crystals, and we shall include this form of interatomic binding in our scheme of classification of crystals, though we shall defer any further discussion of the hydrogen bond until Chapter VII. The interatomic distances in molecular crystals are much greater than those within the molecule, thus:

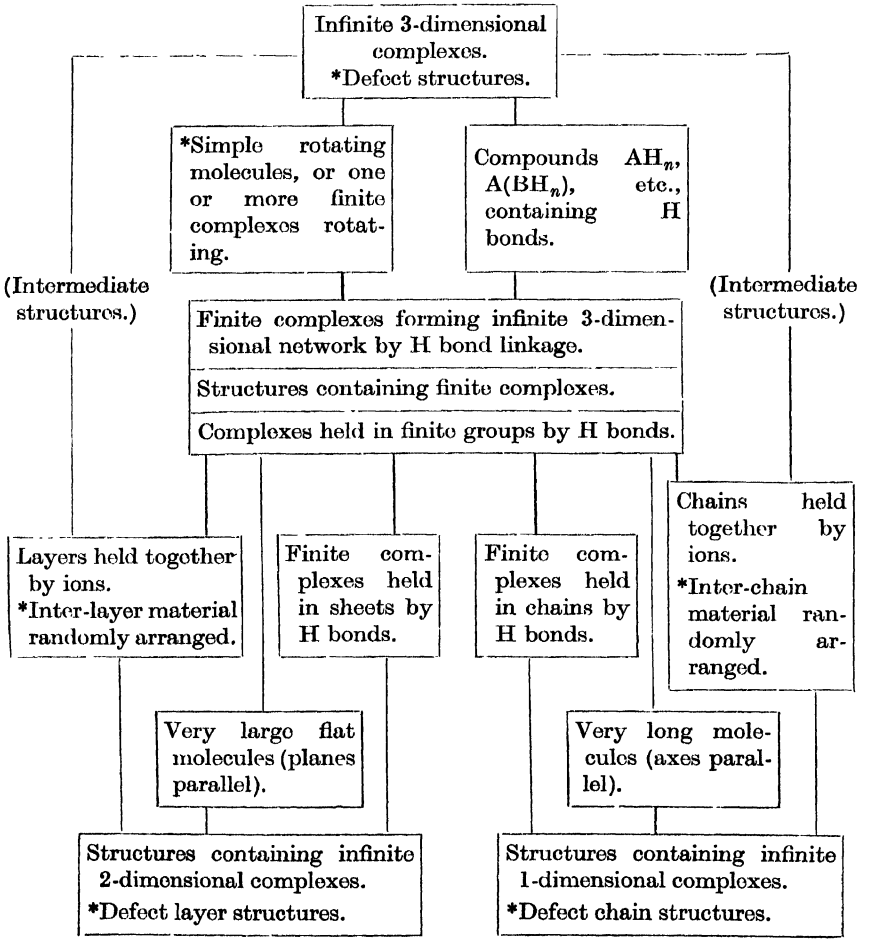


The molecules thus distinguished on the basis of the interatomic distances in the crystal are those known to exist in the liquid or vapour states or in solution in appropriate solvents. It should be noted that we make no statement about the nature of the intra-molecular bonds. They may range from purely homopolar (molecules of elements, e.g. Cl_2) to essentially ionic (SiF_4 molecule) according to the difference between the electronegativities of the atoms. As regards finite complex ions, many are known to exist in solution (CO_3, SO_4, NO_3, etc.), though we do not, of course, require this corroborative evidence before we recognize an ion as existing in a crystal. We have already remarked that an ion which is stable in a crystal is not necessarily stable in solution in a particular solvent. When we come to infinite complexes we have no longer any confirmatory evidence from other states of aggregation and we have to rely entirely on the geometry of the structures and the properties of the crystals. By the geometry of a structure we mean not only the distances between atoms but also the arrangement of the atoms relative to one another. Thus in the chain and layer lattices of $PdCl_2$ and $CdCl_2$ respectively there is the evidence not only of the large Cl—Cl distances between different complexes but also the fact that the only bonds between different complexes are Cl—Cl bonds. There is no linking between metal atoms of one complex and chlorine atoms of another. In crystals in which complexes of lesser extent cannot be distinguished we describe the complex as 3-dimensional. The

simplest crystals of this sort are those in which all the bonds are of the same type throughout, as in NaCl (ionic), diamond (homopolar), inert gases (van der Waals), and the metals. The bonds may, of course, be intermediate in nature as, e.g., in many crystals with the zinc-blende structure (BeO, etc.). The other important group of crystals containing 3-dimensional complexes comprises the so-called framework crystals of which the zeolites are examples. In these a proportion of the atoms are linked to form a rigid framework in the interstices of which are accommodated the remaining atoms, held with various degrees of firmness.

In the accompanying chart we set out the various types of crystal structure, arranged according to the kind of complex they contain, viz. finite (molecules or complex ions), infinite 1-dimensional (chains), infinite 2-dimensional (layers), or infinite 3-dimensional complexes. We

CHART



N.B.—The groups of defect structures are distinguished by asterisks.

shall now only refer briefly to the various groups of structures, but it may be found convenient later to refer back to the chart when particular structures are described. In the chart certain groups of structures are marked by asterisks; the reasons for distinguishing these 'defect' structures will be explained in the next chapter, where we deal in more detail with the solid state.

Crystals containing Finite Complexes

Finite complexes comprise all molecules and finite complex ions. As we have already remarked, these are the only types of complex which can exist in other states of aggregation. Molecular crystals include most solid organic compounds and also the crystalline forms of most simple non-metallic oxides, sulphides, halides, and hydrides. In the simplest type of molecular crystal there are identical non-polar molecules held together by van der Waals bonds. The structures of these crystals are determined by the most efficient packing of units of a given shape held together by undirected forces. When the molecule is roughly spherical the same structure types may occur as in crystals with 3-dimensional complexes, a group of atoms replacing the single atom (compare the structures of Sb_4O_6, page 415 and diamond, page 431). As the shape of the molecule deviates from spherical, so the structures bear more analogy to those of crystals containing infinite 1- or 2-dimensional complexes. An extreme example is the hydrocarbon $C_{1000}H_{2002}$, which for most purposes may be regarded as an infinite chain. Thus the X-ray powder patterns, for example, of long-chain hydrocarbons remain practically constant for molecules over 130 atoms long. More complex types of molecular crystal arise when there are molecules of more than one kind packed together, as in $CHI_3.3S_8$, and when there are hydrogen bonds between certain pairs of atoms of different molecules. In the latter case quite different, and less close, packing of the molecules is found and many interesting structural types arise, which are described in Chapter VII.

The second large group of crystals containing finite complexes includes the hydrates of many salts and acids. Owing to the interest and variety of these compounds they are considered in some detail in Chapter XI.

Finally we have all salts of inorganic and organic acids containing finite complex ions, and ionic coordination compounds generally. We have already said something about complex ions in the previous chapter, where we saw that crystals containing these ions may have structures simply related to those of AX_n compounds with 3-dimensional complexes, e.g.

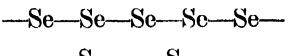
CaC_2 Calcite	NaCl structure	$[Mg(NH_3)_6]I_2$—CaF_2 structure
Aragonite—NiAs structure		$[Al(NH_3)_6]Cl_3$—YF_3 structure.

Where the complexes are approximately spherical in shape the structure may be strictly similar to that of the corresponding AX_n compound, in which case radius ratio criteria are applicable. If, however, the complex

ion is appreciably anisotropic in shape the structure is a distorted version of the simple AX_n structure, as with CaC_2 and $CaCO_3$.

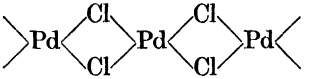
Crystals containing Infinite 1-dimensional Complexes

Here we are concerned with crystals in which chains or bands of atoms extend throughout the crystal, the complexes being recognizable on account of the larger distances between atoms of different chains than between the nearest atoms within the chains. The simplest chain structures are those consisting of infinite linear molecules held together by van der Waals bonds. These are the analogues of simple molecular crystals; examples are Se, SiS_2, $PdCl_2$, SeO_2, Sb_2O_3, in which the chains are of the following types:

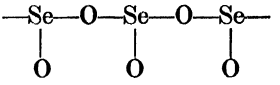




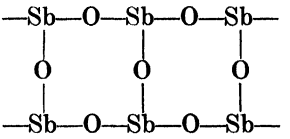
(tetrahedral Si bonds)



(planar Pd bonds)



and



No other types of inorganic chain structures are yet known containing only infinite linear complexes, but in proteins consisting of infinite polypeptide chains there are probably hydrogen bonds forming the lateral links between the chains. No crystals containing chain ions of opposite charge have yet been discovered.

There is, however, another possibility in crystals containing chain and layer complexes, viz. that infinite ions are held together by finite complexes or simple ions situated between them. Examples of structures of this type are the fibrous silicates (pyroxenes and amphiboles), page 473, $Ca(B_2O_4)$, page 492, and $NH_4(CdCl_3)$, page 287. For a diagram of a portion of the diopside structure see Fig. 145.

Crystals containing Infinite 2-dimensional Complexes

Three main classes of crystals containing only 2-dimensional complexes may be recognized, according as the layers are held together by van der Waals, hydrogen, or ionic bonds.

(a) *van der Waals Bonds between Layers*

Many chlorides, bromides, and iodides AX_2 and AX_3 and a number of sulphides, oxyhalides, and hydroxides belong in this category. In the

corresponding oxides and fluorides, in which the A—X bonds are more ionic, 3-dimensional complexes are more usual. The structures of some of the simple AX_2 and AX_3 layers are illustrated (in plan) in Fig. 34.

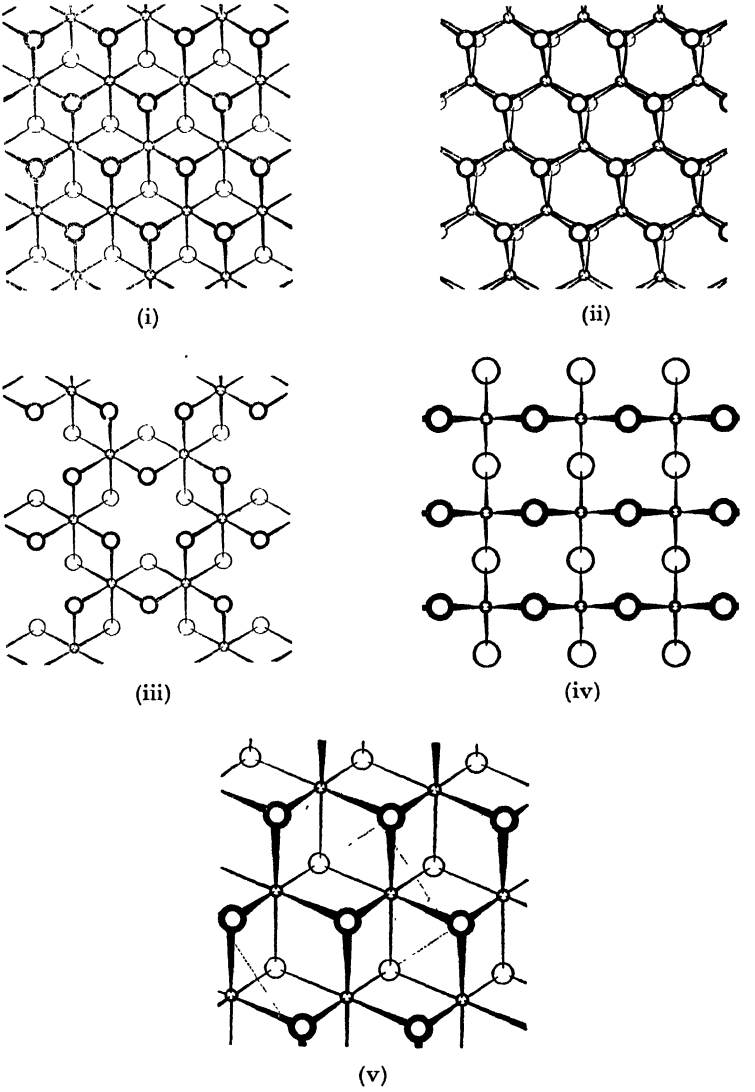


FIG. 34. The structures of some simple AX_2 and AX_3 layers. In each diagram the small circles represent metal atoms in the plane of the paper, and the larger circles halogen, oxygen, or sulphur atoms which lie in planes above and below that of the metal atoms. The layers shown are (i) $CdCl_2$ (or CdI_2), (ii) MoS_2, (iii) $CrCl_3$, (iv) HgI_2, and (v) $HgBr_2$. The non-metal atoms are projected normally on to the plane of the metal atoms except in (ii), where the S atoms are slightly displaced to avoid superposition.

(1) The layers in $CdCl_2$ and CdI_2 are similar, the structures differing in

the way in which the layers pack together. For examples of compounds with these structures see pages 279 (halides), 386 (disulphides), and 353 (dihydroxides).

(2) The characteristic of the structure of MoS_2 (and of the isomorphous WS_2) is the disposition of the Mo bonds towards the corners of a trigonal prism—contrast the octahedral coordination in $CdCl_2$ and CdI_2.

(3) The structure of the layers in the $CrCl_3$ and BiI_3 structures is closely related to that of the $CdCl_2$ and CdI_2 layers, one-third of the possible positions for metal atoms being unoccupied in the former.

(4) The HgI_2 layer is the analogue of (1) for an element forming tetrahedral bonds.

(5) The $HgBr_2$ layer is closely related to (1) and is shown in the figure in a similar orientation. The structure may be regarded as intermediate between a layer and a molecular lattice, since two of the six bromine neighbours of a mercury atom are much closer (2·48 A.) than the remaining four (at 3·23 A.).

(*b*) *Hydrogen Bonds between Layers*

The structures of a number of hydroxides differ from those in (*a*) (1) in two ways: firstly in the way in which the layers are packed together, and secondly in the distance between OH groups of adjacent layers. The arrangement of the OH groups in a layer of $Mg(OH)_2$ and of $Al(OH)_3$ is similar, but whereas in the former structure the OH groups of neighbouring layers are close-packed, in the latter a much more open packing is found. Furthermore, the distance between OH groups in adjacent layers in $Mg(OH)_2$ is 3·22 A. and in $Al(OH)_3$ only 2·80 A. These facts indicate the presence of directed O—H—O bonds between the layers in the latter compound. The structures of γ FeO.OH and FeOCl differ in a rather similar way. For further discussion of hydroxides and related compounds see Chapter XI.

(*c*) *Ionic Bonds between Layers*

Structures of this type, consisting of oppositely charged layer ions, are rare, the only examples yet known being the chlorite minerals, described on page 479.

Just as we find crystals containing chain ions held together by simple ions, so we may have structures containing infinite layer ions and finite complexes or simple ions. The micas are the only large group of crystals of this sort, the complex layers being interleaved with metal ions (page 478). Some of the related clay minerals may also be of this type, and also certain derivatives of graphite (see p. 438).

Crystals containing Infinite 3-dimensional Complexes

This class comprises the following groups:

(*a*) Inert gases.

(*b*) Metals and alloys.

(*c*) Ionic and homopolar crystals, including the 'framework' structures.

(*a*) The first group calls for little discussion. The inert gases Ne, A, Kr, and Xe all crystallize with cubic close-packed structures and a number of crystals containing rotating binary molecules (N_2, CO, HCl, CH_4, PH_3, etc.) are structurally similar. It is immaterial whether such crystals are placed in this group or with crystals containing finite complexes. When there is no rotation of the molecules, however (halogens, HI), less close-packed structures result.

(*b*) Some of the structural features of metals are described in Chapter XVII.

(*c*) In the following table are shown some of the more important structure types for binary compounds in which the infinite 3-dimensional complex extends throughout the whole crystal.

A *bonds*	X *bonds*				
	2 non-linear	*2 linear*	*3 triangular*	*4 tetrahedral*	*6 octahedral*
4 tetrahedral .	Forms of SiO_2	—	—	ZnS, ZnO	—
6 octahedral .	—	ReO_3	TiO_2	Al_2O_3	NaCl
8 cubic . .	—	—	—	CaF_2	—

Examples of framework structures will be found in Chapter XIV: felspars (p. 481) and zeolites (p. 482).

Intermediate structures

No attempted classification of crystal structures, unless it be elaborated to an undesirable degree, can allow for all the possible types of structure which can be adopted even by the elements and the simpler compounds. We have mentioned that a structure like that of $HgBr_2$ may be regarded as intermediate between a purely molecular lattice and a layer lattice. Other structures are intermediate between molecular crystals and infinite 3-dimensional complexes. In a simple molecular crystal such as solid CH_4 the molecules are well defined, but in As_4O_6 and Sb_4O_6, which we have quoted as examples of finite complexes, there is evidence (from bond angles and interatomic distances) that bonds are formed between metal atoms of one complex and oxygen atoms of another (see p. 416). These bonds between atoms of different complexes are weak compared with those within the complexes but utilize definite electron-pairs of oxygen atoms and are on this account to be distinguished from pure van der Waals bonds. The limit of this weak inter-complex binding is the formation of a 3-dimensional complex in the cubic form of Bi_2O_3. The structures of elementary arsenic, antimony, and bismuth and of Zn and Cd illustrate the transition from a 2-dimensional to a 3-dimensional complex. In ideal close-packing each atom has twelve equidistant nearest neighbours. In metallic arsenic there are fairly well-defined layers, each atom having three neighbours in the layer at a distance of 2·51 A. and three in an adjacent layer at 3·15 A. In antimony and bismuth the layers become

progressively less well defined, as shown by the increasingly smaller difference between the corresponding pairs of distances—2·87 and 3·37 A. in Sb, 3·10 and 3·47 A. in Bi. In zinc and cadmium each atom has six nearest neighbours in the basal plane and six further removed, three above and three below the plane of the others. The distances of these two sets of neighbours are respectively 2·660 and 2·907 A. in zinc and 2·973 and 3·287 A. in cadmium, indicating stronger bonds in than between the layers, as suggested by the physical properties. Accordingly, allowance is made in the classification for 'intermediate' structures of various types.

We shall conclude this chapter with remarks on a few points related to the topics we have been discussing.

THE PACKING OF COMPLEXES IN CRYSTALS

The atoms of an inert gas, molecules of approximately spherical shape, and those which become effectively spherical owing to free rotation can pack together in the closest way possible. Apart from the fact that it is

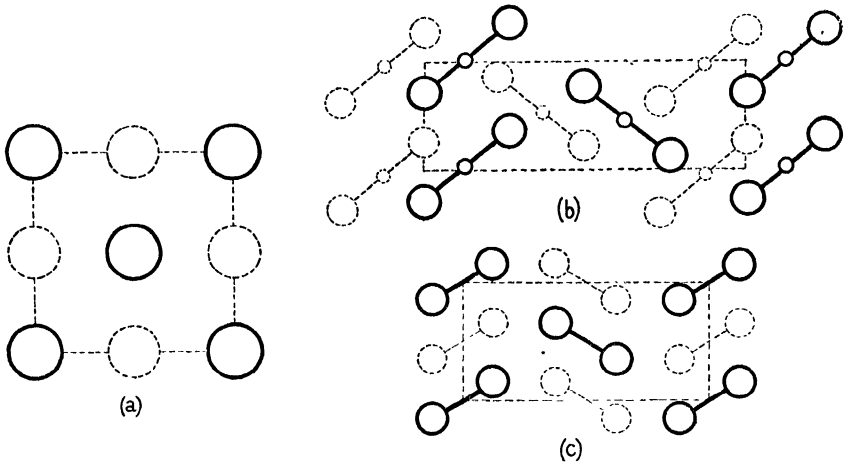


FIG. 35. (*a*) Plan of cubic closo-packing normal to four-fold axis. (*b*) Plan of the structure of mercuric chloride. (*c*) Plan of the structure of iodine.

interesting to see how units with other shapes pack together, the mode of packing also shows in some cases why the crystals take up solvent of crystallization, a matter of more obvious interest to the chemist. In Fig. 35 (*a*) we show a plan of atoms or molecules arranged in cubic close-packing, viewed along a 4-fold symmetry axis—not normal to the close-packed planes of Fig. 24. The atoms shown as dotted circles lie in planes above and below that of the atoms indicated by full circles, so that every atom has twelve (equidistant) neighbours. At (*b*) and (*c*) are shown, in plan, the arrangements of molecules in the structures of mercuric chloride and iodine. It is seen that the packing of these linear Cl—Hg—Cl and I_2 molecules is very similar to that of spherical molecules in (*a*). A

somewhat different mode of packing is found for a square planar group, as is seen from Fig. 36 (*a*) and (*b*), where we show the plan and elevation of the structure of $CuCl_2.2H_2O$. The structure of ammonium triodide illustrates one way of arranging spherical (NH_4^+) and linear groups (I_3^-) (Fig. 36 (*c*)). It is interesting to compare the structure of $[Pd(NH_3)_4]Cl_2.H_2O$

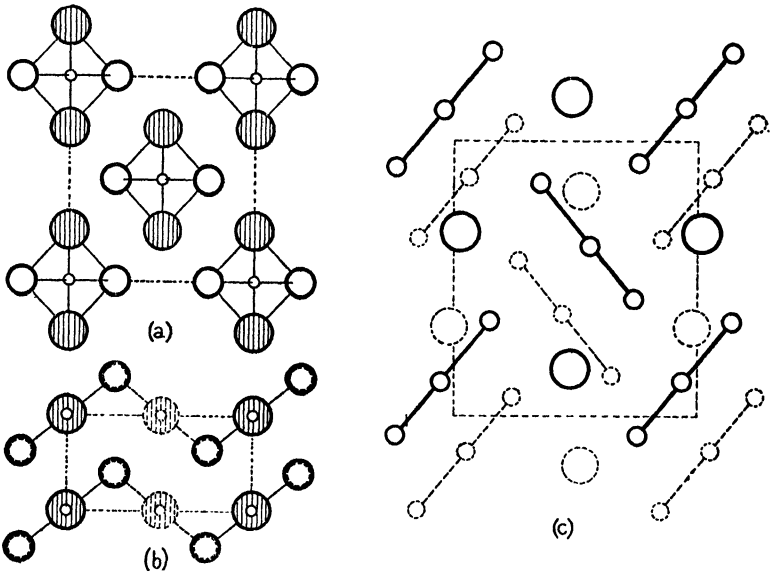


FIG. 36. (*a*) and (*b*) plan and elevation of the structure of $CuCl_2.2H_2O$, (*c*) plan of the structure of NH_4I_3 (large circles represent NH_4^+ ions, and dotted circles indicate atoms at heights $a/2$ above or below the plane of the paper.

with that of $K_2[PtCl_4]$. The arrangement of the square $[Pd(NH_3)_4]^{2+}$ and the Cl^- ions is exactly the same as that of the square $[PtCl_4]^{2-}$ and the K^+ ions. The square planar ions are arranged in the same way as the full circles in Fig. 35 (*a*) above, but they are arranged vertically above one another in successive layers. In crystals of the palladium compound there is room for water molecules, as shown in Fig. 37 (*a*). The structure of silver diammino sulphate provides a good example of one way in which linear (NH_3—Ag—NH_3^{2+} ions) and tetrahedral (SO_4^{2-}) groups may be packed (Fig. 37 (*b*)). Finally, when we come to chain structures we find quite analogous structure types. We may compare the structures of $Cd(NH_3)_2Cl_2$, in which there are chains of octahedra linked by sharing opposite edges, and of SiS_2, with 'tetrahedral' chains, with that of $PdCl_2$ in which there are chains formed by linking up planar $PdCl_4$ groups.

In all these structures the chains lie with their axes parallel, and in Fig. 38 we show the structures viewed along the length of the chain. When the chains are infinite 1-dimensional ions they are held together by ions of opposite charge. In the resulting structure there may be room for solvent molecules, as is the case in crystals of $K_2SnCl_4.H_2O$ and related compounds. A plan of the structure of this compound is given in Fig. 39.

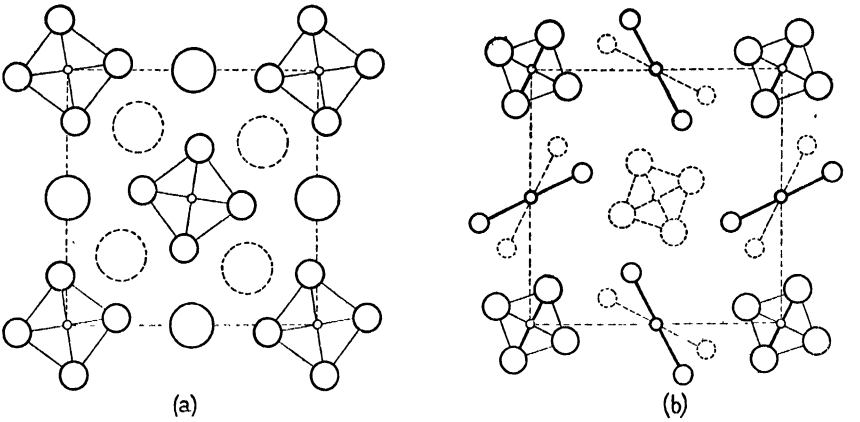


FIG. 37. (*a*) Plan of the structure of $Pd(NH_3)_4Cl_2.H_2O$. The water molecules (large full circles) and planar $[Pd(NH_3)_4]^{2+}$ ions lie in the same plane. The Cl^- ions (dotted circles) lie in planes midway between those of the other atoms. (*b*) Plan of the structure of $\{Ag(NH_3)_2\}_2SO_4$. Full and broken lines indicate groups at different heights.

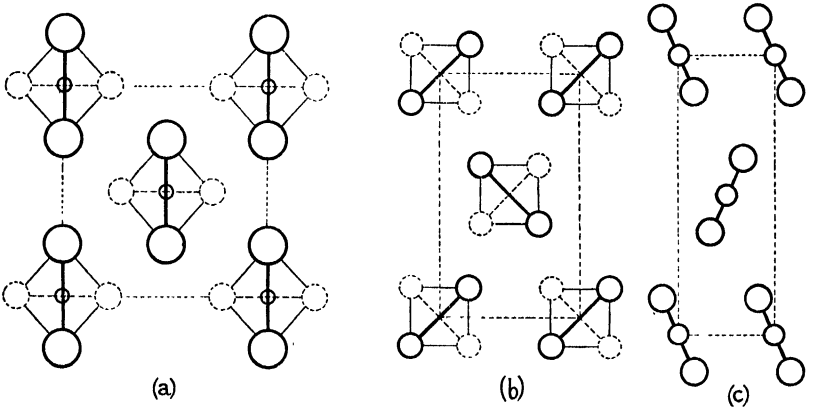


FIG. 38. The structures of (*a*) $Cd(NH_3)_2Cl_2$, (*b*) SiS_2, and (*c*) $PdCl_2$, viewed along the directions of the infinite chains.

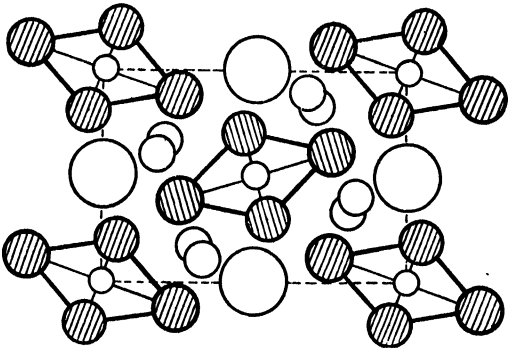


FIG. 39. The structure of $K_2SnCl_4.H_2O$ viewed along the direction of the infinite chains. The K^+ ions (pairs of overlapping circles) and H_2O molecules (large circles) lie, at various heights, between the chains.

GEOMETRICALLY RELATED STRUCTURES

We have seen that the structures of some crystals containing finite complexes are related in a simple way to the structures of AX_n crystals, single atoms being replaced by groups of atoms. The distortion of the structure depends on the shape of the finite complex. Thus CaC_2 and SrO_2 have structures similar to that of rock-salt but elongated in one direction owing to the substitution of linear C—C or O—O ions for Cl^- ions, and the symmetry falls from cubic to tetragonal. On the other hand $[Mg(NH_3)_6]I_2$ has the cubic CaF_2 structure because the complex cation is approximately spherical and the ratio of the radii of the ions lies within the range for stability of the fluorite structure. We may note here some examples of structures which are related in rather different ways to simpler structures.

(1) $A \rightarrow AB \rightarrow AB(C_2)$, etc. The structure of zinc-blende is related to that of diamond as follows. Instead of all the atoms being identical, atoms of two kinds alternate regularly. This process is continued a stage further in $CuFeS_2$ (see p. 394). In the ZnS structure it is necessary that the mean number of orbital electrons is four per atom, so that compounds like AlP and CuI crystallize in the same way.

The relation of BN to graphite is exactly analogous to that of AlP to diamond. A precisely similar substitution of two atoms for one is found in $AlPO_4$ and other structures derived from cristobalite, SiO_2. If in a silica framework we replace some of the Si atoms by Al, instead of equal numbers by Al and P, there results a charged framework in the interstices of which an equal number of alkali ions must be accommodated in order to maintain electrical neutrality. The silicate $NaAlSiO_4$ exists in high- and low-temperature forms—the former being related to the high-temperature form of cristobalite and the latter to tridymite, another of the polymorphic forms of silica. Replacement of half of the silicon atoms by calcium instead of aluminium necessitates the introduction of twice as many sodium ions, and we find Na_2CaSiO_4, also related to cristobalite. Examples of structures related in these various ways are summarized below:

C (Diamond), (Si, grey Sn) — ZnS, AlP——$CuFeS_2$, CuI

C (Graphite) —BN

Al_2O_3 —$FeTiO_3$—(Fe, Mg)TiO_3

SiO_2 — $AlPO_4$, BPO_4, $BAsO_4$

$NaAlSiO_4$—Na_2CaSiO_4

WO_3 — $NaTaO_3$, Tungsten bronzes

(2) The structures of some complex compounds are built up of portions of structures of simpler crystals, so that such structures are related in quite a different way from those in (1). We cannot describe such structures in detail here, but must refer the reader to the structures of (*a*) the minerals of the chondrodite series (p. 469) for examples in which the complex structures arise from the linking of layers of the simple structures, and (*b*) magneto-plumbite (p. 335), where the units of the simple structures are small blocks.

STRUCTURAL FORMULAE OF SOLIDS

The following points may be worth noting with regard to the 'structural' formulae of solids.

Only for crystals containing finite complexes does a simple formula express the composition of the units of structure, and this formula is not necessarily the simplest, empirical, formula, in which case it should not be reduced to its simplest form, e.g. S_8, Sb_4O_6, etc. When chain, layer, or framework ions exist in crystals it is convenient to write their formula in such a way as to indicate which atoms are associated together in the complex, as in the following examples: $Mg(SiO_3)$, $KAl_2[AlSi_3O_{10}(OH)_2]$, and $K(AlSi_3O_8)$. Another reason for not reducing all formulae to their simplest forms is that the same element may be present in two valency states, as in $Tl^I(Tl^{III}Se_2)$, page 516, or $Cs_2Au_2Cl_6$. The latter formula is preferably written as $Cs_2(Au^ICl_2)(Au^{III}Cl_4)$, indicating that uni- and tri-valent gold atoms are present and that two types of complex ion exist in the crystal.

A second point is that similarity in formulae does not necessarily indicate that compounds have similar structures. Thus $RbCdCl_3$ has the same type of empirical formula as the gold compound just mentioned but an entirely different kind of structure (see p. 288). The compounds $CaCO_3$, $CaSiO_3$, and $CaTiO_3$ illustrate this point very well, as shown in the following table:

ABO_3	*Type of complex ion*	*Coordination number of B*
$CaCO_3$	Finite CO_3 groups	3
$CaSiO_3$	Finite Si_3O_9 rings	4
$CaTiO_3$	None—infinite 3-dimensional complex (perovskite structure, see p. 330)	6

It is clear that the number of bonds formed by the atom B can be deduced from the chemical formula only if the complex ion is finite and mononuclear, i.e. of the form (BO_n).

It should at this stage be unnecessary to say that the existence of compounds like $LaAlO_3$ or $SrTiO_3$ does not mean that Al or Ti are 'acidic' any more than the existence of $ZnCr_2S_4$ (with the spinel structure, p. 332) implies the existence of an acid $H_2Cr_2S_4$.

Finally we see that various types of atomic arrangement are possible for a particular empirical formula. In the case of elements we may have

atoms linked together to form 3-dimensional complexes as in metals, diamond, and so on, or we may have layers (black phosphorus, p. 399), chains (Se, Te, p. 538), or finite molecules (Cl_2, S_8 in rhombic sulphur, or P_4). Even if the coordination number of A in a complex AX_n is fixed there are various ways of arranging the A and X atoms to give a certain ratio of X to A atoms. Thus from octahedral AX_6 groups we may obtain complexes with the compositions AX_3 in a number of ways, e.g.

Mode of linking AX_6 *groups*	*Type of complex*	*Example*
Sharing corners with 6 other AX_6	3-dimensional	ReO_3 (p. 331)
,, edges ,, 3 ,, ,,	2-dimensional	$FeCl_3$ (p. 279)
,, faces ,, 2 ,, ,,	1-dimensional	--

If we allow arrangements involving different coordination numbers, then the number of possibilities becomes much greater. For example, for a compound AX_5 the following are among the possible structures:

All A atoms with same environment:
- AX_5 molecules.
- infinite chains of AX_6 octahedra sharing two opposite corners.
- discrete AX_4 and X.

A atoms of two types: $(AX_4)(AX_6)$.

CHAPTER V

THE CRYSTALLINE STATE

It is customary to describe solids as either amorphous or crystalline. Typical examples of 'amorphous' solids are charcoal, glasses, and opal Glasses have already been mentioned in the previous chapter; they are alternatively described as supercooled melts, the rate of cooling having been too great to permit rearrangement to the ordered state of a crystal. It is probable that the immediate environment of many of the atoms in an element or compound is the same whether the substance be in the amorphous, glassy, or crystalline state, and that the distinction between these various forms rests on the degree of order existing throughout the whole body. Thus coke consists of minute fragments of the graphite structure, or at least of aggregates of atoms linked in somewhat the same way as in graphite, but the orderly arrangement of atoms extends only over distances comparable with the C—C distance. When a regular atomic arrangement persists over distances very great compared with interatomic distances, the substance is described as crystalline. As we shall see later, small and usually random departures from regularity occur even in most crystalline bodies.

Crystals may be formed from solution, by cooling the molten material or by deposition from the vapour, and according to the conditions, single crystals or polycrystalline material may be obtained. Since there will in general be random orientation of the individual crystallites in a polycrystalline mass, the properties of the material in bulk may resemble those of an amorphous rather than a crystalline substance. Any particular crystallite would, however, possess the same characteristic properties (other than external form) as an isolated crystal of the substance. Well-developed external form is therefore not an essential criterion of crystallinity, but since the symmetry of the external form of a single crystal of a substance is characteristic of that substance and is related to its internal atomic arrangement, we shall consider first the macroscopic symmetry of single crystals.

THE EXTERNAL SYMMETRY OF CRYSTALS

Crystals are solid bodies bounded by plane faces. (The curvature of the faces of natural diamonds has been attributed to solvent action.) A characteristic feature of the crystals of a particular substance (or of a particular form of a substance if it is polymorphic) is that the angles between corresponding pairs of faces are the same in all crystals. The relative sizes of corresponding faces may, however, vary from crystal to crystal. In Fig. 40 we give two simple examples of this variation in *habit* to show how quite different appearances may result from varying the

relative sizes of crystal faces. Whatever the habit of the crystals of a given substance, however, the essential symmetry is the same for all.

The symmetry of a solid body may be defined in terms of the elements of symmetry it possesses. A cube may be brought into coincidence with itself by rotation through one-quarter of a revolution about an axis

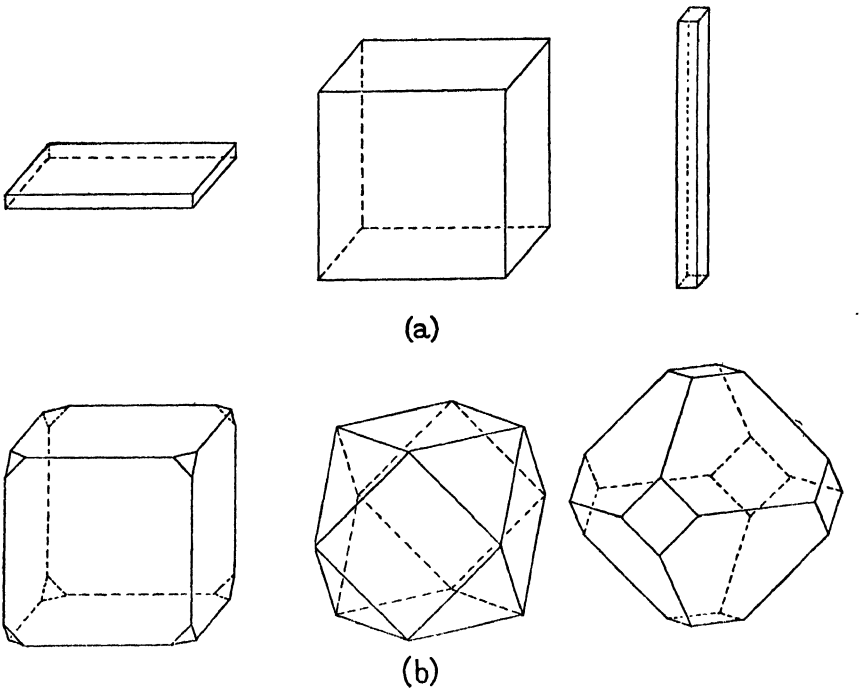


FIG. 40. Variation in habit of crystals. Different relative development of (*a*) cube faces, and (*b*) cube and octahedron faces.

passing through the centres of opposite faces or by one-third of a revolution about a body-diagonal. Such axes are called 4- and 3-fold axes of symmetry respectively. It can be shown that the only axes of symmetry possible in crystals are 2-, 3-, 4-, and 6-fold axes, and it is found that the symmetry of all crystals can be described in terms of the following symmetry elements or combinations thereof:

2-, 3-, 4-, and 6-fold axes of simple rotation, and axes of rotatory inversion, written $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, and $\bar{6}$.

An n-fold axis of rotatory inversion combines, as its name implies, a rotation through $360°/n$ with inversion through the centre of the crystal. It may easily be verified that $\bar{1}$ is equivalent to a centre of symmetry, $\bar{2}$ to a plane of symmetry (written m), and $\bar{6}$ to a simple 3-fold axis perpendicular to a plane of symmetry (written $3/m$). Starting with one face of a crystal, the operation of a set of symmetry elements reproduces all the other possible faces of the crystal. We say possible faces because all

the possible faces of a particular group of related faces are seldom developed, or developed to the same extent, in a given crystal (see Fig. 40).

According to the symmetries of their external forms crystals may be grouped into seven systems, the minimum characteristic symmetries of which are set out below:

Cubic system: four axes of 3-fold symmetry arranged parallel to the body-diagonals of a cube. These necessarily introduce, in addition, either three 2-fold axes or three 4-fold axes which are mutually perpendicular and parallel to cube edges.

Tetragonal system: single axis of 4-fold symmetry.

Hexagonal and Rhombohedral systems: single axis of 6-fold symmetry or one (but not more than one) of 3-fold symmetry.

Orthorhombic system: three mutually perpendicular 2-fold axes or two perpendicular planes of symmetry (but no axes of higher symmetry).

Monoclinic system: one 2-fold axis and/or a plane of symmetry perpendicular to it.

Triclinic (anorthic) system: no simple axis or plane of symmetry.

THE REGULAR INTERNAL STRUCTURE OF CRYSTALS

The properties of crystals already mentioned, and also the property of cleaving into fragments of characteristic shapes, suggested to early observers that crystals were made up by the regular repetition in space of some unit of structure. Hauy (1801) noticed that crystals of calcite of quite different habits could be cleaved into precisely similar cleavage rhombohedra which could be stacked together to reproduce the original crystal forms. This cleavage-block theory could not, however, be extended to all crystals, for some (e.g. quartz) exhibit no cleavage. Also, fluorite may be cleaved into octahedra or tetrahedra, but neither all octahedra nor all tetrahedra can be packed together without leaving gaps; both units, in the ratio of one octahedron to two tetrahedra, are required to fill space. Later, attention was devoted to the packing of spheres rather than parallelepipeds (e.g. Wollaston, 1812), and then attention was transferred to the positions of the centres of such spheres, leading to the lattice theories of Frankenheim (1835) and Bravais (1842).

We now know that a crystal is an assembly of atoms arranged in a regular manner in three dimensions, and it follows that there must be some unit of structure, some representative group of atoms characteristic of each crystal, which if extended in all directions leads to the macroscopic crystal. If we start from an arbitrary origin in the crystal and proceed in any direction we shall arrive, after travelling a certain distance, at a point with the same environment as the point of origin. We may perform this process in two other directions, inclined to the first, and find the corresponding repeat distances. These three axes of reference and the three repeat distances define a parallelepiped which contains a representative portion of the crystal structure and which if indefinitely repeated in those

directions will reproduce the crystal. This parallelepiped is termed the *unit cell*, and the repeat distances or *cell dimensions* (the sides of the unit cell) are written a, b, and c, corresponding to the axes with those symbols. The angles between the axes, taken in pairs, are called α, β, and γ (between bc, ca, and ab respectively). The choice of axes in the crystal is not arbitrary, except in the triclinic system, but is determined by the positions of the symmetry elements. The shape of the unit cell, and hence the constants required to define it, depend on the symmetry of the crystal, and the following table summarizes the data required in the various systems:

Triclinic	$a, b, c, \alpha, \beta, \gamma$
Monoclinic	a, b, c, β $(\alpha = \gamma = 90°)$
Orthorhombic	$a, b, c,$ $(\alpha = \beta = \gamma = 90°)$
Rhombohedral	a $(= b = c)$, α $(= \beta = \gamma)$
Hexagonal	a $(= b)$, c, $\gamma = 120°$, $\alpha = \beta = 90°$
Tetragonal	a $(= b)$, c, $(\alpha = \beta = \gamma = 90°)$
Cubic	a $(= b = c)$, $(\alpha = \beta = \gamma = 90°)$.

If there is an atom at the centre of each unit cell of the same kind as those at the corners the crystal is said to be based on a body-centred lattice. If there are atoms at the mid-points of the faces of the same kind as, and additional to, those at the corners, the lattice is described as face-centred. It may perhaps be helpful to mention here two points in connexion with diagrams of crystal structures. It will be noticed that there are not always atoms at the corners of unit cells in illustrations of crystal structures, and it might seem more logical to choose an atom as the point of origin in the crystal. We have seen that the choice of axes is determined by the symmetry elements. The shape of the unit cell is fixed by the mutual orientation of the symmetry elements, and the size by the distances at which the atomic pattern repeats along directions parallel to the sides of the unit cell. Translations of the unit cell parallel to the axes are therefore permissible since a unit cell of particular size, shape, and orientation will always be a representative portion of the structure. In Fig. 41 is shown a simple 2-dimensional arrangement of atoms. Clearly the rectangle enclosed by the broken lines is a repeat unit, but since the points marked by small black circles are symmetry centres (and points where 2-fold axes perpendicular to the plane of the paper intersect that plane) the unit cell chosen is that shown by the full lines.

The second point concerns the number of atoms in a unit cell. Difficulty is sometimes experienced in reconciling the number of atoms per unit cell, as stated in an account of an X-ray crystallographic study of a compound, with the number shown in a diagram of the unit cell of the structure. Thus in Fig. 42 the numbers of atoms per unit cell are respectively 1, 2, 3, and 4. It is only necessary to remember the following 'rules':

(*a*) An atom the centre of which lies within the unit cell belongs to that unit cell only.

(*b*) An atom lying on a face of a unit cell belongs equally to two unit cells, and therefore counts as $\frac{1}{2}$ atom for a particular unit cell.

(*c*) An atom lying on an edge is common to 4 unit cells.

(*d*) An atom lying at a corner is common to 8 cells.

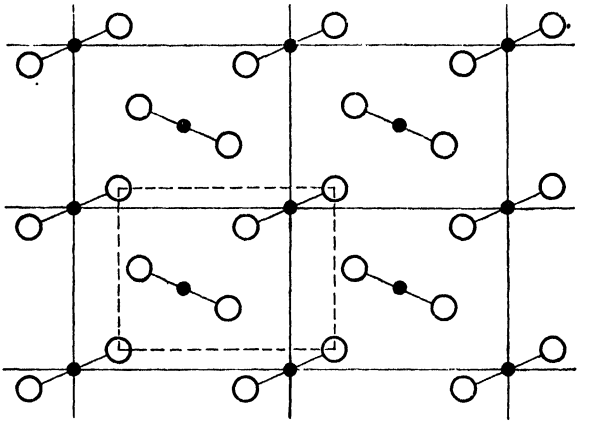
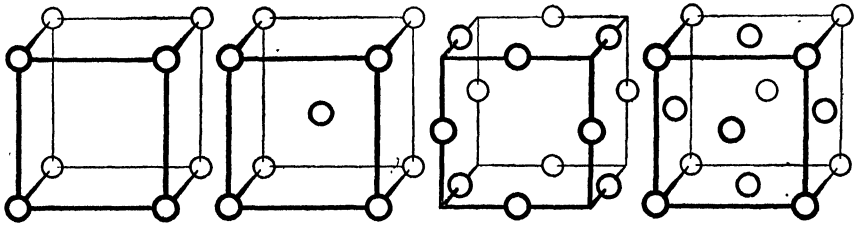


FIG. 41. Choice of unit cell (diagrammatic).

Thus in (*c*), Fig. 42, the 12 atoms shown count at 12/4 per unit cell and in (*d*) the 4 atoms per unit cell are made up of 8/8 = 1 (corners) and 6/2 = 3 (on faces).



(*a*) (*b*) (*c*) (*d*)

FIG. 42. Unit cells containing respectively 1, 2, 3, and 4 atoms.

Just as the external form of the crystal has a certain symmetry, so the arrangement of the atoms in the unit cell is characterized by certain symmetry elements. Now all symmetry elements describing the external form of a crystal pass through a point: this follows from the fact that a crystal is finite. There are only thirty-two possible combinations of the permitted axes of rotation and rotatory inversion, the thirty-two classes of point symmetry. The symmetry elements in the unit cell of a crystal, however, operate not on faces of a crystal but on atoms, and the restriction that they must all pass through a point is removed. Whereas two parallel planes of symmetry would convert a face into an infinite series of parallel faces, which is meaningless, we can obviously have two parallel planes of symmetry passing through each unit cell of a crystal (see Fig. 43, below).

Furthermore we may also have symmetry elements involving translation —glide planes and screw axes. For these reasons the number of combinations of symmetry elements relating to the internal structure of crystals (the 230 space-groups) is very much larger than the number of arrangements describing their external symmetry (the 32 point-groups). Just as one face of a crystal is related to, and converted into, a definite number of

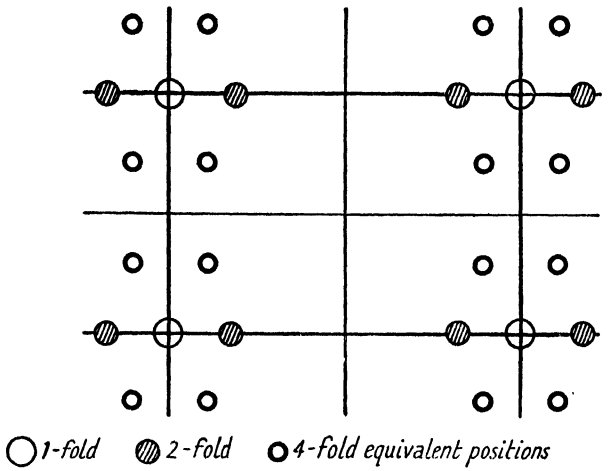


FIG. 43. Equivalent positions in a unit cell.

others by the point symmetry of the crystal, so one position in the unit cell of a crystal is related to a number of others by the symmetry elements in the crystal lattice. Such positions are called *equivalent positions*. Fig. 43 represents the projection of a unit cell of a crystal. Vertical planes of symmetry intersect that of the paper in full lines. The numbers and arrangements of the different kinds of circles show how the numbers of equivalent positions depend on the position of the atom relative to the symmetry elements. It will be apparent that according to classical structure theory all the equivalent positions of a given set should be occupied by atoms of the same kind.

REAL AND IDEAL CRYSTALS—DEFECT STRUCTURES

We may sum up our picture of a crystal as follows. It consists of an extended array of atoms arranged with regular periodicity in all directions. This implies the existence of a unit of structure, repetition of which in three dimensions reproduces the crystal. The unit of structure or unit cell is characteristic of a particular crystal, and each unit cell has by definition the same size and the same content of atoms similarly arranged. We shall refer to such a crystal as an ideal crystal, for few, if any, actual crystals comply with the above requirements. The departures are of two types:

(1) Measurements of the intensity of reflection of X-rays from cleavage

surfaces of natural crystals give results different from those expected for ideal crystals. If a crystal is rotated slowly in a beam of monochromatic X-rays and the reflected beam is collected in an ionization chamber the intensity of reflection may be plotted against the angle of rotation. The 'half-width' of the peak from a given plane can be calculated for an ideal

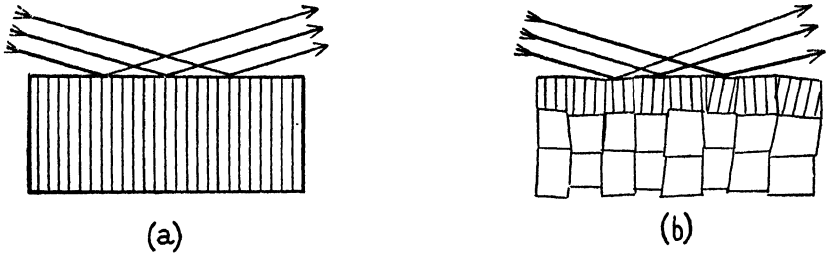


FIG. 44. Reflection of X-rays by (*a*) ideal and (*b*) mosaic crystal.

crystal. For an ordinary surface of rock-salt reflection is observed over say $\frac{1}{2}°$ instead of a few seconds of arc and the intensity of the reflected beam is far greater than the theoretical value. Freshly cleaved calcite, unpolished, is generally much more nearly perfect, and some specimens of rock-salt have been found to be nearly so. It is now known that crystals normally have a mosaic structure, illustrated diagrammatically in Fig. 44 (*b*). Instead of the atoms being perfectly aligned throughout the whole crystal the latter is broken up into a large number of 'mosaic' units, of about 10^{-5} cm. side, which are roughly oriented in the direction of the cleavage plane. The alignment of these blocks is not perfect and they may make angles of a few seconds or even minutes of arc with one another. The mosaic structure also gives rise to an effect called extinction, which is actually of two kinds, primary and secondary. Extinction affects the intensity of reflection from a plane by modifying the linear absorption coefficient and therefore provides additional experimental evidence for the mosaic structure of crystals.

(2) Within each portion of a mosaic crystal the structure may be perfectly regular, but in a number of crystals further departures from structure theory are found. In what follows we shall disregard mosaic structure and consider the arrangement of the atoms within the mosaic blocks.

According to classical structure theory the atoms are arranged at definite points in the lattice consistent with the symmetry of one of the 230 space-groups, whence it follows that all unit cells should contain the same numbers and kinds of atoms arranged in the same way. The theory also requires that a given set of equivalent positions must be occupied, and completely occupied, by atoms of the same sort. It is found experimentally that some crystals do not satisfy these conditions and such crystals are said to have 'defect' lattices. These cases were first considered rather exceptional, but it is now realized that many

crystals are of this type, and though at first sight they may appear to be of crystallographic rather than chemical interest, we shall see that they are of fundamental importance in relation to our interpretation of the laws of chemical combination. Defect structures may depart from the requirements of structure theory in one of the following ways:

(1) The mean position of a given atom (or atoms) cannot be located at a definite point. (Vibration of an atom about a fixed mean position—thermal motion—does not constitute a departure from structure theory.)

(*a*) There is random motion of the atoms (translation).

(*b*) The locus of the centre of an atom is stationary, e.g. circle or surface of a sphere, the atom being off the axis of rotation of a rotating group.

(2) The mean position of every atom is a fixed point, but the content of a particular unit cell is not the same as that of every other, differing in number, position, and/or kind of atom. This includes all structures containing atoms arranged at random.

In each of the above classes two main subdivisions may be made, according to whether each set of equivalent positions, if occupied at all, is completely filled or only contains part of its full complement of atoms. Further, more detailed classification is possible but would lead us to a complete geometrical classification of all solid bodies which is not necessary in this book. We shall shortly give examples of some of the types of defect structures, but first we must mention that the study of certain physical properties of crystals has suggested the existence of deviations from the ideal 3-dimensional lattice of a different order of magnitude from those we have been considering.

The existence of the various types of defect lattice enumerated above has been established by X-ray methods, which means that the deviations from the ideal crystal (1) are large enough to affect appreciably the intensities of the X-ray reflections, to the extent of 0·1 per cent. or more, and (2) persist over a time interval comparable with the time taken to record the X-ray reflections. The phenomena of the conductivity of ionic crystals and of semi-conductors, the existence of colour-centres, and the fluorescence of solids containing small amounts of impurity all suggest that in a crystal in thermodynamic equilibrium there exist two types of defect, named after those who postulated their existence:

Frenkel defect, consisting of an interstitial atom and, some distance away, the vacant lattice position from which the atom originated.

Schottky defect, consisting of a vacant lattice position only, the atom from which has migrated to the surface of the crystal.

These are illustrated diagrammatically in Fig. 45. Under the influence of an applied electric field these defects can move through the crystal, accounting for the electrolytic conduction of ionic crystals. The migration of a vacant lattice position is, of course, equivalent to the movement of an ion in the opposite direction. The number of such defects and therefore the magnitude of the electrolytic conductivity is a definite function

of the temperature for a given crystal, and molten polar salts are good conductors of electricity—e.g. 3·5 ohm^{-1} $cm.^{-1}$ for NaCl at 850° C. At temperatures just below their melting-points their conductivities are of the order of 10^{-4} ohm^{-1} $cm.^{-1}$ and they decrease rapidly with falling temperature. In a salt MX the conductivity may be due to one or both ions, and one method of investigating this point is as follows. Two plates

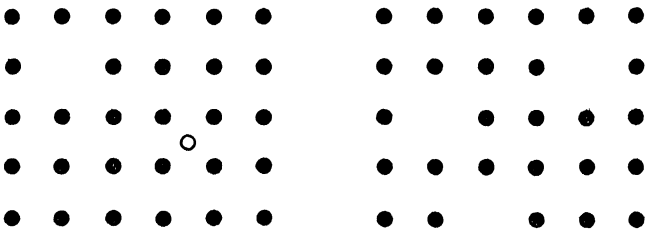


FIG. 45. Frenkel and Schottky defects in a crystal.

of crystal of equal thickness are placed in contact between two electrodes of the metal M. A current is then passed and the thicknesses of the electrodes and the crystal sections are determined. If only the negative ions have moved, the crystal plate nearer the anode is found to be thicker than the other, since the negative ions have combined with the metal of the anode. On the other hand, if only the metal ions have moved, then the thicknesses of the crystal plates remain unchanged but metal is transferred from anode to cathode. If both types of ion move the thicknesses of the plates change by intermediate amounts from which the transport numbers of the ions can be deduced. Experiments of this sort show that only the negative ions are mobile in $BaCl_2$, $PbCl_2$, $PbBr_2$; the positive ions only in AgCl, AgBr, AgI, α-CuBr, α-CuI, most alkali halides below 500° C., and both types of ion in PbI_2 and the alkali halides at high temperatures. The high-temperature forms of AgI and Ag_2HgI_4 show abnormally high ionic conductivities to which we refer later.

Colour Centres. A number of alkali halides become coloured when heated in the vapour of the metal or halogen owing to the absorption of a stoichiometric excess of one of the constituents. Thus NaCl becomes yellow when heated in sodium vapour and KCl blue-purple in potassium vapour, the amount of excess metal being of the order of 1 in 10^{-4}. Similar colorations are produced by electron bombardment of the crystals.

Phosphors. If pure zinc sulphide is heated to a temperature of say 800°–1000° C. it acquires the property of fluorescing when exposed to ultra-violet light or cathode rays. Fluorescence involves the absorption of radiation and the emission of radiation of longer wavelength, and in this case it is apparently associated with non-stoichiometric composition, there being interstitial zinc atoms and/or vacant sulphur positions. If the zinc sulphide is heated with a small amount of copper this is absorbed into the lattice and the crystals now fluoresce a brilliant yellow-green

instead of blue as in the case of the pure material. Moreover, they continue to emit light after irradiation has ceased (phosphorescence). A concentration of copper of only 1 in 10^{-6} will produce appreciable fluorescence and the optimum concentration is around 1 in 10^{-4} (compare colour-centres), but amounts much in excess of this reduce and finally destroy the fluorescence.

Semi-conductors. A number of compounds, notably oxides and sulphides, which are normally insulators, become conducting either when they contain a small amount of certain impurities or when they have become non-stoichiometric as the result of heating under appropriate conditions. The properties of such semi-conductors are dependent on their previous heat treatment and are to be associated with lattice defects, as are the colour-centres and fluorescence just referred to. Oxides, for example, may be grouped under two heads: (*a*) reduction semi-conductors, the conductivity of which increases on heating *in vacuo* (ZnO), and (*b*) oxidation semi-conductors, which are similarly affected on heating in oxygen under pressure (Cu_2O). The lattice defects postulated to account for these properties of crystals of non-stoichiometric composition are, as we have said, of a different order of magnitude from those we propose to describe now. The former involve departures from ideal crystals only of the order of 1 in 10^{-4}, and there is evidence from diffusion data that the time required for an ion to move from one position in the lattice to another is of the order of 10^{-10} seconds. Such defects are of little importance to the chemist and they cannot be detected by X-ray methods.

In the following remarks on defect structures we shall not adhere to any rigid crystallographic classification. Instead we shall divide our examples into four groups, viz.

(1) Crystals in which there is translatory motion of one or more types of atom (or ion) in a rigid lattice formed by atoms of another sort.
(2) Crystals in which there is rotation of some or all of the groups of atoms (molecules or complex ions).
(3) Mixed crystals.
(4) Miscellaneous defect structures and non-stoichiometric compounds.

(1) Translatory Motion of Atoms in Crystals

A number of iodides, sulphides, selenides, and tellurides are remarkable for forming high-temperature modifications with properties strikingly different from those of the ordinary low-temperature forms. Two of these compounds are worthy of rather detailed description.

Silver iodide normally forms hexagonal crystals with the wurtzite structure, the so-called β-AgI, in which the iodine atoms form a close-packed lattice—each being equidistant from twelve others. At 145·8° C. these crystals transform, sharply and reversibly, into the α- or high-temperature modification in which the coordination number of the large iodine ions has fallen to eight. This α-AgI has an exceptionally high ionic conductivity (1·3 ohm^{-1} $cm.^{-1}$ at 146° C.). In the iodine lattice of

this α-form there are possible positions of 2-, 3-, and 4-fold coordination for the silver ions, and X-ray measurements show that they move freely between all these positions. The high conductivity and self-diffusion of α-AgI confirm that the silver ions are not restricted to any definite positions in the rigid iodine lattice but move between the easily deformed

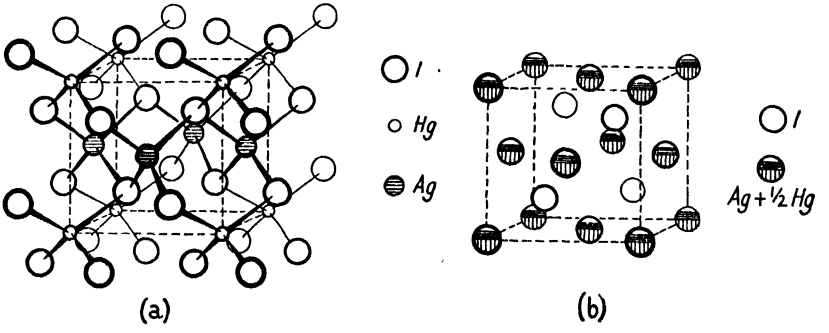


FIG. 46. The crystal structures of (*a*) the low- and (*b*) the high-temperature forms of Ag_2HgI_4.

iodine ions. The iodine lattice retains its rigidity up to the melting-point, 555° C. On heating AgI, therefore, we have the following sequence of events. At the transition point, 145·8° C., the iodine ions suddenly rearrange themselves to form a new stable lattice but the lattice of the silver ions melts, and from 145·8° to the melting-point (at which temperature the iodine lattice also collapses) the silver is in a fluid form in the solid iodine lattice.

The double iodide Ag_2HgI_4 shows a rather different behaviour. In the low-temperature (β) modification of this compound the iodine atoms form a cubic close-packed lattice and the Ag and Hg atoms occupy some of the tetrahedral holes in a perfectly regular manner, giving the crystal tetragonal symmetry (Fig. 46 (*a*)). The Hg atoms are situated at the corners of the unit cell and the Ag atoms at the mid-points of the vertical faces. Above 50·7° C. Ag_2HgI_4 exists as the α-modification in which the positions of the iodine atoms are the same as in the β-form, but the Ag and Hg atoms occupy at random not only the positions occupied in the low-temperature modification but also the tetrahedral holes at the mid-points of the remaining two sides of the unit cell (Fig. 46 (*b*)). In a cubic close-packed lattice there are twice as many tetrahedral holes as close-packed atoms, so that in this α-form, although the $2n$Ag+nHg atoms occupy statistically three-fourths of one set of tetrahedral holes, there is another set of $4n$ tetrahedral holes which are not occupied at all. This is in marked contrast to α-AgI, where the Ag atoms occupy at random all positions of sufficient size to accommodate them. This greater freedom in α-AgI may account for the very large conductivity, 1·3 ohm^{-1} $cm.^{-1}$ just above the transition point compared with that of $0{\cdot}79\times10^{-3}$ ohm^{-1} $cm.^{-1}$ for

α-Ag_2HgI_4 just above its transition point. Even so, the change in conductivity of Ag_2HgI_4 from $0{\cdot}98 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$ at 49·9° to a value 100 times greater just above 50·7° C. gives the compound a conductivity about 1,000 times greater than that of any normal ionic conductor at such a temperature. Although an averaged structure in which the number of available lattice points exceeds the number of metallic ions is a necessary condition for a solid with a high ionic conductivity, this alone is not sufficient. There may be a high activation energy required to surmount the potential barriers between the different points of the metal ion lattice. This is apparently the case in γ'-Al_2O_3 (see below), which has only a small cationic conductivity at high field strengths, though larger than that of the completely ordered α-Al_2O_3 (corundum). Silver mercuric iodide differs from silver iodide in another important respect. In the α- and β-forms of Ag_2HgI_4 the arrangement of the iodine ions is the same, whereas in AgI there is a change in the iodine lattice at the transition point. Hence the transition in AgI is sharp, but in the case of Ag_2HgI_4 a continuous and rapid change in conductivity and colour begins at about 40° and ceases only when the transition point is passed. The specific heat also increases rapidly over this temperature range but drops sharply at 50·7° C. These changes in Ag_2HgI_4 may be compared with order-disorder phenomena in alloys and with those accompanying the onset of rotation of molecules in crystals.

Other compounds with related types of defect lattices include the high-temperature forms of the sulphides, selenides, and tellurides of copper and silver. (The high-temperature form of cuprous iodide (440–602° C.) appears to be quite similar to α-AgI, forming a complete range of mixed crystals with that compound and possessing high ionic conductivity.) These compounds adopt one of two structures according to whether the ratio r_{cation}: r_{anion} is greater or less than 0·6. In the former case, exemplified by α-Ag_2S and α-Ag_2Se, the structure is similar to that of α-AgI with the Ag ions arranged at random in the interstices of a cubic body-centred arrangement of anions. In the latter case (α-Ag_2Te, α-Cu_2Se, and α-Cu_2S) the anions together with half of the metal ions form a zinc-blende structure in the interstices of which the rest of the metal ions are statistically distributed. It is interesting to note that Cu_2S is normally deficient in copper, approximating to the formula Cu_9S_5 (compare FeS, below).

(2) The Rotation of Molecules and Ions in Crystals

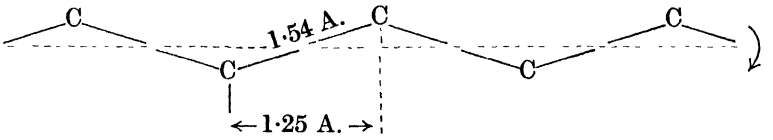
The decrease with rising temperature of the intensity of monochromatic X-rays reflected by a plane of atoms in a crystal is satisfactorily interpreted as due to the increased amplitude of vibration of the atoms about their mean positions. There is also the possibility that groups of atoms can take up energy of rotation, this first resulting in small oscillations and later in free rotation about one or more axes. In the case of hydrogen it is probable that in the solid the molecules rotate even at the absolute zero; in other crystals rotation sets in only at higher temperatures. The

possibility of free rotation will be determined by the relative magnitudes of the potential energy of the molecule in various orientations, and it will be most likely to occur in crystals containing highly symmetrical molecules or ions with small moments of inertia, and particularly in simple molecular crystals in which the molecules are held together by the relatively weak, undirected van der Waals forces. Definite proof of the rotation of groups of atoms in many crystals has been obtained by X-ray crystallographic examination. Free rotation increases the symmetry of a group of atoms and may, though it does not necessarily, increase the symmetry of the crystal as a whole. Some cases of polymorphism (see p. 183) are due to the rotation of one or more groups of atoms in one form of the substance. Free rotation also alters the apparent size and shape of a molecule or complex ion. Naturally the sidetracking of some thermal energy into rotational in addition to vibrational degrees of freedom as the crystal is warmed up will affect the variation of the specific heat with temperature; and the study of the specific heats of molecular crystals shows that the problem of the rotation of molecules in crystals is more complex than it was at first thought to be. We shall therefore first describe the structural changes in certain crystals which establish beyond doubt that there is rotation of groups of atoms in these crystals.

We have mentioned that the molecules of hydrogen in the solid element are rotating down to the lowest temperatures reached, as indicated by the hexagonal close-packing of the molecules. This type of packing is to be expected only for molecules with spherical symmetry, and the structure of hydrogen should be contrasted with that of, say, chlorine, in which the dumbbell-shaped molecules are packed in quite a different way. The high-temperature forms of many molecular crystals, such as HCl, HBr, HI, CH_4, etc., are also close-packed, but in these there are also thermal transformations at lower temperatures to which we refer below. There are many examples of crystals in which complex ions (CN^-, CO_3^{2-}, NO_3^-, ClO_4^-, SO_4^{2-}) rotate. An ion like CO_3^{2-} or NO_3^- may first begin to rotate about its 3-fold axis and this apparently happens in crystals of $NaNO_3$ over the temperature range 180–275° C. It may also rotate freely about its centre, when it behaves as a large spherical ion of effective radius about 2·3 A. This is so in the form of NH_4NO_3 stable above 125° C. which has the caesium chloride structure, indicating complete rotation of both the NH_4^+ and NO_3^- ions. This salt is remarkable for existing in at least five crystalline forms, at atmospheric pressure, in some of which the NH_4^+ and/or the NO_3^- ions rotate. All the ammonium halides, with the exception of the fluoride, are dimorphous and crystallize with both the NaCl and CsCl structures. The former is the high-temperature form and the transition temperatures are 184·3°, 137·8°, and −17·6° C. for the chloride, bromide, and iodide respectively. In all these salts the NH_4^+ ions are rotating at ordinary temperatures and the rotation presumably sets in over the temperature range in which these salts show a specific heat anomaly (see below), which for the chloride is from −40° to −30° C.

Ammonium fluoride, on the other hand, has a quite different structure, rotation of the NH_4^+ ions being prevented by the formation of N—H—F bonds. More is said of these 'hydrogen bonds' in Chapter VII.

In some organic compounds rotation of carbon chains occurs, and the mono-alkyl-ammonium halides provide an interesting example of the way in which the rotation of the chains was demonstrated. The apparent spacing of the carbon atoms along the direction of the chains is 1·25 A., whereas the carbon atoms in a $—CH_2—CH_2—CH_2—$ chain are normally 1·54 A. apart. The distance 1·25 A. is clearly the projection of the normal C—C separation on the axis of rotation:



These examples are sufficient to show that rotation of certain molecules and complex ions does occur in crystals, but less is known about how and at what temperatures rotation begins. When a study is made of the variation with temperature of the specific heat of a crystalline substance of this sort, it is found that in some cases there is a sudden intake of heat at a definite temperature. This is so with HCl, N_2, and CF_4, for example. This might reasonably be associated with the onset of rotation of the molecule, but in other cases another kind of thermal transformation is observed which takes place over an appreciable temperature range. Heat is absorbed, and the specific heat (usually) rises to a maximum value and then falls suddenly and continues to follow the usual curve. Such a specific heat anomaly for CH_4 is shown in Fig. 47 (*a*). Moreover, the same crystal may undergo more than one transformation of this second type or in some cases (O_2, H_2S) both types of transformation may be exhibited. Until the precise nature of these changes is understood we can only say that it is possible that with the second type of change there are more alternative orientations for the molecule at temperatures above than at temperatures below the transition point. The change from the state in which the molecules perform only small oscillations to that in which they rotate freely is rather analogous to the process of melting of a solid. We may expect that the thermal energy required to enable the first few molecules to rotate will be quite large but that by their rotation the forces restraining the neighbouring molecules are reduced so that the number of molecules free to rotate increases very rapidly once the process has begun. Ideas such as these receive support from experiments on mixed crystals. If the lattice of methane is diluted with inert gas atom (by forming solid solutions of methane with argon or krypton) the straints between neighbouring methane molecules are reduced. T now plot the specific heats of such mixed crystals containing d proportions of inert gas, we find that the temperature r

anomaly increases with increasing content of inert gas. In addition, the height of the peak decreases and the position of the peak is moved towards lower temperatures, as shown in Fig. 47 (*b*). If the content of krypton in the crystals is 50 per cent. or more the anomaly disappears entirely.

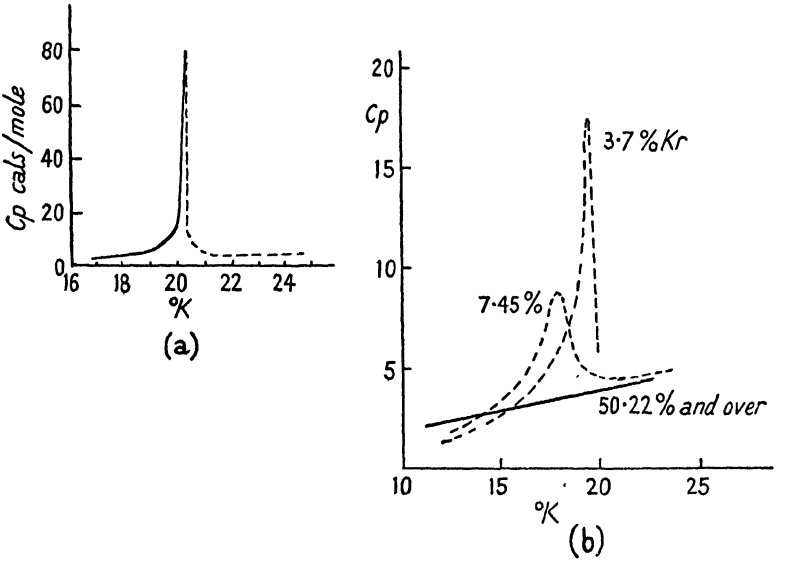


FIG. 47. Thermal transformations in (*a*) methane and (*b*) mixed crystals CH_4—Kr.

(3) Mixed Crystals

The chemist is usually introduced to the phenomenon of mixed crystal formation in connexion with isomorphism, and it is often stated that the formation of mixed crystals by two substances indicates that they are isomorphous. This is not so, nor is it true that if two substances do not form mixed crystals they are not isomorphous. We leave further remarks on isomorphism to a later section, but here we shall give a few examples of mixed crystal formation. The nature of mixed crystals can be appreciated only if we consider their crystal structures, for they are interesting examples of defect lattices. The simplest examples of mixed crystals are those of metals, the substitutional solid solutions which are formed by many pairs of metals. Silver and gold, for example, are miscible in all proportions (i.e. they form a continuous series of solid solutions) as are K and Rb, As and Sb, Mo and W, Ni and Pd, and many other pairs of chemically similar metals the atoms of which are of approximately the ·me size. When two such metals A and B have the same structure, ·ition of A to B produces a solid solution in which the geometrical ·ement of the atoms is the same as in pure A or B with the two ˆ atoms arranged at random. The melting-points and cell dimen- ·ns solid solutions vary regularly with composition. The random

arrangement of the atoms is invariably found if the molten mixture has been cooled quickly, but in some cases rearrangement to form a more regular structure takes place if the melt is cooled slowly or if the quenched material is annealed. This formation of 'superlattices' is dealt with in Chapter XVII. These substitutional solid solutions are examples of our second class of defect lattices, since all the crystallographically equivalent positions are occupied but by atoms of different kinds. Of a similar type are the mixed alkali halides, e.g. mixed crystals (K, Na)Cl, in which the K and Na ions are distributed at random over the Na positions in a rock-salt lattice. More interesting are the compounds $Li_2Fe_2O_4$ and Li_2TiO_3. Both crystallize with the rock-salt structure and there is random arrangement of the positive ions. These compounds form a continuous series of mixed crystals not only with each other but also with MgO, which crystallizes with the same structure. In Li_2TiO_3 the unit cell contains $1\frac{1}{3}$ formula weights, i.e. $2\frac{2}{3}$ Li^+ and $1\frac{1}{3}$ Ti^{4+} ions together occupy the octahedral positions between the close-packed oxygen ions. A more complex arrangement is found in some of the spinels, compounds of the general formula AB_2O_4, which are described in Chapter IX. In the normal spinel structure, as found for $ZnAl_2O_4$, $FeAl_2O_4$, and others, the eight A ions in the unit cell occupy positions of tetrahedral coordination and the sixteen B ions positions of octahedral coordination. In other cases ($TiMg_2O_4$, $MgFe_2O_4$) eight of the B ions occupy the tetrahedral positions and the other eight together with the eight A ions occupy the sixteen octahedral positions.

There are also mixed crystals in which not only is there random arrangement of different kinds of atoms in equivalent positions but in addition some of these positions are unoccupied. Crystals of CaF_2 (and SrF_2) containing small amounts of the trifluorides of scandium, yttrium, or the rare earths belong in this category. The structure of YF_3 is very similar to that of CaF_2 (p. 99), the extra F ions being situated at the centre and the mid-points of the edges of the unit cell. Mixed crystals CaF_2—YF_3 containing up to 40 atomic per cent. of the latter may be formed, and in these some of the positions which would all be occupied in pure YF_3 must be vacant. In another group of mixed crystals of compounds of different formula type, of which $MgCl_2$—LiCl is an example, there must similarly be either vacant lattice positions or additional interstitial ions. If a small amount of $MgCl_2$ dissolves in LiCl, which we may write as Li_2Cl_2, then since the packing of the large Cl ions determines the structure, there will be one vacant lithium position for every Mg^{2+} ion which enters the lattice. At the $MgCl_2$ end of the series, on the other hand, two Li^+ will enter for every two Cl^- in order to maintain electrical neutrality and there will be an excess of positive ions in the lattice. The conductivity of crystals of AgCl and AgBr containing small amounts of $CdCl_2$, $CdBr_2$, $PbCl_2$, or $PbBr_2$ has been measured. There will be a vacant Ag position for every Cd^{2+} or Pb^{2+} ion in the lattice. The conductivity of such a crystal at high temperatures will be due both to these

silver 'holes' and to the ordinary thermal defects mentioned above (Frenkel and Schottky defects), but at low temperatures the latter will not be important and can be assumed to be of the same order of magnitude in the mixed crystal as in the pure silver halide. The addition of 1 per cent. $CdCl_2$ increases the conductivity of AgCl at 210° C. by a factor of about one hundred. This fact not only provides evidence for the existence of defects of the type postulated by Frenkel and Schottky but also shows that they are of the same type as the large-scale defects we have been considering in mixed crystals.

Finally there are examples of mixed crystal formation between compounds of similar formula-type but different crystal structures, e.g. AgBr and AgI, AgBr and CuBr, CdS and ZnO. The first case is rather complicated by the fact that while AgBr has the rock-salt structure AgI appears to be capable of crystallizing in four different forms: the β- (low temperature) and α-forms, the zinc-blende structure, and also (under 3,000 atmospheres pressure) with the rock-salt structure. Under ordinary conditions, however, AgI certainly does not crystallize with the same structure as AgBr, yet the latter will dissolve up to 70 per cent. of AgI, though AgI dissolves very little AgBr. There is, of course, no reason why such solubilities should be reciprocal; compare the mutual solubilities of metals in one another. The system AgBr—CuBr presents some interesting points. Silver bromide crystallizes with the rock-salt structure ($a = 5{\cdot}76$ A.) and cuprous bromide with the zinc-blende structure ($a = 5{\cdot}68$ A.), so that in both compounds the bromine atoms are similarly arranged. In AgBr each Ag atom is surrounded by six Br and in CuBr each Cu by four Br, and it might be supposed that when CuBr dissolves in AgBr the Cu atoms would go into the positions of 6-fold coordination like the Ag atoms. In this case the mixed (Ag, Cu)Br crystal would be of the same type as one of (K, Na)Cl. There is evidence, however, that the Cu atoms go into tetrahedral positions between four bromine atoms, and since there are sufficient equivalent octahedral positions for all the Ag and Cu atoms it follows that for every Cu in a tetrahedral position there must be an octahedral position unoccupied. Measurements of the electrical conductivity and density of pure AgBr are interpreted as showing that at 400° some 16 per cent. of the octahedral positions are unoccupied and that the corresponding Ag atoms have gone into tetrahedral positions. Since the conductivities, measured at a fixed temperature, of mixed crystals (Ag, Cu)Br increase with rising Cu concentration just as the conductivity of pure AgBr rises with temperature, it seems probable that the Cu atoms are behaving in the same way as the Ag atoms in AgBr.

(4) Miscellaneous Defect Structures

In our introduction to defect structures we mentioned that we could distinguish between structures in which (*a*) each set of equivalent positions, if occupied at all, is completely filled, and (*b*) those in which some of these sets of equivalent positions are only partially occupied. Examples of the

former are the substitutional solid solutions of metals and mixed crystals such as (K, Na)Cl or K(Br, Cl), and of the latter the high-temperature forms of AgI and other crystals of this type, mixed crystals of substances of different formula-type such as CaF_2—YF_3, and interstitial solid solutions (e.g. metals containing small atoms in the interstices of the structure). In the case of crystals of the latter kind, (*b*), where we have, say, one set of equivalent positions only partly filled, we may obviously describe the structure in two ways. We may regard it as derived from one structure by the addition of a number of atoms or from another by the removal of certain atoms. An interstitial solid solution of carbon in γ-Fe is conveniently regarded in the former way because the γ-Fe structure (cubic close-packed) is stable without the carbon atoms. On the other hand, ferrous sulphide, which occurs naturally as the mineral pyrrhotite or magnetic pyrites, seldom if ever has the exact composition corresponding to the formula FeS. Formulae such as Fe_6S_7 to $Fe_{11}S_{12}$ have been assigned on the basis of chemical analyses. Careful measurements of the densities and cell dimensions of various specimens show that in these non-stoichiometric crystals some of the Fe positions in the lattice are unoccupied. This is possible because the approximately close-packed sulphur atoms form a stable lattice which is sufficiently rigid to tolerate the absence of some of the Fe atoms. However, this sulphur lattice is not stable (as pure sulphur) unless the majority of the metal atoms are present (the range of stability of the FeS 'phase' is only from 50 to 55·5 atomic per cent. S), so that $Fe_{11}S_{12}$, for example, is best described as FeS deficient in iron and not as sulphur+interstitial Fe atoms. Incidentally it is interesting to note that FeS has for so long been taken as an example of a chemical compound to illustrate the Law of Fixed Proportions. Further descriptions of defect structures will be found elsewhere in this book, see for example spinels (p. 332), γ-Al_2O_3 and γ-Fe_2O_3 (p. 334), the tungsten bronzes (p. 331), and interstitial compounds (p. 565).

THE LAWS OF CHEMICAL COMBINATION

The formulae of chemical compounds are based on chemical analyses which consist in the weighing (or measuring) of the masses (or volumes) of substances involved in chemical reactions. In interpreting the results of analyses we assume that in any reaction the total mass of the products is equal to the total mass of the materials with which we started. This Law of Conservation of Mass has been checked for a small number of reactions and has been shown to be true within the limits of accuracy attainable; it is assumed to hold in all cases. In Chapter I we saw that there is a simple relation between mass and energy, so that since in general energy is absorbed or evolved during chemical reactions (as heat or light), the mass-equivalence of this energy should be taken into account in the strict application of this law. However, the discrepancy arising from neglecting the mass-equivalence of such energy is too small to be

detected by the methods of chemical analysis. For example, in the formation of one gram-molecule (18 grams) of water from hydrogen and oxygen the loss of mass is only $0{\cdot}3 \times 10^{-8}$ grams. The careful analytical work of the late eighteenth and the nineteenth centuries led to the formulation of three fundamental laws of chemical combination, the Laws of Constant Composition and of Multiple and Reciprocal Proportions. These laws and their interpretation in terms of the atomic theory marked the beginning of chemistry as a precise science. They were founded on the study of simple molecules (the elementary gases N_2, O_2, Cl_2, gaseous oxides such as those of carbon, nitrogen, and so on) and simple solids like halides and oxides.

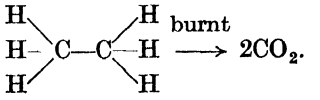
In view of what we have said of the structure of solids it is relevant to inquire whether these laws, hitherto regarded as the basis of quantitative chemistry, apply to all solid compounds, and indeed to inquire what we mean by the term compound when applied to a solid. Let us consider the Law of Constant Composition in this light. This law states that the composition by weight of a particular compound is always the same regardless of the method of preparation, and together with the atomic theory it implies that the ratios of the numbers of atoms of different kinds in a given compound are always the same. Before proceeding further it will be necessary to discover what we mean by a chemical compound. May we, for example, use the Law of Constant Composition to define a compound? We shall see that constancy of composition is no criterion of compound formation and, equally, variation in composition does not mean that a substance is not a chemical compound. It is instructive to examine some of the ways in which a chemical compound is distinguishable from a mixture, and it appears conventional to take FeS and a mixture of finely divided iron and sulphur as an example. The constituents of such a mixture may be separated in a number of ways: by flotation, which utilizes the difference in density; by dissolving the sulphur in carbon disulphide, in which iron is insoluble; or by using a magnet to extract the particles of iron. All these methods depend on the fact that the mixture of iron and sulphur consists of discrete particles which, though small judged by ordinary standards, each contain millions of atoms of iron and sulphur respectively. These particles therefore all retain the properties of iron and sulphur in bulk, properties which arise from the interaction between neighbouring, similar atoms. When, however, the iron and sulphur have interacted to form FeS, every Fe atom is now surrounded by six S and every S by six Fe atoms. Properties which depended on the way in which the outer electrons of, for example, a sulphur atom interacted with those of surrounding sulphur atoms have now been modified. So we find that the solubility, hardness, melting-point, boiling-point, and so on of a compound are different from those of the constituent elements. Nevertheless one set of properties of the compound will remain the same as in the original elements, for all properties characteristic of the nuclei or of the inner electronic structures of the atoms will be substantially

unaffected by changes in the configuration of the outer electrons which are those responsible for the interatomic binding. These properties have already been distinguished in Chapter I as non-periodic properties of the elements, and they include properties like radioactivity and the wavelengths of the characteristic X-ray lines. It is clear also that certain properties of an element (e.g. the ferromagnetism of iron) may be lost on compound formation, while the rearrangement of the atoms may give rise to entirely new properties (e.g. the optical activity of cinnabar, HgS). The so-called 'chemical' properties come in this category, but we shall have more to say on this point shortly. The action of dilute hydrochloric acid on iron results in the evolution of hydrogen gas, but if FeS is treated in the same way H_2S is evolved. As regards the properties of a compound compared with those of the constituent elements we may therefore say that certain properties of the elements are retained in the compound, others are lost, new ones are acquired, and properties like solubility and melting-point are modified. Now it is an entirely different matter to say that a definite melting-point is a characteristic of a compound. A compound certainly has a definite melting-point, but so have other types of solids such as 'molecular compounds' (see below) and eutectic mixtures.

It is commonly stated that mixtures differ from compounds in that less severe treatment, i.e. the expenditure of less energy, is required to resolve a mixture into its constituents than is the case with a compound, and there is a tendency to distinguish between 'physical' and 'chemical' processes in this connexion. Just as we shall find it difficult to define the term chemical compound, so it is equally difficult (and equally unprofitable) to draw a hard-and-fast line between these supposedly different kinds of process. It is more important to appreciate what happens in a process than to characterize it as a particular kind of process. To this end we shall consider briefly a few processes to see whether there are any satisfactory criteria we could use to distinguish physical from chemical changes. Experimental physics is usually concerned with studying the properties of substances without altering their composition (nuclear physics stands in an exceptional position in this respect), whereas chemistry is more concerned with processes in which the products have different atomic compositions and therefore different properties from those of the starting materials. We shall see that in both physical and chemical processes of the simplest kinds bonds between atoms are broken, but the chemical process then involves a rearrangement of the atoms to form new combinations.

Processes such as cleavage, melting, vaporization (which includes boiling and sublimation), and dissolution all involve the separation of atoms from one another and therefore the breaking of interatomic bonds of some kind. Not all crystals exhibit cleavage, and when it is observed the ease with which it can be brought about depends on the nature and strength of the bonds broken in the process. We have seen that crystals may be roughly classified according to the extent of the groups of atoms held together by bonds of the same type. In a crystal such as diamond all

the atoms are linked by homopolar forces into one large grouping which extends throughout the whole crystal. Cleavage of this crystal therefore breaks C—C bonds of the same kind that are broken in any reaction involving the splitting up of a carbon compound into simpler ones, e.g.



The melting of ice and the boiling of water involve the breaking of hydrogen bonds and the sublimation of a crystal of zinc-blende the rupturing of Zn—S bonds. The process of dissolution of a crystal illustrates in a similar way the different types of structure found in solids. The dissolution of a molecular crystal is merely a matter of separating molecules already held together only by feeble van der Waals forces. If a crystal of NaCl is dissolved in water we again merely separate ions already existing as such in the crystal, though the forces between them are of a different kind from, and much stronger than, those operating between the molecules in a molecular crystal. When we dissolve HCl gas in water, however, a more profound change takes place, molecules being dissociated into H^+ and Cl^- ions.

Now let us compare two simple chemical reactions. First we shall take the combustion of methane, CH_4, to CO_2. Without going into the mechanism of the change we may say that all the C—H bonds are broken and C—O bonds formed. Now suppose that we make aqueous solutions of $NaNO_3$ and KCl, mix them, and finally obtain some crystals of NaCl and KNO_3. This would be called a chemical reaction, for it certainly results in the formation of two compounds different from those with which we started and with different properties. (In this connexion we may remind the reader that the properties of, e.g. KCl *in solution* are strictly not those of KCl but those of the K^+ and Cl^- ions. By the properties of KCl we should mean those of the solid and those of the KCl molecule, but the latter have been little studied. Thus the property of precipitating AgCl from a solution of $AgNO_3$ is not a property peculiar to KCl but more generally of the Cl^- ion and is common to all soluble ionized chlorides.) What processes does the reaction

$$NaNO_3 + KCl \rightarrow NaCl + KNO_3$$

involve? We shall assume that we start with the crystalline salts. In $NaNO_3$ there are discrete Na^+ and NO_3^- ions, and in KCl, K^+ and Cl^- ions. In the process of dissolution these ions are separated and they are eventually recombined to form crystals of NaCl and KNO_3. At no stage has there been any appreciable alteration in the electronic configurations of these ions. We see that the changes described as chemical reactions differ greatly in the extent to which the arrangement of the outer electrons of the atoms is altered, and the same is true of processes loosely described as physical changes. In vaporization we have all degrees from the one

extreme, the vaporization of a molecular crystal, through the boiling of an associated liquid like water to the sublimation of ZnS or PCl_5.

Now let us see how constant composition is related to compound formation. If two elements or compounds form a series of solid phases intermediate in composition between the pure substances, it is conventional to regard these phases as compounds only in certain cases. If the composition can be varied continuously over either a small or a large range the phase is called a solid solution or mixed crystal. If, however, only a small number of phases with definite compositions are obtained these *may* be compounds. From an aqueous solution containing CsCl and $CoCl_2$ the compounds Cs_3CoCl_5 and Cs_2CoCl_4 may be crystallized according to the temperature and relative concentrations of the two salts. We may digress here to remark that there seems to be no general agreement as to which compounds of this type should be called 'double salts' and which 'complex salts'. It is often stated that double salts redissolve to form a solution of the original salts, whereas in the latter case the solution contains complex ions not present in those salts. It is, however, unsound to distinguish between two kinds of solid by their behaviour in solution, for we have seen in the previous chapter that there is no simple relation between the structure of a solid and the form in which the same compound exists in solution. On the one hand, a complex ion may exist in the crystal but be unstable in solution, so that a solid which is a true complex salt may in solution give all the reactions of the simple ions. On the other hand, the solution of a simple salt may itself contain complex ions as is the case with a hot blue solution of $CoCl_2$ in which there are complex ions $CoCl_4^{2-}$ in addition to simple Cl^- and hydrated Co^{2+} ions. The term complex salt is best retained for any crystalline salt which contains complex ions which do not exist in the crystals of the simple salts from which it was prepared.

To return to the mixed crystals, the system KCl—KBr will serve as an example. A mixed crystal KCl_xBr_{1-x} can be grown with any desired composition between KCl and KBr. Suppose that we have a crystal with the empirical composition K_2ClBr. The equal numbers of Cl and Br ions are arranged at random so that although on the average every K has three Br and three Cl ions as neighbours a particular K ion may have, say one Br and five Cl or five Br and one Cl. Such a mixed crystal therefore differs from a salt like PbFCl in which there is a regular arrangement of F and Cl ions throughout the crystal. Is the fact that the environment of every K ion in the mixed crystal is not the same, sufficient reason for saying that it is not a compound, and would it become a compound if, on annealing, the Cl and Br ions did arrange themselves regularly so that every K ion had three Cl and three Br neighbours? (The same considerations would apply to the disordered Cu_3Au solid solution and the ordered superlattice; see Chapter XVII.) We must remember that in many crystals the environments of all the atoms of one kind are not the same, and this is true of some elements as well as compounds. For example, in one form of metallic tungsten the atoms are of two kinds, some having

twelve equidistant nearest neighbours and the others having a quite different environment. In α-Mn the atoms are of four kinds and in β-Mn of two kinds. It may be true that in these at present inexplicable complex structures the different environments of the various sets of atoms may be due to the fact that the element can exhibit more than one valency, but this cannot be the explanation in a crystal such as andalusite, Al_2SiO_5, in which one-half of the Al atoms are surrounded by six and the others by five oxygen atoms. Many other examples could be given. We cannot therefore insist that in a compound every chemically similar atom must have the same environment, and equally we cannot say that regular atomic arrangement in a solid is a sufficient criterion for compound formation. This would, of course, imply definite proportions of the atoms of different sorts, but it would mean that we should regard as compounds such solid phases as molecular crystals, e.g. $SbI_3.3S_8$, in which SbI_3 and S_8 molecules are packed quite regularly but held together only by van der Waals forces, and all ordered alloys. We should exclude all statistical and non-stoichiometric crystals, and this would be inconvenient in chemistry, for some very simple compounds normally have defect structures. Moreover, in the silicates and sulphide ores isomorphous (random) replacement is the rule rather than the exception (see the next section). In such cases the actual crystals represent departures from ideal limiting compositions which are not necessarily always, or ever, attained. The difficulties we encounter in attempting to define the term compound arise from the fact that the structures of solids are not determined solely by the electronic configurations of the atoms. This is the case only with discrete molecules or complex ions, which are the only compounds to which the Law of Constant Composition can be strictly applied. The law is also usually obeyed by simple ionic compounds, since here the requirement of electrical neutrality ensures stoichiometric proportions of the ions, assuming that no foreign ions are present and disregarding the thermal defects mentioned above. We have noted that under exceptional conditions extra K^+ ions, though very few, may be introduced into the interstices of the KCl lattice, the balance of charge then being maintained by the presence in the lattice of free electrons.

Let us consider a crystal consisting of identical units packed together. In the simplest case these are atoms, but they may be finite groups or infinite chains or layers. The first point to notice is that if when the crystal is being formed there are present other atoms of suitable size, then these may fit into the lattice as easily as the original atoms, resulting in the formation of a substitutional solid solution. If the proportions of the two kinds of atom are such that a regular arrangement of them is possible, and if such an arrangement is more stable at low temperatures than the random arrangement, then rearrangement may take place on cooling. Rearrangement of atoms in the solid state is usually a slow process, and the annealing of alloys consists in maintaining the alloy at a temperature just below its melting-point to facilitate the attainment of

equilibrium. The second point is that when we have formed our crystal of identical atoms there are interstices between the atoms which may be large enough to accommodate other atoms. Small atoms like those of H, B, C, and N can enter many metallic lattices, forming what are called interstitial solid solutions. As might be expected, these have wide ranges of composition, but in the limit, when all similar holes have been occupied, the empirical formula is simple and the structure perfectly regular. Thus if C atoms, for example, occupy the tetrahedral holes in a cubic close-packed metal M we have MC_2 as the limiting case, so that the description of MC_2 as a compound and $MC_{1.7}$, say, as a solid solution is not consistent with the recognition of, say, FeS as a compound. The geometrical analogy between a non-stoichiometric crystal such as FeS and an interstitial solid solution like $MC_{1.7}$ must not be exaggerated, for FeS tends always towards the limiting composition FeS, whereas the composition of the solid solutions is often variable over a wide range. In the latter case the packing of the metal atoms is the same as in the pure metal, so that the structure is stable without any interstitial atoms, whereas this is not so with the sulphur lattice of FeS. Just as metal atoms of different sizes can often pack together to form simple structures (e.g. the fluorite structure of Mg_2Sn, etc.), so if two kinds of molecules have suitable shapes and sizes they may be able to form a regular crystalline arrangement. Thus the molecular crystal $SbI_3.3S_8$ is in no sense a chemical compound of the two components. Geometrical requirements lead in such cases to a definite (usually simple) formula.

These considerations have not led us to any simple definition of what constitutes a solid compound. They have shown that constant composition does not necessarily imply compound formation and that it may be convenient for some purposes to regard as compounds many solids of non-stoichiometric composition. Equally we find it difficult to apply any simple geometrical criterion to all the various types of solid. These conclusions are not surprising when we remember, for example, that few, if any, crystals are ideal crystals, that the ionic bond is a concept rather than a type of interatomic bond operating in actual crystals, that the perfect gas does not exist, and so on throughout the whole of physics, chemistry, and the other sciences. What is important is to realize the meaning we give to the terms we use.

ISOMORPHISM

Isomorphism is of more than crystallographic interest. At the time of Dalton's Atomic Theory only equivalent weights of elements were known. True atomic weights as we now know them could be determined only after the idea of molecules had developed as a result of the study of the combining volumes of gases. Only then could formulae be assigned to gaseous molecules showing the correct relative numbers of atoms, and these led to the conception of valency and the relation between equivalent and atomic weights. Avogadro's Hypothesis stated that at a given

temperature and pressure equal volumes of different gases contain equal numbers of molecules. This implies that the molecular weights of different gases bear the same relation to one another as their densities. Adopting the atomic weight of hydrogen as unit Cannizzaro (1858 and onwards) was able to determine the molecular weights of volatile compounds of the elements. The molecular weights of a considerable number of volatile compounds of a given element were determined and the smallest weight (referred to H = 1) of the element found in any of these molecules was taken as the atomic weight. Since vapour densities could not be determined with the precision possible in the case of equivalents, the exact atomic weight was determined as follows. The approximate atomic weight was found as already described and this must be an integral multiple of the equivalent. Assuming that the molecular weight was known sufficiently accurately to give the value of this number (the valency) unambiguously, then the exact atomic weight was simply the product of equivalent $\times$ valency.

Now this method could be applied only to those elements which form a considerable number of volatile compounds, i.e. the non-metals, and to establish with certainty the atomic weights of the metals other ways had to be found. The first of these made use of the 'Law of Atomic Heats' of Dulong and Petit, which we have already mentioned. The relation:

$$\text{specific heat} \times \text{atomic weight} = \text{atomic heat} \approx 6$$

could be used to determine the atomic weight with sufficient accuracy to give the valency, leading to the exact atomic weight as described above.

Isomorphism provided another way of linking up the atomic weights of metals and non-metals. Mitscherlich in 1819 found that certain pairs of salts developed the same crystalline form and concluded that such salts had similar chemical formulae, one kind of atom in one compound being replaced by another kind in the isomorphous salt. Analyses of such a pair of salts immediately gave the relative atomic weights of these two atoms. For example, the atomic weight of selenium was established in this way in 1828, following the discovery of the isomorphism of sodium sulphate and selenate, and also of the corresponding silver salts. The way in which the atomic weights of many metals can all be linked to those of a non-metal is well illustrated by the following examples. Potassium permanganate, $KMnO_4$, is isomorphous with potassium perchlorate, $KClO_4$, giving the atomic weight of Mn assuming that of Cl to be known. Also the manganate, chromate, sulphate, and selenate of potassium are all isomorphous, thus connecting the atomic weights of Mn, Cr, and Se to that of S. Finally a whole series of divalent metals form double sulphates of the general type $M^{I}_2M^{II}(SO_4)_2.6H_2O$ (the 'schönites'), where M^{I} is an alkali or similar metal (see the alums, below) and M^{II} may be Mg, Mn, Fe, Co, Ni, Cu, or Zn, the atomic weights of which may be linked through Mn to those of S and Cl. The alums (p. 180) and spinels (p. 332) are other examples of large groups of isomorphous crystals.

Another interesting case of isomorphism led to the correction of the atomic weight of vanadium and the clarification of the chemistry of that element. The formulae set out below were assigned to these minerals by Berzelius:

Apatite	$3Ca_3(PO_4)_2.CaF_2$
Pyromorphite	$3Pb_3(PO_4)_2.PbCl_2$
Mimetite	$3Pb_3(AsO_4)_2.PbCl_2$
Vanadinite	$3Pb_3V_2O_6.PbCl_2$

(Actually the formula of apatite would now be written $Ca_5(PO_4)_3F$ and not in the above form which suggests that the crystal is built up of units of $Ca_3(PO_4)_2$ and CaF_2. The crystal is an assemblage of Ca^{2+}, PO_4^{3-}, and F^- ions, and there is no association of certain calcium ions with PO_4^{3-} ions and of others only with F^- ions.) The fact that these four minerals are isomorphous led Roscoe to investigate the chemistry of vanadium, and he found that Berzelius had mistaken the oxide VO for metallic V and therefore assigned to vanadium an atomic weight 16 units too high. The correct formula for vanadinite then becomes $3Pb_3(VO_4)_2.PbCl_2$ or $Pb_5(VO_4)_3Cl$, of the same type as those of the other three minerals.

It appeared at first that in cases of isomorphism there was strong chemical resemblance between isomorphous salts, for in most cases their formulae differed only in the substitution of one kind of atom for another as in the examples quoted. Examples like $CaCO_3$ and $NaNO_3$ were considered exceptional, but many examples could now be given to show that chemical resemblances between isomorphous salts are not at all essential. In this connexion the following sets of isomorphous salts are of interest: K_2SO_4, K_2BeF_4, and $[N(CH_3)_4]_2HgCl_4$; $K_2TiF_6.H_2O$, $K_2NbOF_5.H_2O$, and $K_2WO_2F_4.H_2O$, and the 'alums' $K_2BeF_4.Al_2(SO_4)_3.24H_2O$ and $K_2ZnCl_4.Al_2(SO_4)_3.24H_2O$.

Criteria for Isomorphism

We now know that the requirement for isomorphism is similarity in internal, or atomic, structure of the crystals rather than similarity in chemical properties. Thus $CaCO_3$ and $NaNO_3$ are isomorphous because both crystals are built up of geometrically similar units, discrete ions and planar XO_3 groups, just as K_2SO_4 and K_2BeF_4 both contain K^+ ions and tetrahedral AX_4 groups. Various criteria for isomorphism have been suggested at different times, and it is worth while examining these in the light of our knowledge of the internal structure of crystals.

(1) *Similarity in Crystalline Form*

This is a vague phrase and requires careful interpretation. On the basis of external form crystals are classified into thirty-two symmetry classes, which are grouped into seven crystal systems. The structures of crystals in different systems are referable to unit cells of different types. The unit of structure in a cubic crystal is a unit cell with three equal edges mutually perpendicular, i.e. a cube. The angles between corresponding

pairs of faces (e.g. cube and octahedron faces) are necessarily the same on all cubic crystals whatever their internal structure. In a tetragonal crystal the unit cell is a tetragonal prism of base a and height c and the ratio $c:a$ may have any value. It will be clear that the angles between certain pairs of faces of tetragonal crystals are independent of the value of this axial ratio. For example, faces perpendicular to the a and c axes must always be perpendicular to one another, and angles between faces parallel to the c axis do not involve the axial ratio. The angles between faces inclined to both the a and c axes will, however, be dependent on the value of $c:a$. Thus in a series of tetragonal crystals all having the same external symmetry but with slightly different axial ratios we shall find small variations in some of the interfacial angles. Similar considerations apply in the other crystal systems. In the rhombohedral system, for example, the sides of the unit cell are equal and equally inclined to one another but the angle of the rhombohedron may vary. So in a series of isomorphous carbonates we find the following angles between corresponding pairs of faces:

$CaCO_3$ . . .	74° 55′
$FeCO_3$ . . .	73° 00′
$ZnCO_3$ . . .	72° 20′

A further point concerning crystalline form now arises. Examination of the external form of a crystal enables us to assign it to one of the thirty-two symmetry classes, but many different kinds of atomic arrangement can exhibit the same external symmetry: we have seen that there are 230 arrangements of 'internal' symmetry elements or space-groups. For example, metallic copper (cubic close-packed), α-Fe (body-centred cubic), NaCl, and CaF_2 all exhibit full cubic point-symmetry but have very different atomic arrangements and are in no sense isomorphous. It is interesting to note that the large class of double sulphates termed the alums, $A^IA^{III}(SO_4)_2.12H_2O$ (where A^I is NH_4, Na, K, Rb, Cs, etc., and A^{III} is Al, Ga, In, V, Cr, Mn, Fe, etc.) are often given as examples of isomorphous salts. These salts are all cubic but the arrangement of the structural units, A^I, A^{III}, SO_4^{2-} ions, and H_2O molecules is not the same in all cases, there being three different alum structures. Although all the alums listed below exhibit the same external symmetry they fall into three groups distinguished by small differences in internal structure:

α alum structure:	$KAl(SO_4)_2.12H_2O$
	$NH_4Al(SO_4)_2.12H_2O$
	$KCr(SO_4)_2.12H_2O$
	$RbAl(SO_4)_2.12H_2O$
	$TlAl(SO_4)_2.12H_2O$
	$KAl(SeO_4)_2.12H_2O$
β alum structure:	$(NH_3CH_3)Al(SO_4)_2.12H_2O$
	$CsAl(SO_4)_2.12H_2O$
γ alum structure:	$NaAl(SO_4)_2.12H_2O$

Comparison of the immediate environments of the monovalent ions, viz.

γ structure: $Na—6H_2O$ at 2·45 A.
α structure: $K—6H_2O$ at 2·94 A.
β structure: $NH_3CH_3—\begin{cases}6H_2O \text{ at } 3{\cdot}55 \text{ A.} \\ 6\ O(SO_4) \text{ at } 3{\cdot}58 \text{ A.}\end{cases}$

shows that the structural differences are due to the variation in size of these ions. In the γ and α structures the singly charged positive ions are surrounded by groups of six water molecules, the $M^+—H_2O$ distances being greater for the latter structure. In the β structure the very large Cs^+ and $(NH_3CH_3)^+$ ions are in contact with six O atoms of SO_4^{2-} ions in addition to six H_2O molecules, the $M^+—H_2O$ distance being still greater. If we restrict the term isomorphous to crystals in which there is similar arrangement of geometrically similar structural units, then the alums are not all isomorphous. (A complex ion such as NH_4^+ or CN^- which attains spherical symmetry by rotation, or a large ion such as $N(CH_3)_4^+$ or $Co(NH_3)_6^{3+}$ which is roughly spherical in shape, may be considered to be geometrically similar to simple spherical ions.) Such a definition of isomorphism is the only satisfactory one. It should be noticed that it makes no mention of the chemical nature of the crystals, but since it implies similarity in chemical formulae many isomorphous crystals will be closely related chemically. It does not require, however, exactly similar formula types. For example, in $K_2TiF_6.H_2O$ the structural units are K^+ ions, octahedral TiF_6^{2-} ions, and H_2O molecules, and the TiF_6^{2-} ions may be replaced by other ions provided they are octahedral and of similar size and charge. Ions such as $NbOF_5^{2-}$ and $WO_2F_4^{2-}$ fulfil these requirements. According to our definition all crystals with the same geometrical structure are isomorphous, e.g. all the alkali halides at ordinary temperatures (except CsCl, CsBr, and CsI), AgF, AgCl, AgBr, PbS, CaO, and ScN—to take a few examples at random—have the rock-salt structure. Mixed crystal formation has also been considered a criterion for isomorphism, but certainly these crystals do not all form mixed crystals with one another, and we must examine this matter in more detail.

(2) *Mixed crystal formation*

First we may state that mixed crystals will be formed by isomorphous crystals (defined as above) only if the interatomic bonds are of similar character in the two crystals. Thus KCl forms mixed crystals with KBr but not with PbS. Secondly our definition implies similar *relative* sizes of corresponding atoms or complex ions—e.g. the ratio of the sizes of the ions in the rock-salt structure must lie between certain limits as otherwise another structure will be more stable—but says nothing about their *absolute* sizes in the different isomorphous crystals. It is found that complete miscibility of isomorphous metals is possible only if the sizes of the atoms differ by not more than about 15 per cent. (of the radius of the smaller). In simple ionic crystals there are similar restrictions to mixed

crystal formation. This accounts for the fact that some compounds can form a wide range of solid solutions while others more closely related chemically are miscible only to a small extent, if at all. Thus we find that NaCl and AgCl form a wide range of mixed crystals, and that KCl and KBr are miscible in all proportions, whereas there is only limited miscibility of KCl and KI or of NaCl and KCl, in agreement with the radii of the ions.

Finally we should mention that even though the dimensions of the unit cells of two isomorphous crystals are sufficiently close to permit the formation of mixed crystals, it may not be possible to grow them. This will be the case if one of the salts is insoluble or is decomposed before melting, since mixed crystals are made from a solution or molten mixture of the two salts. Thus the cell constants of calcite and sodium nitrate are very nearly the same:

$CaCO_3$,	$a = 6{\cdot}361$ A.,	$\alpha = 46° 07'$
$NaNO_3$,	$a = 6{\cdot}32$ A.,	$\alpha = 47° 15'$

but mixed crystals cannot be made, though oriented overgrowths of $NaNO_3$ on calcite may be grown. The formation of oriented overgrowths also requires correspondence, within certain limits, of the cell dimensions of the isomorphous crystals. We conclude therefore that isomorphism does not imply the ability to form mixed crystals and conversely—as we have seen in our earlier discussion of mixed crystals—the formation of mixed crystals by two compounds does not mean that the compounds are isomorphous (cf. CaF_2—YF_3, AgBr (rock-salt structure)—AgI (zinc-blende structure)).

Isomorphous replacement is of very common occurrence in minerals. Many minerals were formed at high temperatures from melts containing atoms of many kinds; others crystallized from solutions containing many ionic species.

Anti-isomorphism

Just as a number of difluorides and dioxides crystallize with the fluorite structure in which each positive ion is surrounded by eight negative ions and each negative ion by four positive ions, so the oxides, sulphides, etc., of some monovalent metals crystallize with the 'anti-fluorite' structure in which the geometrical arrangement of the ions is similar but the positions of the positive and negative ions are interchanged.

Fluorite structure:	CaF_2, ThO_2, etc.
Anti-fluorite structure:	Li_2O, Li_2S, Na_2S, Cu_2S, etc.

Crystals of these two classes may be described as anti-isomorphous.

Polymeric Isomorphism

Structural investigations of certain series of related compounds have shown that there may be simple relations between their cell dimensions, as in the cases of $CuFeS_2$ and $CuFeSnS_4$ with structures simply related to that of zinc-blende (see p. 394), and $FeNb_2O_6$ which is related in a similar way to TiO_2. Owing to the close correspondence of the cell dimen-

sions of one compound with some multiples of those of the other in such cases portions of the two structures can fit together, so that the formation of oriented overgrowths may be possible. The formation of mixed crystals of such compounds is apparently rarely observed.

POLYMORPHISM

The term polymorphism was introduced by Mitscherlich in 1823 to describe cases where a substance, elementary or compound, crystallized in more than one form. We may adopt the definition due to Barth, that polymorphism includes every possible difference encountered in the crystalline lattice of a substance of constant chemical composition except homogene-

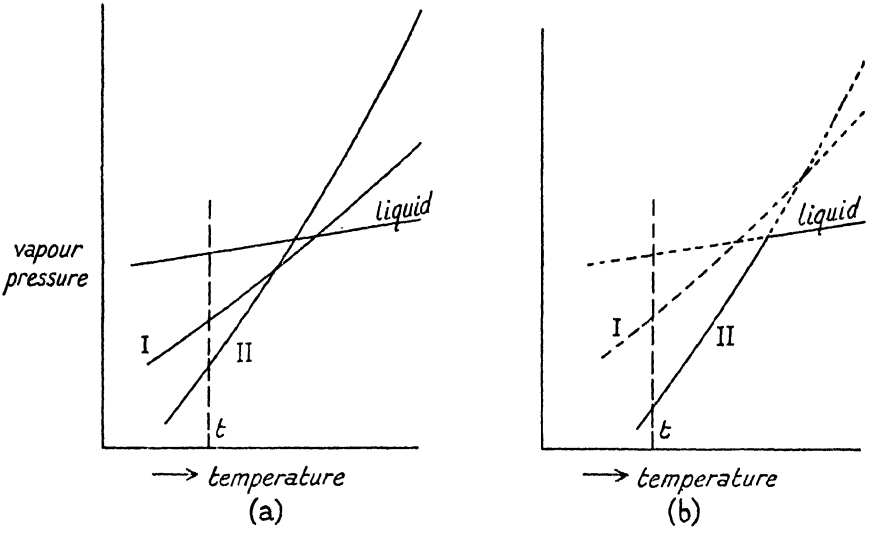


FIG. 48. Vapour pressure-temperature curves for the forms of (*a*) an enantiotropic solid and (*b*) a monotropic solid.

ous deformations. It will be as well to mention here another term, allotropy, which is still often used, though there appears to be little need for it. It is a less precise term than polymorphism and is applied wherever an element exists in more than one 'form' (Berzelius, 1841), as in the cases of carbon (diamond and graphite), phosphorus (white and black), or oxygen (O_2 and ozone, O_3). Apart from oxygen and ozone, the molecules S_2 and S_8, and possibly other similar cases, all cases of allotropy are merely examples of polymorphism since they refer to differences in crystalline form, and they are best described as such. A substance is described as di- or tri-morphic according to the number of distinct polymorphic forms.

We may distinguish two kinds of polymorphic substances according to whether or not the two forms (taking a dimorphic substance as example) are reversibly interconvertible. If we plot curves showing the variation of vapour pressure with temperature for each form and for the liquid, then we can represent these two possibilities in the manner shown in Fig. 48. In (*a*) the curves for the two forms (I and II) intersect at a

temperature below the melting-point of either form, and at this temperature the two forms are in equilibrium with one another. The polymorphic forms in this case are said to be enantiotropic—e.g. grey and white tin, rhombic and monoclinic sulphur. In (*b*) there is no such transition point and the substance is described as monotropic. Thus whereas in (*a*) the transition from I to II may be observed at a temperature below the melting-point, in (*b*) the form II cannot be converted into I without passing through the liquid or vapour phase. In either (*a*) or (*b*) both forms may be obtained at, say, a temperature t by supercooling the liquid or vapour, and the rate at which the less stable reverts to the more stable form may vary widely. Moreover, the rapidity with which an enantiotropic change takes place varies in different cases. Some such changes occur sharply and are easily reversible; that of α into β quartz is of this kind. Others, involving more radical changes in structure, are sluggish and exhibit hysteresis, as in the case of the quartz-tridymite change.

Polymorphic changes could be classified in various ways, but for our purposes we may divide them into the following groups:

(1) Changes from 'ideal' to defect lattices, involving
   (*a*) rotation of one or more of the units of structure (molecules or complex ions);
   (*b*) rearrangement of an ordered lattice into a disordered one;
   (*c*) breakdown of the lattice formed by one constituent.
(2) Changes in the packing of the units of structure and hence in the number and/or arrangement of nearest neighbours.
(3) Changes in structure leaving the immediate environments of the atoms sensibly unaltered.

We should perhaps remark that one reason for dividing examples of polymorphism into these classes is that they are so numerous and so varied in type that some sort of classification is necessary in order to present an intelligible account of a subject which usually receives very scanty treatment. A second, and in our opinion a far more important, reason is that we shall see the relation of polymorphism to other aspects of the structures of solids, a point on which we enlarge later.

(1) Changes from Ideal to Defect Structures

(*a*) We have already described briefly the phenomenon of rotation of molecules and complex ions in crystals. The rotation of a group of unsymmetrical shape will, of course, lead to a different kind of packing, so that all changes in class I involve changes in number and/or arrangement of nearest neighbours. They are distinguished from those in class II since these latter are not defect structures. Various ammonium salts (NH_4Cl, NH_4Br, NH_4I, NH_4NO_3), cyanides, and hydroxides exhibit this type of polymorphism.

(*b*) In a disordered solid solution higher symmetry may be achieved by the statistical arrangement of the atoms, the ordered arrangement

having lower symmetry, as in the case of Cu_3Au. The random solid solution has full cubic symmetry and the superlattice tetragonal symmetry (see p. 557).

(*c*) The structural changes in certain iodides, sulphides, and related compounds, in the high-temperature forms of which some or all of the metal ions are mobile in a still rigid anion lattice, have already been described in some detail. Examples are α-AgI, α-Ag_2HgI_4, α-Ag_2S, α-Ag_2Se, etc.

(2) Changes in the Packing of the Units of Structure and hence in the Number or Arrangement of Nearest Neighbours

Here the term unit of structure requires some explanation. In a metal or simple ionic structure it is the atom or simple ion, but in a crystal containing complex ions or molecules these are regarded as the structural units. We have therefore the following types of substance showing polymorphism of this kind.

(*a*) *Metals.* A considerable number of metals crystallize in two forms characterized by different coordination numbers, e.g. Fe with the cubic and hexagonal close-packed structures with 8- and 12-coordination respectively. The changes from grey to white tin and from α to β W also involve changes in coordination number.

(*b*) *Simple ionic crystals.* The simplest example here is the change from the rock-salt (6:6) to the caesium chloride (8:8) structure. Caesium chloride itself changes from the latter to the former structure at 460° C., and the chloride, bromide, and iodide of rubidium show the opposite effect when subjected to high pressure (5,000 kg./cm.^{2}).

(*c*) *Molecular crystals.* Certain organic crystals in which the molecules are held together by hydrogen bonds exist in more than one form. The polymorphic change merely involves rearrangement of the molecules and is therefore comparable with the above cases. (See p. 263 for the relation between the structures of α and β resorcinol.)

(*d*) *Crystals containing complex ions.* A crystal such as that of calcite is built up of Ca^{2+} and CO_3^{2-} ions which we regard as the units of structure, and we have seen (p. 105) that there are two simple ways of packing these ions. Both the calcite and aragonite structures are of the 6:6 coordinated type (deformed NaCl and NiAs respectively), but the arrangement of the six CO_3^{2-} ions relative to a Ca^{2+} ion is different in the two cases. The 6-coordination of Ca^{2+} by CO_3^{2-} must not be confused with the actual coordination number of the Ca^{2+} ions by oxygen. Since the Ca^{2+} ions lie between CO_3^{2-} ions their immediate neighbours are oxygen atoms and the number of these neighbours may be different even though the number of surrounding CO_3^{2-} ions is the same. This is shown diagrammatically in Fig. 49 for a 2-dimensional analogy. Thus in calcite a Ca^{2+} ion is in contact with six and in aragonite with nine oxygen atoms. On the other hand, in both pyrites and marcasite, the two forms of FeS_2, which represent

alternative ways of arranging Fe atoms and S_2 groups, the coordination number of Fe by S is the same.

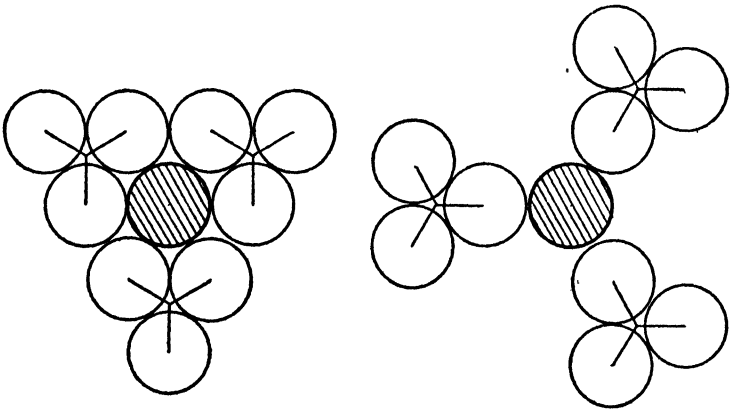


FIG. 49. Distinction between the number of surrounding AX_3 groups and the number of nearest X atoms.

(3) Changes in Structure leaving the immediate Environments of the Atoms sensibly Unaltered

This class includes some of the best-known examples of polymorphism. The simplest case is that of a metal which crystallizes with both the cubic and hexagonal close-packed structures. We have seen that in these close-packed arrangements of identical atoms the atoms are arranged in layers and the difference between the two kinds of packing arises from the way in which the successive layers are superposed. In hexagonal close-packing the sequence of layers is *ABAB*... and in cubic close-packing *ABCABC*... (p. 109). Hence a cubic close-packed structure may be converted into the hexagonal structure by sliding certain of the layers over one another, a process termed gliding. In view of this simple relationship between the two arrangements it seems remarkable that a metal should exist in the two distinct forms (as is the case with Ca, Co, Ni, Sc, La, and Ce), and even more remarkable that the regular sequence *ABAB*... or *ABCABC*... should be maintained throughout the whole of the crystal. If, for example, the first few layers of a crystal are *ABCABCAB*, then the next layer will be an *A* or a *C* layer according to the positions of its atoms relative to those of the last (*B*) layer. If this layer breaks the sequence and goes on as an *A* layer, then we get a crystal which is a mixed cubic-hexagonal close-packed structure, and it is interesting that this type of defect appears to have been observed in only one case, that of metallic cobalt.

A rather similar relation exists between the structures of zinc-blende and wurtzite, the two crystalline forms of ZnS. In both of these structures the Zn atoms are surrounded tetrahedrally by four S and the S atoms similarly by four Zn. In the cubic zinc-blende structure the positions of

the S atoms are those of cubic close-packing, and the same is true of the Zn atoms, which may be regarded as occupying one-half of the tetrahedral holes in the sulphur lattice. In wurtzite, on the other hand, the positions of the S atoms are those of hexagonal close-packing. As in the case of

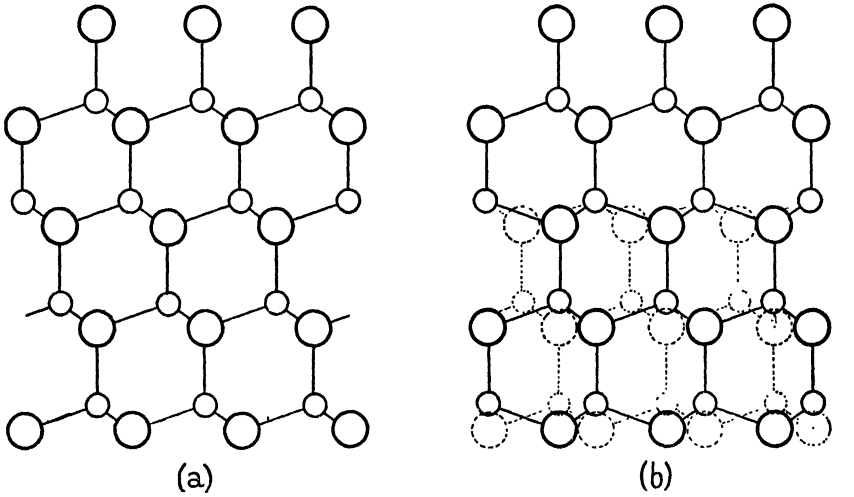


FIG. 50. Elevations of the structures of (*a*) zinc-blende and (*b*) wurtzite. (Two of the four tetrahedral neighbours of an atom are superposed in these diagrams.)

simple close-packed metal structures, therefore, one structure is related to the other by translatory movements of portions of the structure parallel to the layers of close-packed atoms. This may be seen from the elevations of these structures shown in Fig. 50.

The three crystalline forms of silica, each of which also has a low- and high-temperature form, are a classic example of this kind of polymorphism, for in each form the environment of the silicon atoms is similar but the SiO_4 tetrahedra are linked together in different ways. The structures of these crystals are described in Chapter XIV. Another oxide of a Group IV element is remarkable for existing in three crystalline forms—titanium dioxide. All three forms occur as minerals, rutile, anatase, and brookite, and in all cases the Ti atoms are surrounded by six oxygen atoms forming an approximately regular octahedral coordination group.

The polymorphism of antimony trioxide has already been mentioned in connexion with the classification of crystals. It is our first case of polymorphism in which the two forms contain complexes of different types—in this case finite groups and infinite chains. The polymorphism of certain of the non-metals provides further examples of this sort. Of the various varieties of phosphorus which have been described, two are certainly characterized by definite crystalline form, white phosphorus and black phosphorus. In the brilliant cubic crystals of the former the units of structure are certainly P_4 molecules while the latter has a more complex layer structure, illustrated diagrammatically in Fig. 119 (p. 399). In both

forms the P atoms form three strong bonds, but the bond angles are rather different in the two structures. Arsenic is normally obtained in the 'metallic' form which has a layer structure in which every As atom has three nearest neighbours, but rapid condensation of the vapour produces an unstable yellow modification which probably has a molecular As_4 structure similar to that of white phosphorus. Sulphur forms at least two kinds of crystals, rhombic and monoclinic. The structure of the latter is not yet known, but in rhombic sulphur there are S_8 molecules (p. 538) consisting of rings of eight sulphur atoms. We have seen that the only other arrangement apart from rings possible for atoms forming only two bonds is a chain. The structure of plastic sulphur is incompletely determined, but certainly consists of chains of S atoms, and crystalline selenium and tellurium are built up of infinite chains.

These examples are sufficient to show that polymorphism is a phenomenon of some interest and intimately related to the stereochemistry of the elements. We wish now to touch upon one or two other subjects closely connected with polymorphism.

REACTIONS IN THE SOLID STATE

In reactions in which one solid is converted into another in the *solid* state the only atoms which can take part in the first stages are those on the surfaces. For further action to take place it may be necessary for atoms to diffuse from the surface of the original solid through the layer of product. Such reactions, therefore, like other cases of diffusion in solids and electrolytic conduction in ionic crystals, depend on the movement of atoms through a crystal and they are closely related to polymorphic changes which must also involve the movement of atoms relative to one another. We have said that at first only surface atoms are concerned in 'solid reactions'. It might appear that this is not always true and that the reaction takes place throughout the bulk of the solid, but in the study of such reactions two points must be remembered.

Firstly, many reactions apparently taking place in the solid phase actually involve the gaseous or liquid phase or require the presence of moisture. In a simple change of one solid (A) into another (B), A may first melt and then B crystallize out, and if B has a higher melting-point than A, only careful observation will detect the intermediate liquid phase. The transition temperature for the change zinc-blende–wurtzite is very close to 1020° C., but crystals of the latter are often found in ZnS which has been heated to temperatures well below 1020°, e.g. 900° C. The explanation here is that the wurtzite has been deposited from the vapour phase, some ZnS having sublimed. In particular, all experiments involving grinding must be regarded with suspicion since quite high temperatures may be developed locally. Finally reactions, such as the rusting of iron, requiring the presence of moisture are concerned with ionic processes in solution and are of quite a different kind from those we are considering here.

Secondly, many solids possess extensive 'internal surfaces', particularly if they have been formed as a result of a chemical or polymorphic change. Consider, for example, the conversion of crystalline $Mg(OH)_2$ into MgO by heating—say to 500° C. This hydroxide has a layer structure and MgO the rock-salt structure. The MgO formed in this way consists of micro-crystals, since the temperature is far too low to allow recrystallization and the formation of compact crystals to take place. The conversion of $Mn(OH)_2$ into MnO_2 (via MnO(OH)) similarly leads to a very finely divided product. Although all these three manganese compounds have rather similar arrangements of oxygen atoms, there is not sufficiently close correspondence between the structures to permit the formation of compact crystals. The carbon obtained from burning organic matter also possesses very considerable internal surfaces and such products have great activity as catalysts and absorbents.

We may mention here that a characteristic of polymorphic changes and of true 'solid reactions' is that there is generally a quite definite crystallographic relation between the original crystal and the orientation of the crystals of the product. This merely expresses the fact that there is as little disturbance as possible during the changes. Thus when zirconium changes (at 862° C.) from the body-centred form to the hexagonal close-packed form the most densely populated planes of the former structure (the (110) planes) become the close-packed (0001) planes in the hexagonal structure. In the conversion of $Mg(OH)_2$ into MgO the most densely packed planes (111) of the latter are parallel to the layers of oxygen atoms in the original $Mg(OH)_2$ layer structure. A more complex example is provided by the conversion of aluminium metal first, by cold oxidation, into the γ' oxide, then into the γ form and finally into α-Al_2O_3:

Al	*Cubic* γ' Al_2O_3 ($Al_{\frac{8}{3}}O$)	*Cubic* γ Al_2O_3 (spinel structure)	*Rhombohedral* α Al_2O_3 (corundum)
Cubic close-packed	Cubic close-packed oxygen lattice with Al at random in $\frac{2}{3}$ of octahedral holes.	Also cubic close-packed oxygen, but Al in tetrahedral and octahedral holes.	Hexagonal close-packed oxygen with Al in $\frac{2}{3}$ of octahedral holes.

These examples show that chemical reactions involving solids have a geometrical as well as a chemical aspect. Knowledge of the structures of solids is necessary to an appreciation of the geometry of solid reactions, and the classification of crystals adopted in the previous chapter is of use in this connexion. Thus the absorption of material by graphite and clay minerals with expansion of the lattice in one direction only is typical of layer structures, whereas framework structures such as zeolites can absorb material without expansion of the lattice. A close-packed structure such as a metal, on the other hand, cannot accommodate, in the holes in the structure, foreign atoms of size comparable with its own atoms but can absorb very small atoms. Thus hydrogen diffuses through metallic palladium and carbon into iron.

To discover the actual mechanism of solid reactions is a problem of some complexity, but progress has been made in some cases. Suppose, for example, that we have a portion of solid silver in contact with liquid sulphur. The silver is gradually converted into its sulphide. It is clear that as soon as a complete film of Ag_2S covers the surface of the metal further action can take place only if silver or sulphur atoms diffuse through this layer of sulphide. Experiments show that it is the silver which can move through the Ag_2S. Many cases of the diffusion of atoms through salts could be given, but the following are typical. The diffusion of Pb through PbI_2 crystals has been shown by using radioactive Pb. If a crystal of NaCl is electrolysed at 600° C. using a gold anode, Au atoms diffuse into the salt crystal, and a similar effect is obtained with Ni above 640° C. (the melting-point of NaCl is 801° C.). Finally, if a crystal of Ag_2S containing 1 per cent. Cu_2S in solid solution is placed in contact with a crystal of pure Ag_2S and the combination is kept at a temperature of 200–300° C. for some hours, it is found that the Cu has become distributed throughout both crystals.

When a metal surface is oxidized there must be diffusion of either metal or oxygen atoms (or both) through the oxide layer if the oxidation is to continue. Interesting differences are found between the behaviours of different metals when they are oxidized. When copper is heated in air or oxygen the thickness of the oxide layer increases steadily with time, and the rate of growth of the layer increases if the oxygen pressure is increased. In the case of zinc, however, the rate of oxidation is almost independent of the oxygen pressure, provided there are sufficient oxygen atoms to react with all the zinc atoms which diffuse to the surface. There is a corresponding difference between Cu_2O and ZnO as semi-conductors, the former being a semi-conductor only if it is deficient in copper (or alternatively contains a stoichiometric excess of oxygen) and ZnO only if it contains excess zinc. It is reasonable to suppose, therefore, that the mechanism of the oxidation of such metals is similar in some way to that of semi-conductivity. The conductivity of Cu_2O is due to the movement of ions and electrons (it is mainly electronic), and the oxidation of copper proceeds by the diffusion of equal numbers of copper ions and electrons through the Cu_2O layer. Thus the semi-conductivity of Cu_2O and the rate of oxidation of Cu are similarly affected by variation in oxygen pressure at a given temperature. Aluminium, however, behaves quite differently. On oxidation the oxide layer grows until it reaches a certain thickness (about 40 A.), when the process stops. This is attributed to the fact that the work required to remove an electron from the metal into the oxide layer is very large. Quantum mechanics suggests a mechanism for some electrons to penetrate the oxide layer without receiving any thermal energy of activation, and predicts a maximum thickness for such a layer of the same order of magnitude as that observed.

We have digressed deliberately from polymorphism to semi-conductivity with the object of showing that many phenomena which are at first sight

quite unrelated and often kept in 'watertight' compartments as branches of chemistry, physics, crystallography, or some other branch of science, are in fact different aspects of one type of process. We see that the study of physical processes like the semi-conductivity of oxides may throw considerable light on the mechanism of the oxidation of metals, a problem which at first sight might appear to come within the province of the chemist rather than the physicist. The study of processes involving the movement of atoms in solids embraces polymorphic changes, order-disorder phenomena in alloys, defect structures, semi-conductivity and the properties of phosphors, and finally all the various reactions involving solid phases.

CHAPTER VI

THE EXPERIMENTAL METHODS OF STRUCTURAL CHEMISTRY

In this chapter we shall consider some of the more important ways of determining the arrangement of atoms relative to one another. We shall not be concerned with details of experimental technique or of theory, but rather with the principles on which the various methods are based, with their advantages and disadvantages and with the type of information they provide. Also, all methods are subject to certain limitations and sources of error or ambiguity, and some appreciation of these is at least as important as a knowledge of the experimental methods themselves.

The sum total of our knowledge of the geometrical arrangement of the bonds formed by an atom is conveniently referred to as the stereochemistry of that atom. As we have seen, the angles between the bonds from atoms of a given element depend not only on the number of bonds formed but also on the valency state of the atom and on the nature of the bonds—whether covalent or ionic, single or multiple. Prior to the development of physical methods of determining structure the experimental methods of studying the stereochemistry of an atom were few in number, and we may mention here some of the major differences between classical stereochemistry and modern structural chemistry. Firstly, the experimental methods were deductive in the sense that the spatial arrangement of certain atoms around others was inferred from (*a*) the existence of a molecule in a certain number of stereoisomeric forms, (*b*) the optical activity of a molecule or complex ion, or (*c*) the conversion of the compound under investigation into others whose configurations could be determined as in (*a*) or (*b*). Secondly, the information obtained was only qualitative. The proof, from the optical activity of a molecule *Cabcd*, that the carbon atom formed four tetrahedral bonds was not a proof that the interbond angles were all 109° 28′ but only that the bonds were not coplanar and were directed, at least approximately, towards the apices of a tetrahedron. Classical stereochemistry could not utilize the *absolute* values of physical constants. Differences in physical properties such as melting-points were, of course, required to establish the individuality of a number of isomers and the molecular rotatory power of a compound was measured, but deductions were not made from the absolute values of these constants. Use cannot be made of such values until theory has developed sufficiently to predict them for the various possible configurations of a molecule: only then does it become possible to obtain useful information from them.

In contrast to the qualitative nature of classical stereochemistry we

have the modern metrical structural chemistry, in which the interest has now shifted to small departures from expected interatomic distances and interbond angles.

Thirdly, classical stereochemistry was restricted, by the very nature of its experimental methods, to the study of finite groups of atoms—molecules and complex ions. The extension of the scope of stereochemistry to include also the infinite complexes has become possible only with the study of the solid state.

There are three stages in the determination of the structure of a molecule. Chemical analysis tells us the ratios of the numbers of atoms of different kinds. Next the determination of the molecular weight is necessary to find the actual numbers of atoms of each kind in a molecule. The molecular weight may be found by the cryoscopic or ebullioscopic methods, by determining the vapour density or nowadays by the X-ray method (see below). Ignorance of correct molecular weights has caused trouble in the past when deducing the configurations of molecules from the number of isomers, as, for example, when one of the supposed isomers was in reality a polymer (see p. 223). The third stage is the actual determination of the spatial arrangement of the atoms, with which we are now concerned. Our knowledge of the structure of matter is derived from observations of the way in which matter interacts with energy. We may examine how a group of atoms behaves in an electric or magnetic field, how the electrons of the atoms take up energy from, and thereby modify, a beam of light, X-rays or electrons, or how the molecule acquires rotational or vibrational energy.

An atom consists of a nucleus, in which practically all the mass of the atom resides, surrounded by a number of orbital electrons. Atoms cannot approach indefinitely close to each other owing to the repulsion of the orbital electrons and of the nuclei, so that we can assign sizes to atoms—though, as we have already seen, the effective size of an atom is not constant. We may distinguish between properties dependent on the presence of a massive nucleus and those arising from the presence of the orbital electrons. The former include mass and the power of scattering other nuclei (e.g. α-particles) and fast electrons. Of the properties associated with the orbital electrons we shall be most concerned with the scattering of X-rays, the absorption or emission of energy due to the movement of electrons from one orbit to another, and the magnetic properties arising from the movement of the electrons, which are equivalent to electric currents and therefore possess magnetic moments.

Let us now see how these properties may be utilized to find the structures of substances. We may start with the simple system A—B consisting of two atoms and inquire how we can determine the distance between the atoms. In this system, consisting of two nuclei surrounded by orbital electrons, the arrangement of some of the outer electrons is different from that in the isolated atoms since these constitute the bond between the atoms, but the arrangement of the inner orbital electrons and the structures

of the nuclei are not appreciably affected. We may therefore determine the separation of the atoms from

(*a*) The moment of inertia of A—B. This is a function of the masses of the atoms and of their distance apart. For a diatomic molecule consisting of atoms of masses m_1 and m_2 a distance d apart, rotating about an axis perpendicular to the line of centres, the moment of inertia is given by

$$I = \frac{m_1 m_2}{m_1+m_2} d^2.$$

The way in which I is found will be considered later.

(*b*) The scattering of electrons. The diffraction of high-velocity electrons is almost entirely due to the atomic nuclei, the relative positions of which can therefore be deduced now that the theory of scattering of electrons has been developed.

(*c*) The scattering of X-rays. This depends on the arrangement of the orbital electrons, so that the variation of electron density in the system may be found. The positions of the nuclei of the atoms can therefore be determined if we assume these to be at the centres of their respective electronic systems.

Other properties of a bond which are of interest from the structural standpoint are its polarity, which we shall consider in more detail shortly, and its heat of formation. The latter will interest us only in cases where a comparison of the observed heat of formation of a compound with the values calculated for various possible molecular models enables a decision to be made between them.

When we come to more complex groups of atoms there are more ways of obtaining information about structure, though the problem is necessarily one of greater complexity. As before, we may utilize moments of inertia and data from electron and X-ray diffraction. If, for example, we knew the moments of inertia of a complex molecule about a sufficient number of axes it would, in principle, be possible to determine completely the structure of the molecule. In practice, however, the problem is too difficult except for comparatively simple molecules. The electron and X-ray diffraction methods will be discussed shortly. Other properties of complex groups of atoms may be grouped under three heads:

(1) Additive properties, i.e. those which may be expressed as the sum of the properties of the individual atoms or of the separate bonds:
(*a*) heat of formation,
(*b*) mean diamagnetic susceptibility.

(2) Vector properties, which are the resultant of directed properties of the individual bonds:
dipole moment.

(3) A third group contains properties which cannot be expressed as the scalar or vector sum of properties of the component atoms or bonds. These are shape and symmetry and related properties:

(*a*) stereoisomerism,
(*b*) optical activity,
(*c*) optical and magnetic anisotropy.

We shall now consider the more important structural methods in more detail.

X-RAY DIFFRACTION

Matter in all states of aggregation may be studied by means of X-ray diffraction. For technical reasons X-rays have been superseded by electrons in the study of the structures of gases and vapours, and we have mentioned in Chapter IV the diffraction of X-rays by liquids. In the present section we shall be concerned only with the diffraction of X-rays by crystalline solids.

A crystal is a regular 3-dimensional array of atoms. Just as a series of parallel lines ruled on a plane surface acts as a diffraction grating for visible light, so a crystal acts as a 3-dimensional grating for X-rays. The wavelengths of X-rays are of the same order of magnitude as the interatomic distances in crystals, and along any direction in a crystal the atoms repeat at regular intervals. For a line grating of periodicity a the condition for the formation of a spectrum is

$$a(\alpha - \alpha_0) = n\lambda,$$

where α and α_0 are the direction cosines of the diffracted and incident beams, n is an integer (the order of the spectrum), and λ is the wavelength of the light. If a crystal is rotated about a principal axis and monochromatic X-rays are incident perpendicular to the axis (Fig. 51 (*a*)) the diffracted beams lie on cones of half angle θ_1, θ_2, etc., corresponding to $n = 1, 2$, etc., in the equation

$$n\lambda = a \sin\theta \quad (\alpha = \sin\theta \text{ and } \alpha_0 = 0 \text{ in above equation}),$$

where a is the period along the axis of rotation. The diffracted beams may be conveniently recorded on a photographic film wrapped inside a cylindrical camera surrounding the crystal (Fig. 51 (*b*)). In Figure 53 (*a*) is shown a typical photograph obtained in this way. For convenience in interpreting the photographs it is more usual to oscillate the crystal to and fro through a small angle (often 15°) rather than to take a complete rotation photograph. The angle θ may then be measured as $\tan^{-1}x/r$, r being the radius of the camera, whence the spacing a of equivalent atoms along the axis of rotation is determined. In this way the dimensions of the unit cell of the crystal may be found. If the axes of the crystal are not orthogonal the interaxial angles may be measured goniometrically or from the angular relations between various sets of diffracted beams.

Since a crystal behaves as a 3-dimensional grating, three equations must

be satisfied simultaneously if a spectrum is to be formed by monochromatic X-rays, viz.

$$a(\alpha-\alpha_0) = h\lambda$$
$$b(\beta-\beta_0) = k\lambda$$
$$c(\gamma-\gamma_0) = l\lambda.$$

The order of each spectrum is therefore denoted by a set of three integers, *hkl*. These integers are related in a simple way to the ordinary crystallo-

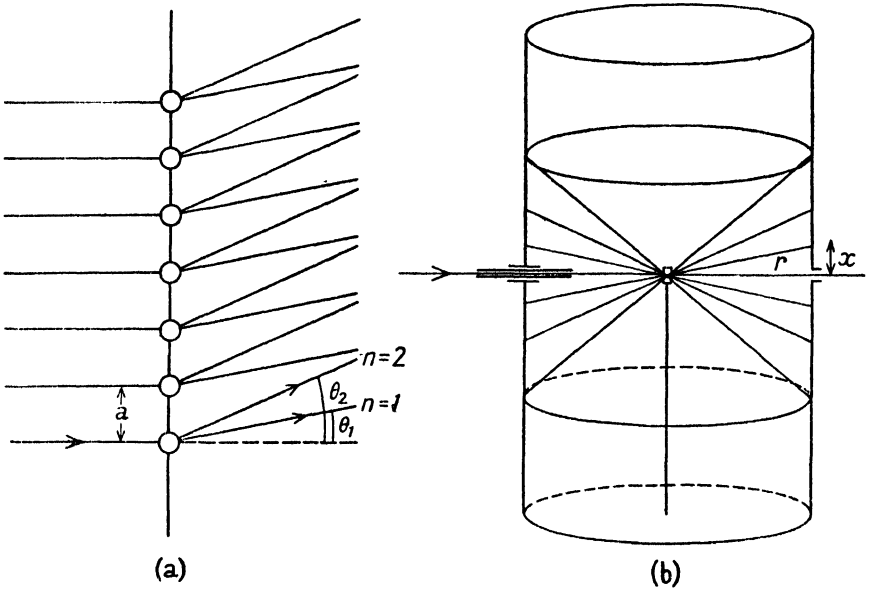


FIG. 51. X-ray rotation (or oscillation) photograph, showing the formation of layer lines in a cylindrical camera.

graphic indices of crystal faces. Laue showed that the above equations are equivalent to the conditions for reflection of the X-rays by the plane with indices *hkl*. Thus the diffracted beams of X-rays may be regarded as reflections from all the various possible planes of atoms in the crystal. Whereas, however, the indices of a crystal *face* simply define its orientation, the X-ray indices also show the order of the spectrum from a given plane. For example, the (111) plane gives rise to a series of diffracted beams, the first order reflection being 111, the second 222, and so on. In general for a stationary crystal and monochromatic X-rays few planes are in a position to reflect the X-rays so that we use either (*a*) a stationary crystal and 'white' radiation—Laue photograph—or (*b*) monochromatic radiation and rotate the crystal.

In regarding the crystal in this way as a three-dimensional diffraction grating we have represented the scattering material as concentrated at points. In fact the orbital electrons are responsible for the scattering, so that we must replace the points in our grating by atoms with radial

electron distributions of the type described in Chapter I. Since the electrons are distributed throughout the space between the centres of the atoms we may alternatively regard the crystal in a rather different way. The concentration of electrons varies quite irregularly from point to point within the unit cell, depending on the positions and nature of the atoms therein, but it varies periodically throughout the crystal, since the crystal is built up by regular repetition of the unit cell in three dimensions. On account of this periodicity it should be possible to resolve the electron distribution into its Fourier components, each one of which is responsible for a particular diffracted beam. From a knowledge of the amplitudes and phases of these diffracted beams we should, therefore, be able to determine the variation of electron density in the crystal. So far we have considered only the directions of the diffracted beams, these depending only on the shape and dimensions of the unit cell. We now have to see how we can determine the internal structure of the unit cell, i.e. the arrangement and nature of the atoms, or alternatively the distribution of electron density, in the unit cell.

The diffracted X-ray beams differ not only in direction but also in intensity and phase. Their intensities may be measured by means of an ionization chamber or by photographic methods, but the phase constant cannot be directly determined experimentally.* The expression for the intensity of a diffracted beam is the product of a number of terms including the wavelength of the X-rays, the scattering power of a single electron, and others which need not concern us here, and in addition a term called the structure factor, $F(hkl)$. This structure factor, which is a function of the structure only, is a complex quantity characterized by an amplitude and a phase constant. Since we cannot in general determine these phase constants directly from the experimental measurements, we cannot reconstruct the distribution of electron density in the crystal from the observed intensity measurements, for these give us only the *amplitudes* of the structure factors. It is necessary first to determine the approximate positions of the atoms (or at any rate of the heavier atoms) in order to calculate the phase constants of the various diffracted beams. The structure factor $F(hkl)$ may be expressed as the sum of a number of terms which are functions of (1) the scattering powers of the individual atoms, and (2) the relative positions of the atoms in the unit cell. The former, the atomic structure factors, are known. They have been calculated for most atoms and also in some cases determined experimentally, and are plotted as the f-curves of the atoms (see p. 21). If calculated from an atomic model the atomic structure factor gives the scattering power of the atom at absolute zero and must be corrected for temperature.

* For an exception to this general rule see the determination of the structure of the phthalocyanin molecule (Robertson, ref. 165). There is also another method, so far of very restricted application, depending on the variation in the scattering power of an atom with the wavelength of the X-rays.

The coordinates of the atoms in the unit cell are found by altering the positions of the atoms until reasonable agreement is obtained between the calculated and observed values of the amplitudes of $F(hkl)$ of the most intense reflections. In simple structures, e.g. rock-salt or diamond, there may be only one reasonable way of arranging the atoms. There are not necessarily any variable parameters to be determined. This depends on the number of atoms of a given sort to be placed in the unit cell and the

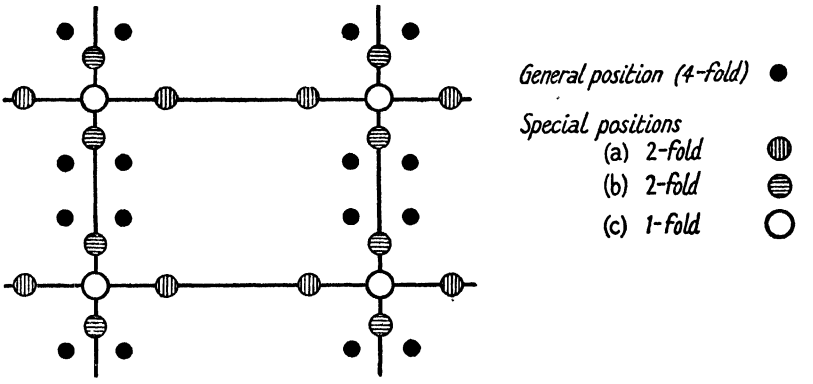


FIG. 52. General and special positions in a space group.

number and types of symmetry elements present. Suppose, for example, that the vertical sides of the unit cell shown in plan in Fig. 52 are planes of symmetry. If we have only one atom of a particular kind in this unit cell then it can go in one place only, on the plan, at the point of origin. (It has, of course, a variable parameter perpendicular to the plane of the paper, i.e. along the line of intersection of the two planes of symmetry, and this is true of all the atoms in Fig. 52. The 1-fold equivalent position would have no variable vertical parameter if an additional symmetry element were introduced in the plane of the paper.) Two atoms of the same sort must also be placed in 'special' positions, on one or other of the planes of symmetry. Four atoms may be placed either in the 'general' position as shown or they may occupy various combinations of 2-fold and/or 1-fold positions. This question of special and general positions is of some importance to the chemist because the symmetry of a molecule or complex ion may sometimes be deduced without a complete determination of the structure being made. If we had only one molecule to place in the above unit cell, then it follows that the molecule must lie along the intersection of the two planes of symmetry, i.e. it must itself possess two mutually perpendicular planes of symmetry. We return to this point later.

For many years the 'trial' method, i.e. the variation of atomic parameters to give agreement between observed and calculated intensities was the only one used. In complex structures there must always be some doubt as to whether the best combination of parameters has been found

since it is impossible to try every possible variation of the parameters. In recent years a rather different technique has been developed. As soon as enough is known of the structure to enable the phase constants of the strongest reflections to be calculated, a preliminary Fourier synthesis is made utilizing the experimentally determined intensities of these reflections. This generally leads to more exact values of the parameters of the atoms and enables us to calculate the phase constants of some of the weaker reflections. The Fourier synthesis is repeated incorporating the structure factors of more reflections than before. In this way the Fourier synthesis is used in a process of successive approximation. Assuming that the correct phase constants have been assigned to the reflections, and this will be so if the first approximate structure was sufficiently near to the truth, then the final Fourier synthesis represents the best way of utilizing all the available data and gives a unique solution.

We must now consider the types of information obtainable from X-ray studies. It is convenient to deal with the various points in order, according to the extents to which the available data are utilized. We shall therefore first see what sort of information can be derived from (*a*) the simple comparison of photographs, and then what additional information results from the measurement of (*b*) the positions of the X-ray reflections on the photographs and (*c*) their intensities.

(a) Use of Powder Photographs for Identification, etc.

If a single crystal of a substance is rotated in a beam of monochromatic X-rays the diffracted beams may be recorded on a photographic film as a collection of spots the arrangement of which depends on the orientation of the crystal relative to the axis of rotation. If the substance is not available in the form of crystals large enough to manipulate (and this may be done under the microscope with a high-power objective) another type of photograph may be taken, the powder photograph. The single crystal is replaced by a small amount of the finely divided crystalline powder, mounted as a cylindrical specimen on a hair or in a thin-walled capillary tube of Lindemann glass with its axis of rotation at the centre of the camera. When a plane photographic plate is used the photograph consists of a number of concentric rings, but it is more usual to use a cylindrical camera since all the diffracted beams may then be recorded. Only a narrow strip of film need be used, and the photograph has the appearance shown in Fig. 53 (*d*).

For purposes of identification the powder photograph is obviously as useful a characteristic of the substance as a physical property such as its melting-point. Comparison of the photograph of a substance with standard photographs can therefore be used to identify it and incidentally establish its purity. Other applications of powder photographs are in the establishment of phase-rule diagrams, in the study of polymorphic changes, and in following the course of chemical reactions.

The study by X-ray methods of the formation of bleaching powder is a good example of the last application. The ordinary equation

$$2Ca(OH)_2+2Cl_2 \rightarrow Ca(OCl)_2+CaCl_2+2H_2O$$

is unsatisfactory for two reasons: the reaction does not go to completion—there being usually some 15–25 per cent. $Ca(OH)_2$ in commercial bleaching powder which is very difficult to chlorinate—and secondly, bleaching powder is not markedly deliquescent, suggesting that there is no free calcium chloride. X-ray investigation showed that the first stage in the reaction is the formation of a basic hypochlorite with the empirical formula $Ca_3(OCl)_2(OH)_4$ (*a*) and a basic chloride $Ca_2Cl_2(OH)_2.H_2O$ (*b*). As chlorination proceeds, more of (*b*) is formed and (*a*) disappears, being replaced by a mixed crystal phase of variable composition consisting largely of hypochlorite. The difficulty of further chlorination is due to the existence of the very stable compound (*b*) and this is not appreciably deliquescent. Actually, very prolonged chlorination produces a deliquescent product containing a higher proportion of $Ca(OCl)_2$ and some $CaCl_2.4H_2O$, which replaces part of (*b*).

(b) Further Information obtained by Measurement of Photographs

By measuring the positions of the lines on a powder photograph, the wavelength of the X-rays and the radius of the camera being known, the constants of the unit cell can, in principle, be determined. For crystals of low symmetry the interpretation of a powder photograph may be very difficult, but in all cases these data can be obtained from single crystal photographs. Relative measurements only can clearly be used to determine the composition of a member of a series of mixed crystals if we have photographs of the end members and assume Vegard's law. From photographs taken at various temperatures coefficients of thermal expansion may be calculated.

Determination of Molecular Weights

The absolute mass of material in the unit cell is known if we determine its volume and the density of the crystal. The lengths of the sides and the angles of the unit cell may be directly determined by X-ray methods with considerable accuracy (to a few parts in 100,000, using precision cameras), but the accurate measurement of density is a matter of some difficulty owing to the imperfection of crystals and the presence of absorbed gases. If large amounts of material are available a pyknometer may be used: otherwise flotation methods may be used for crystals with densities not exceeding about $3\frac{1}{2}$ g./c.c. A refinement of the ordinary flotation method, which involves the use of a centrifuge, has given densities accurate to $\pm 0{\cdot}0001$.

For a molecular crystal the mass of material in the unit cell is an integral multiple of the molecular weight (in absolute units), i.e. the ordinary molecular weight multiplied by 1/16th the mass of an oxygen atom.

The actual number of molecules in the unit cell is found from other considerations such as the space available or the arrangement of symmetry elements. For all crystals, other than certain types of defect crystals already mentioned in Chapter V, the unit cell must contain one 'formula-weight' or an integral multiple of it. Many examples could be quoted of the correction of chemical formulae as a result of X-ray studies, but the following are typical. The formula $Al_4(SiW_{12}O_{40})_3 . 87H_2O$ was formerly applied to the highest hydrate of aluminium silicotungstate. Determination of its dimensions showed that the unit cell of this crystal would contain only 0·66 of the above formula-weight. The formula now adopted is $AlHSiW_{12}O_{40} . 28H_2O$, with two formula-weights per unit cell. Comparison of the analytical figures calculated for the two formulae will show that it would be difficult to distinguish between them by means of ordinary chemical analysis:

	Calculated for	
	$Al_4(SiW_{12}O_{40})_3 . 87H_2O$	$AlHSiW_{12}O_{40} . 28H_2O$
Al_2O_3 . . .	2·00	1·50
SiO_2+WO_3 . .	82·80	83·44
H_2O . . .	15·20	15·06

For another example see ammonium paramolybdate, p. 340.

In the field of silicate chemistry the application of X-ray methods has had very striking results, which are summarized in Chapter XIV. Two examples will suffice here. The mineral amphibole was formerly assigned the ideal formula $CaMg_3(SiO_3)_4$—isomorphous replacement is, of course common as in most silicates. Analysis, however, always shows about 2 per cent. water. X-ray studies showed that this is not present in the form of H_2O molecules but that the correct formula is $(OH)_2Ca_2Mg_5(Si_4O_{11})_2$ Again, the formula of the zinc silicate hemimorphite was formerly written $H_2Zn_2SiO_5$. Its structural formula has now been revised to $(OH)_2Zn_4Si_2O_7 . H_2O$. In this case the relative numbers of atoms in the old formula were correct but the formula was unintelligible chemically.

Determination of the Approximate Shape of a Molecule

From a knowledge of the dimensions of the unit cell it is sometimes although not by any means generally, possible to obtain some idea of the shape of a molecule and hence to eliminate certain plausible structural formulae. This method has been applied to certain complex organic compounds and also to a number of organo-metallic compounds, as illustrated by the following example. The compound dipyridinocupric chloride was studied to determine whether the four bonds from the cupric atom were arranged in a plane or tetrahedrally. The short length of the *c* axis of the unit cell (3·84 A.) shows that the two pyridine rings must be at least approximately coplanar. From a study of models it is found that no molecules in which the copper atom formed tetrahedral bonds could approach to within 3·84 A. of each other, so that the metal bonds must be coplanar (or approximately so). Only one form of the molecule is known,

and it can be shown by the following argument that this form must have the *trans* configuration. We know that the planes of the pyridine rings must be very nearly parallel, but this is impossible in a molecule with the *cis* configuration since it brings carbon atoms of different rings within 1·9 A. of one another instead of the minimum of about 3·7 A. normally found. To obtain the required clearance between the rings it would be necessary to rotate them about the Cu—N bonds through an angle of about 40°, thus increasing the thickness of the molecule and necessitating a c axis of at least 4·5 A.

(c) Results of More Complete Studies

The final result of a complete X-ray crystallographic study of a substance is the determination of the relative positions of all the constituent atoms (or alternatively of the electron density distribution) to the greatest degree of accuracy possible. Assuming that the experimental methods were refined to an extent which made the errors of measurement negligible, the X-ray method has, like an optical microscope, a limiting resolving power. We shall not be concerned in this chapter with the results of complete structure analyses since these form a considerable part of the subject-matter of this book. A certain amount of information about the structure of a substance may, however, in some cases be obtained from incomplete structure analyses. Such studies are sometimes made because a survey of a large number of crystals is required, a complete study of them all being impossible on account of the time factor, or because the particular piece of information can be obtained from the incomplete analysis, the further details of the structure being of little immediate interest.

After the determination of the cell dimensions the next stage is to discover the nature and arrangement of the symmetry elements in the structure. In our brief remarks on general and special positions we saw that in favourable cases the symmetry of a molecule or complex ion may be obvious from the position it must occupy in the structure. For example, if a molecule Ma_4 is found to lie on a 4-fold axis, then it must have a planar and not a tetrahedral configuration. Such deductions must, however, be made with great care, as the following example will show. Suppose that we have a salt $A_2[BX_4]$ and we find that the B atoms lie at symmetry centres. We might be tempted to assume that the BX_4 ions must be planar and not tetrahedral, since the tetrahedron is not centro-symmetrical. This deduction is justified if we know that the BX_4 ions are *finite* complex ions. If they consisted of infinite chains of octahedral BX_6 groups sharing opposite edges (see Fig. 73, p. 288), the B atoms could be at centres of symmetry but deductions about the arrangement of *four* bonds from B would be false.

Finally we must point out one other limitation of X-ray methods. The scattering power of an atom depends on the number of its orbital electrons. It is therefore difficult to locate accurately the position of very light atoms

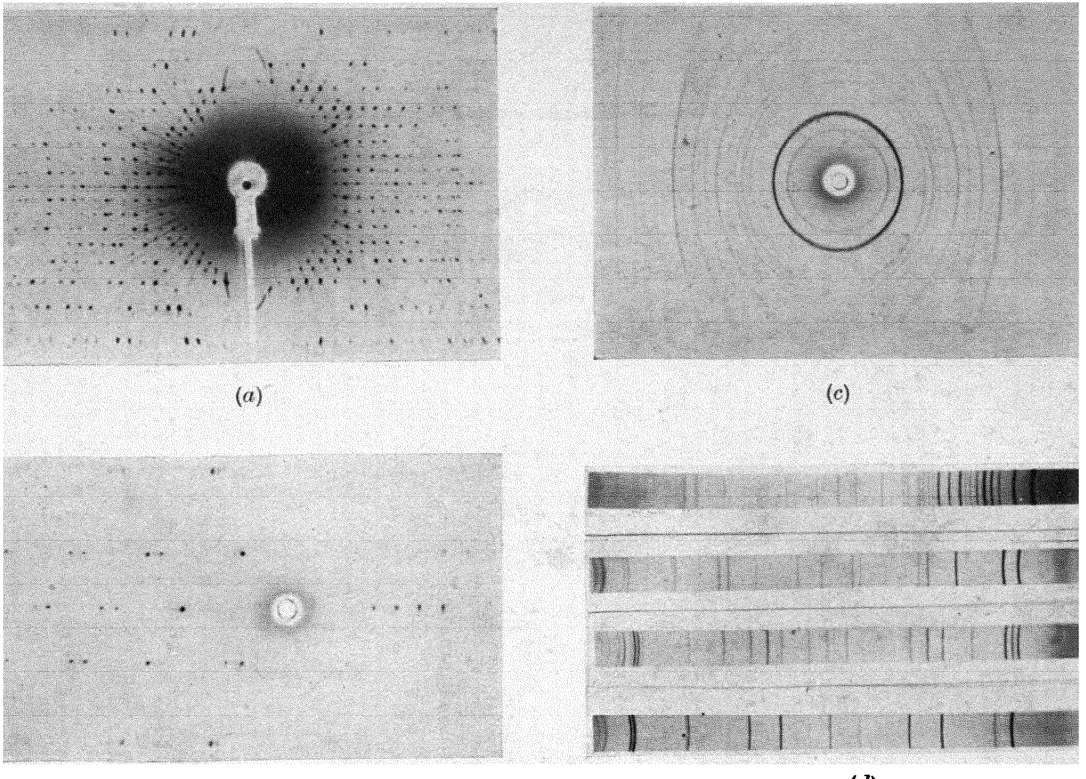


FIG. 53. Examples of X-ray diffraction photographs of crystals.

(*a*) and (*b*), 15° oscillation photographs of single crystals, (*c*) and (*d*), powder photographs taken in cylindrical cameras. Those shown at (*d*) are halves of equatorial strips of photographs of the type (*c*).

beams are small. Hydrogen atoms cannot be detected directly by X-rays (except, perhaps, in solid CH_4 and other such favourable cases), but their positions may in some cases be inferred—from considerations of symmetry (knowing the number to be placed in the unit cell) or from distances between pairs of atoms between which the hydrogen atoms lie. In this connexion see the discussion of the hydrogen bond in Chapter VII.

ELECTRON DIFFRACTION

Interference effects due to electrons were first demonstrated by Davisson and Kunsman, who in 1921 studied the scattering of electrons by a polycrystalline nickel surface, but the observed phenomena were not interpreted as such since the wave nature of the electron was not suggested until 1924. De Broglie's relation, $\lambda = h/mv$, and the experiments of Davisson and Germer on the diffraction of electrons by a single crystal of nickel have already been mentioned in Chapter I. The development of quantum mechanics led to the theory of the scattering of electrons by atoms and molecules and made available a new method of examining the structure of matter. Apart from studies made with the object of testing the de Broglie relation or of examining the physical aspects of the interaction of electrons with matter, work on electron diffraction falls into three groups: the study of solids, of gases with low-velocity electrons (say, of less than 1,000 volts energy), and of gases with high-velocity electrons.

The electron diffraction method may be used to study crystal structure, either of single crystals, polycrystalline material—in which case the diffraction pattern is similar to an X-ray powder photograph—or semi-crystalline matter. We shall not discuss this aspect of the subject since information about the bulk structure of solids is also obtainable by the use of X-rays. One point to note, however, is that electrons are much more strongly absorbed by matter than are X-rays, so that they penetrate to a much smaller distance into a solid. For this reason transmission is possible only through very thin films which have to be prepared by special methods. The alternative is to study the scattering from the surface of the crystal. On account of their small penetrating power electrons are particularly suitable for studying surface structure.

In the interaction of atoms with slow electrons the orbital electrons as well as the nuclei are responsible for the scattering, but the atomic structure factors are not accurately known except for hydrogen. The method is therefore not useful for determining the structures of molecules. In the case of high-velocity electrons the scattering by the orbital electrons is negligible compared with that due to the nuclei, and this type of electron diffraction has provided a great deal of information about the structures of molecules of gases.

A stream of electrons, usually from a hot cathode, is accelerated by a potential of the order of 40 kilovolts in a highly evacuated apparatus. A jet of vapour of the substance being examined is sent perpendicular to the

electron beam from a fine nozzle and is either condensed on the far side of the beam on a surface cooled with liquid air or pumped away through a separate outlet connected to a high-speed pump. Efficient removal of the vapour is, of course, essential to the maintenance of the vacuum. The method is applicable to any substance which can be vaporized without decomposition under reduced pressure so as to give a vapour pressure of 100–200 mm. Owing to the facts that the interaction of electrons with the molecules of a gas is much more intense than that of X-rays and that they have a greater photographic effect, the exposure time required to photograph the diffraction pattern is only of the order of $\frac{1}{5}$ second as compared with hours for an X-ray diffraction photograph of a gas.

In the jet of vapour the molecules are sufficiently far apart for each to scatter independently of the others. The scattering is of two types, described as coherent and incoherent. The latter scattering is accompanied by change of wavelength and this incoherent scattering shows no interference effects characteristic of the molecule. It falls off rapidly as the angle of scattering (θ) increases, and merely adds to the general background on the photograph caused by accidental X-rays or by diffraction taking place away from the immediate neighbourhood of the jet owing to inadequate pumping or condensation. The coherent scattering $I(\theta)$ at an angle θ is given by the expression

$$I(\theta) = k \sum_i \sum_j \phi_i \phi_j \frac{\sin sr_{ij}}{sr_{ij}}$$

where ϕ_i, the electron scattering power of the ith atom, is $(Z_i - f_i) \Big/ \left(\frac{\sin \frac{1}{2}\theta}{\lambda}\right)^2$, Z_i being its atomic number and f_i its scattering power for X-rays,

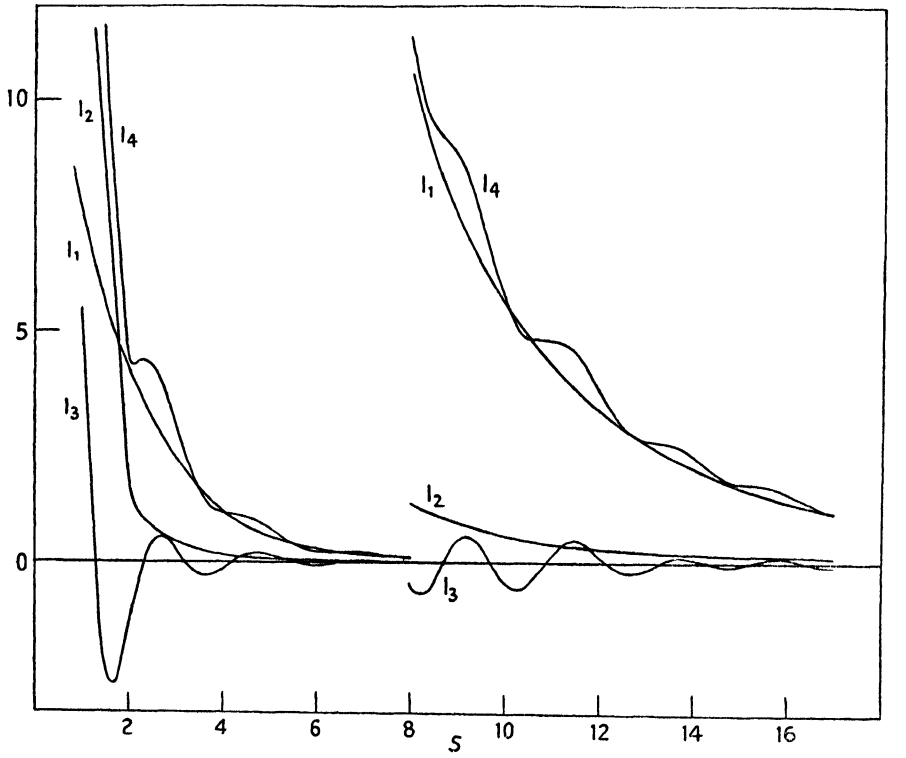
$$s = 4\pi \sin \tfrac{1}{2}\theta/\lambda$$

and r_{ij} is the distance between the ith and jth atoms. From the above expression for $I(\theta)$ we see that there is a term, the so-called interatomic scattering, for each pair of atoms of the type

$$\phi_i \phi_j \frac{\sin sr_{ij}}{sr_{ij}}.$$

This scattering varies sinusoidally, with steadily decreasing amplitude, as θ increases from 0 to π. There is also a term for each atom of the form $k\phi_i^2$, since the limit of $\sin sr_{ij}/sr_{ij}$ is unity as r_{ij} tends to zero. This atom scattering falls off steadily, i.e. non-periodically, with increase in θ according to the way in which the scattering power varies with angle. For a complex molecule, therefore, the diffraction pattern due to the coherent scattering is the result of these various atomic scattering terms and superimposed on these are the periodic terms—one for each interatomic distance. Now f_i falls off as θ increases. X-rays are scattered by the orbital electrons and destructive interference between the wavelets scattered by various parts of the electron cloud around the nucleus takes place to an increasing extent as θ increases. Accordingly in the expression

for the scattering power for electrons, $Z_i - f_i$ increases with θ but the denominator $(\sin \frac{1}{2}\theta/\lambda)^2$ increases so much more rapidly that ϕ_i itself falls off very rapidly. The result is that the sinusoidal variations in intensity due to the interatomic terms do not appear on the photographic plate as



I_1 = coherent atomic scattering; I_2 = incoherent atomic scattering;
I_3 = 'interatomic' scattering; $I_4 = I_1 + I_2 + I_3$.

FIG. 54. Theoretical electron diffraction curves for CCl_4 (after Brockway). The ordinates are multiplied by 100 beyond $s = 8$.

maxima or minima but only as small inflexions on a steeply falling curve. This point is well illustrated in Fig. 54. This topic has been dealt with at some length because the peculiar difficulty in electron diffraction studies is that of determining the relative intensities of the peaks due to the various intensity terms and of estimating their exact positions.

In spite of the shape of the theoretical intensity curve the actual photograph appears to show a set of concentric dark and light rings. It has been found that the positions of the diffraction maxima can usually be determined more accurately by visual observation than from a microphotometer record, which is necessarily of the same form as the theoretical intensity curve. Owing to the labour involved in calculating intensity curves for a large number of possible molecular models, any reasonable assumptions concerning the latter are made in order to arrive as quickly as possible at the approximate shape of the molecule. Variations in the

model are then made until the calculated intensity curve reproduces all the features of the photograph. This in itself does not prove that the correct structure of the molecule has been found, and it is necessary to vary the parameters in the model until definite disagreement between the appearance of the photograph and the calculated intensity curve results. In this way a good estimate of the accuracy of the parameters may be obtained.

The general factors determining the accuracy are (1) the number of independent parameters in the molecule, (2) the relative importance of the interatomic and atomic scattering terms, (3) the physical characteristics of the substance, e.g. a very volatile substance is difficult to condense or remove completely after passing through the electron beam and therefore gives a less clear photograph, and (4) the accuracy with which the wavelength of the electrons is known—which depends on an accurate measurement of the voltage applied to the tube—and the distances in the camera and on the photograph. Comparisons of the results of electron diffraction studies with those of other methods show agreement, on the average, to within 1 per cent.

The following points are relevant when comparing the usefulness of the electron diffraction and X-ray diffraction methods. In a triangular molecule like SO_2 or ClO_2 the central atom has a much greater scattering power than the oxygen atoms, and as a result the two S—O (or Cl—O) terms in the scattering equation have much more effect on the diffraction pattern than has the single O—O term. Hence any alteration in the bond angle makes little difference to the theoretical intensity curve. It is therefore possible to determine the S—O (or Cl—O) distance quite accurately but only to obtain an approximate estimate of the interbond angle. Owing to the dependence of scattering power on nuclear mass it is also impossible to locate hydrogen atoms accurately in the presence of much heavier atoms, though the hydrogen atoms cannot be neglected when calculating the theoretical scattering curves. Finally, just as in X-ray diffraction allowance has to be made, when comparing calculated with observed intensities, for the thermal vibrations of atoms in the lattice, so the thermal vibrations of atoms in molecules must be taken into account in electron diffraction studies. In the latter the effect may be more pronounced than in a crystal, for in certain types of molecules (in the vapour state) the interbond angles are easily distorted. Thus on electron diffraction photographs of SnI_2 and PbI_2 the interatomic scattering due to the I—I term is hardly observable owing to the ease with which the molecule bends.

SPECTROSCOPIC STUDIES

When suitably excited, thermally or electrically, atoms and molecules emit their characteristic spectra. It is necessary to find the most suitable form of excitation for a given substance and among the various methods available are excitation by flame, arc, or spark, and by a discharge through

a gas at low pressure in a Geissler tube. As an alternative to studying the emission spectrum of a molecule we may study its absorption spectrum. Atoms emit spectra consisting of discrete lines, while the spectra of molecules contain groups of lines so close together that they are described as bands.

A molecule can possess internal energy of three kinds, to changes in each of which quantum conditions must be applied; these are electronic energy, the energy of vibration of the nuclei, and rotational energy. Electronic transitions involve the largest energy changes, of the order of 1–10 electron-volts (1 electron-volt = 23 k.cals./mole). Each electronic transition may be accompanied by the simultaneous loss or gain of one or more quanta of vibrational energy, so that the lines in the spectrum corresponding to the movement of an electron from one quantum level to another have associated with them a number of vibrational lines. These correspond to changes in energy of the order of 0·1 electron-volts. Still smaller energy changes are possible, due to alterations in the rotational energy of the molecule around particular axes, and these are of the order of 0·001 electron-volts. They give rise to a group of lines (fine structure) in the immediate neighbourhood of each electronic and vibrational line. The emission or absorption of these small rotational quanta may take place independently of any electronic or vibrational changes, and in this case they produce a set of lines in the far infra-red region of the spectrum. The intermediate possibility is that rotational and vibrational changes take place together, and these are responsible for groups of lines in the near infra-red. The rotational (far infra-red) spectra are studied exclusively as absorption spectra, and this is often the most convenient way of studying the other types of spectra.

The data obtainable from spectroscopic studies include the evaluation of interatomic distances and interbond angles, heats of formation, and the force constants of bonds. We shall not discuss the two latter properties of bonds, but shall indicate briefly how information about the geometry of a molecule may be obtained. If we knew the moments of inertia of a molecule about its various possible axes of rotation we could deduce all the interatomic distances and interbond angles. In practice the structures of only the simplest molecules have been determined in this way from spectroscopic data as the difficulties, both of experiment and of interpretation of the spectra, are considerable, but we may illustrate the principles of the method by reference to simple rotational spectra.

Consider a diatomic molecule consisting of atoms of masses m_1 and m_2 a distance d apart. For rotation about an axis perpendicular to the line of centres its moment of inertia is $I = \dfrac{m_1 m_2}{m_1+m_2} d^2$. If its angular velocity is ω the kinetic energy of rotation is $\frac{1}{2}I\omega^2$. The angular momentum is restricted to multiples of $h/2\pi$, so that

$$I\omega = \frac{mh}{2\pi},$$

where m is an integer, the rotational quantum number. The kinetic energy of the molecule is therefore $m^2h^2/8\pi^2I$. A quantum of radiation of frequency ν is emitted when the molecule changes from a state with quantum number m to the state characterized by the quantum number $m\pm1$. The energy emitted (or absorbed) is

$$h\nu = \frac{h^2(1+2m)}{8\pi^2I}, \quad \text{whence} \quad \nu = \frac{h(1+2m)}{8\pi^2I}.$$

The spectrum in the far infra-red should therefore consist of a series of equally spaced lines separated by intervals of $h/4\pi^2I$. By measuring this quantity the moment of inertia I can be found. Actually the frequency separation of the lines is not quite constant since a molecule is not absolutely rigid and the moment of inertia increases during vigorous rotation. Although the study of the far infra-red spectrum is in principle the simplest and most direct way of determining moments of inertia, the experimental study of this region of the spectrum is difficult. Photographic plates are not sensitive to such long wavelengths, so that the lines must be located either by means of a thermopile or selenium cell and a galvanometer or by indirect semi-photographic methods such as the use of 'solarized' plates or a phosphorescent ZnS screen which is quenched by the infra-red radiation. The accuracy of such measurements is not comparable with that attainable in the study of electronic spectra. Moreover, all molecules do not exhibit simple rotational spectra. This is true of simple diatomic molecules such as N_2, O_2, and Cl_2, but the far infra-red (absorption) spectra of ammonia, water, and the hydrogen halides have been studied.

There are two alternative ways of studying these rotational changes in order to determine moments of inertia:

(1) Measurements of ultra-violet, visible, or near infra-red band spectra, where the rotational changes accompany electronic and vibrational or vibrational transitions. Here we may note a complication. An electronic or vibrational transition involves a change in I, so that in determining interatomic distances in this way we must be sure that they refer to the ground (unexcited) state of the molecule.

(2) Raman spectra. When monochromatic light is passed through a medium, most is transmitted or scattered without change in wavelength, but spectrometric examination of the scattered light shows additional series of lines on both sides of the wavelength of the incident radiation. These changes in wavelength (and therefore of energy) are due to the acquisition or loss of quanta of vibrational or rotational energy by the molecules or other groups of atoms in the medium. It is supposed that the incident radiation $h\nu_i$ raises the molecule from one energy state I to another II from which it returns to the final state III with emission of a quantum $h\nu_s$ of scattered radiation. The net change in the energy of the radiation is $h(\nu_i-\nu_s) = h\Delta\nu$ where $\Delta\nu$, the change in frequency (or Raman frequency), is positive or negative according to the energy of state III

relative to states I and II (see Fig. 55). The following points concerning Raman spectra are relevant.

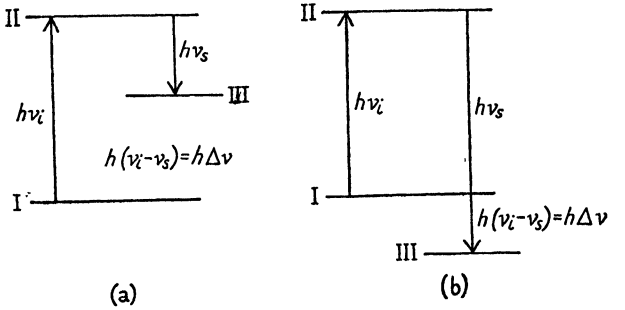


FIG. 55. The formation of (*a*) Stokes line ($\Delta\nu$ positive) and (*b*) anti-Stokes line ($\Delta\nu$ negative) in Raman spectrum.

(*a*) The Raman frequency is independent of the frequency of the incident radiation. We may therefore use any convenient source of monochromatic radiation so that the scattered light is in the region of high sensitivity of a photographic plate. Vibrational or rotational transitions may therefore be studied, without the complication of simultaneous electronic transitions, in a region of the spectrum far more easy to deal with experimentally than the infra-red or far infra-red. Owing to the small intensity of the Raman lines, however, exposures of many hours are necessary.

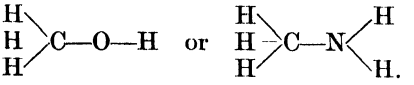
(*b*) The Raman spectrum is independent of the state of aggregation, provided, of course, that the particular molecule or complex ion is stable under the conditions of experiment. Vapours, liquids, solid or molten salts or their solutions may be studied in this way. The observation that the Raman frequencies of a series of solid nitrates are practically identical and the same as those of the solutions and of the molten salts shows that the particular frequencies are to be associated with the NO_3 ion. There is a similar general correspondence between the values for a number of different tetrahedral ions, studied in solutions of their salts (Na_2SO_4, $NaClO_4$, Na_2WO_4) or in the acids (H_2SO_4), but telluric acid is anomalous, showing that it does not contain TeO_4^{2-} ions; see p. 355.

(*c*) In some respects the information obtained from Raman spectra is supplementary to that given by ordinary spectroscopic studies. As already mentioned, some simple molecules do not give pure vibrational spectra but the vibrations of the molecule do give rise to Raman spectra. Again, the infra-red absorption spectra of certain crystalline salts have been studied. It was found that the spectra of a set of carbonates, for example, were almost identical, the lines originating from the vibrations of the CO_3^{2-} ion. One possible type of vibration of the ion is 'inactive' in the sense that it does not contribute to the spectrum. This is presumably the simultaneous symmetrical movement of all the oxygen atoms along

the C—O bonds, a mode of vibration which does not alter the electric moment of the ion. The frequency of this inactive vibration can only be determined indirectly from these spectra, but it occurs as a Raman frequency.

THE USE OF THERMOCHEMICAL DATA IN STRUCTURAL CHEMISTRY

We shall not devote much space to this subject, for, since bond energies are additive, apart from possible allowances for certain structural factors such as strain in ring systems, they are generally not of great use from the structural point of view. For the bond in a diatomic molecule the determination of the heat of formation of the bond (bond energy) necessitates only the measurement of the heat of formation of the molecule from, or of dissociation into, atoms—allowance being made for latent heat of fusion and evaporation if changes of state are involved. (These latent heats must also be corrected for their alteration with temperature in order to reduce all the bond energies to a standard temperature, usually 18–20° C.) Since a molecule cannot be completely dissociated into its atoms merely by heating, the heat of dissociation (or atomization) cannot be measured simply as the heat of the reaction $X_2 \rightarrow 2X$ and must be determined in other ways (see below). In order to find the energies of many bonds we require thermochemical data on complex molecules. For example, we cannot find the energy of the single bonds C—O or C—N from molecules like CO or C_2N_2 because these molecules contain multiple bonds and we have to resort to compounds such as organic hydroxy- and amino-derivatives, e.g.



Such molecules can neither be conveniently formed directly from their constituent atoms nor dissociated into them, and if they could, the measured heat of reaction would be the sum of the energies of all the bonds formed or broken. We therefore have to make use of two principles:

(1) For molecules in which there is no possibility of (or at least no reason to suspect) resonance, the heat of formation is the sum of the heats of formation of the individual bonds.

(2) The heat evolved (or absorbed) in any reaction is constant and independent of the manner in which the reaction is brought about, whether in one or many steps (Hess's Law).

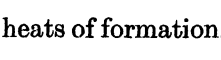
To find the sum of the energies of all the bonds in a molecule we must determine the energy involved either in forming all these bonds from the *separate* atoms or in breaking up the molecule into its constituent atoms. If we determine the heat of formation of the molecule from its elements the latter are in the form of finite molecules, or possibly some more complex grouping if a solid is used (e.g. diamond). In any case therefore

we require to know the heat of atomization of the constituent elements. It is often impossible, however, to synthesize a given molecule from molecules of its constituent elements (e.g. CH_3OH from C, H_2 and O_2), and the heat of formation may then be determined indirectly by applying Hess's Law. The alternative to measuring the heat of formation of the molecule is to measure the energy involved in breaking all the bonds in the molecule. The decomposition of a molecule into its elements would, if it were possible, lead to molecules of the latter, so that a knowledge of their heats of atomization would still be required. In general the most convenient way of disrupting a molecule is to oxidize it and measure the heat of combustion. If we know the heats of formation of the resulting oxides from molecules of the respective elements and oxygen and also the heats of atomization of the elements we can calculate the sum of the energies of the bonds in the original molecule.

The determination of heats of atomization of the elements is more difficult than might at first appear, for a number of reasons. In the first place the bonds in the molecules N_2 and O_2 are not simple electron-pair bonds, so that the energies of the bonds N—N and O—O cannot be determined from these molecules but have to be obtained indirectly from the heats of formation of compounds such as $H_2N—NH_2$ and HO—OH. Secondly, in cases where the bonds are simple electron-pair bonds the molecules cannot be dissociated completely, for at any given temperature a state of equilibrium is reached between the undissociated molecules and the atoms. In such cases (Cl_2, Br_2, I_2) the heat of atomization may be determined indirectly from the change in the degree of dissociation with temperature, applying the Clausius-Clapeyron equation. The heat of atomization of solid elements may be obtained from the heat of sublimation divided by the number of bonds formed by an atom to its nearest neighbours—four in the case of elements with the diamond structure (C, Si, Ge).

As an alternative to these methods involving thermochemical measurements, heats of atomization may be determined spectroscopically. The principle of the method is that if a molecule acquires more and more vibrational energy it will finally dissociate into atoms. Just as in the calculation of moments of inertia it was necessary to discover whether we were dealing with a normal or excited molecule, so here we must know whether the atoms formed are excited or not. In the former case we must allow for the difference in energy content between the atom in the normal and excited states. The energy of dissociation is found by determining the frequency at which a series of vibrational lines of a band system pass into a region of continuous absorption. This is the point at which energy is no longer taken up by the molecule as quantized vibrational energy, but goes to increase the (non-quantized) kinetic energy of the dissociated atoms.

As examples of the direct application of thermochemical data to structural problems we may mention:

(*a*) The choice between a number of possible structural formulae for a molecule on the grounds of the agreement between the observed and calculated heats of formation. The single-bonded structure  for ozone may be rejected because the heat of formation calculated for this molecule is −75·6 k.cals./mole compared with the observed value −34·5 k.cals./mole. For the structure of the ozone molecule see p. 302.

(*b*) The calculation of resonance energies. In Chapter II bond energies were mentioned in two connexions. We saw how bond energies were used to draw up an electronegativity scale, and we also mentioned that a comparison of observed and calculated heats of formation of molecules provided evidence for the existence of resonance by leading to values for resonance energies. In Chapter XIII the structure of the carbon monoxide molecule is discussed in some detail from this point of view.

THE MAGNETIC PROPERTIES OF ATOMS AND MOLECULES

Atoms are systems of electric charges. An electron in motion is equivalent to an electric current in a circuit and therefore possesses a magnetic moment. Since an atom (other than H) contains a number of electrons it may or may not possess a resultant permanent magnetic moment. All substances show polarization in a magnetic field and they may be divided into two groups. Diamagnetic substances tend, in an inhomogeneous field, to move from the stronger to the weaker part of the field, the induced magnetic field being opposed to the external field. Paramagnetic substances show the reverse behaviour. Our interest in diamagnetism will be largely confined to the diamagnetic anisotropy of molecules, to which we refer in a later section.

All atoms exhibit diamagnetism, which results from the modifying influence of the applied magnetic field on the motion of the electrons. It is a function of the distribution of the electron density in the atom and is largely independent of temperature and structure and therefore of change of state. Among the important groups of diamagnetic substances are the inert gases, simple ionic crystals in which the ions have completed electron shells, many homopolar molecules such as H_2 and Cl_2 (O_2, however, is strongly paramagnetic because the electron spins are parallel), most organic compounds, and some metals. The susceptibilities of ionic crystals like the alkali halides are the sums of the susceptibilities of the component ions, and the mean susceptibilities of many molecules are the sums of terms for the separate atoms, an allowance being necessary in some cases for the different types of bonds. This additivity of diamagnetic susceptibilities is expressed in Pascal's Law: $\chi_M = \sum \chi_A + \lambda$, where λ is the 'bond-type' factor referred to above. Many metals exhibit weak diamagnetism or paramagnetism, but in certain semi-metals such as Bi, Sb, and graphite

the valency electrons are not free as in a true metal. In such crystals the energy states of the electrons are functions of the structure of the crystal, which can therefore exhibit pronounced diamagnetic anisotropy. This anisotropy disappears when the crystal melts. In certain molecules, particularly of organic compounds, and planar complex ions there is reason to believe that some of the electrons occupy plane orbits much larger than those in simple atoms. This is so in the planar ions CO_3^{2-}, NO_3^-, and $CH_3.COO^-$ and in molecules like C_6H_6 and those with more complex ring systems. In such cases marked diamagnetic anisotropy is observed.

Some atoms and compounds show paramagnetism in addition to diamagnetism, and the latter is then relatively unimportant. Any atom in which there are unpaired electrons in an incomplete shell possesses a permanent magnetic moment and exhibits paramagnetism. The paramagnetic susceptibility is often large and is dependent on the temperature, since the orienting of these permanent dipoles in an applied field is opposed by thermal motion. The electrons of the completed inner shells are responsible only for a relatively small diamagnetism. According to quantum theory the magnetic moment is made up of two parts. One is due to the spins of the electrons, the other to their orbital motion. The resultant magnetic moment of the atom (μ_B) is measured in terms of the Bohr magneton, the absolute value of which is $eh/4\pi mc$. The study of the relation of μ_B to the number of unpaired electrons in an atom has provided results of great interest. In what follows we shall ignore the contribution, if any, of the orbital moment to the resultant moment of an atom.

The resultant spin moment of n unpaired electrons is $\sqrt{\{n(n+2)\}}$ Bohr magnetons, that for one unpaired electron being 1·73 ($\sqrt{3}$) Bohr magnetons. Before discussing the application of magnetic measurements to structural problems we may note how in the case of the ions of the transition elements from vanadium to copper they confirm the way in which the 3*d* shell is filled. In this shell there are five orbitals. The first five electrons go one into each of these orbitals, these electrons being consequently unpaired. When the number of electrons becomes greater than five the additional electrons go into orbitals already containing an electron. Since no two electrons may have all their quantum numbers identical, the spins of the two electrons in a particular orbital must be opposed; the electrons are then said to be paired. The number of unpaired electrons therefore first rises to five and then falls to zero when the 3*d* shell has acquired its full complement of ten electrons. In the following table the values of the magnetic moments of the ions in solution are compared with the numbers of unpaired electrons in the various ions. The differences between the observed and calculated moments are probably due to the fact that the contributions of the orbital moments have been neglected.

Magnetic data can provide answers, in favourable cases, to two questions relating to the bonds formed by an element: (*a*) Are the bonds essentially

TABLE 13

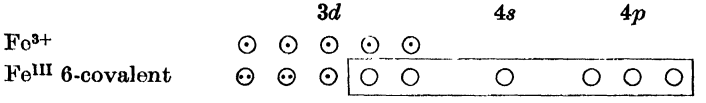
Magnetic moments of ions in aqueous solution

Ion	*Number of 3d electrons*	*Number of unpaired electrons*	*Calculated spin moment (in Bohr magnetons)*	*Observed moment*
K^+, Ca^{2+}, Sc^3, Ti^4	0	0	0·00	0·0
V^4	1	1	1·73	1·7
V^3	2	2	2·83	2·4
V^2, Cr^3	3	3	3·88	3·8–3·9
Cr^2, Mn^3	4	4	4·90	4·8–4·9
Mn^2, Fe^3	5	5	5·92	5·9
Fe^2	6	4	4·90	5·3
Co^2	7	3	3·88	5·0–5·2
Ni^2	8	2	2·83	3·2
Cu^2	9	1	1·73	1·9–2·0
Cu^1, Zn^2	10	0	0·00	0·0

ionic or essentially covalent? and (*b*) How are they arranged in space? The method is applicable only if there are two alternative electronic configurations for the atom which correspond to different numbers of unpaired electrons. We may see how it works by reference to a few examples which are taken from those quoted by Pauling in *The Nature of the Chemical Bond.*

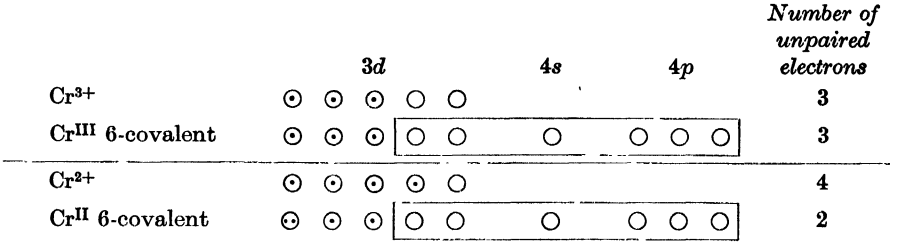
(a) The Nature of Bonds—Ionic or Covalent

The transition metals form many octahedral complex ions, and magnetic measurements show that in some the bonds are essentially ionic and in others covalent. For example, the configuration of the ferric ion is that shown below, with five unpaired 3*d* electrons. This corresponds to a moment of 5·92 Bohr magnetons, with which may be compared the observed moment of 5·86 in crystalline $Fe_2(SO_4)_3$. If, however, Fe^{III} forms six d^2sp^3 bonds, then these five electrons go into three 3*d* orbitals, leaving only one unpaired electron. Moreover, since in these extreme con-



figurations there are different numbers of unpaired electrons, resonance between them is not possible. In ionic compounds the Fe^{III} atom should therefore have a moment of 5·86 and in covalent complexes only 1·73 Bohr magnetons. For $K_3Fe^{III}(CN)_6$ the observed moment is 2·33, indicating covalent bonds, and for complexes containing F or H_2O (in $(NH_4)_3FeF_6$, $(NH_4)_2[FeF_5(H_2O)]$) 5·9 Bohr magnetons. Similar arguments applied to complexes of trivalent cobalt show that $[CoF_6]^{3-}$ and $[Co(H_2O)_6]^{3+}$ contain ionic bonds but $[Co(NH_3)_6]^{3+}$, $[Co(NO_2)_6]^{3-}$, and $[Co(CN)_6]^{3-}$ covalent bonds. In this case the numbers of unpaired

electrons are 4 (ionic) and 0 (covalent). The magnetic criterion is not applicable to octahedral complexes of *trivalent* chromium, for in both the extreme states the number of unpaired electrons is three, but it may be applied to complexes of *divalent* chromium, as may be seen from the following scheme:



In such cases as Cr^{III} it is sometimes possible to argue from the chemical or other properties of the complex. For example, a number of trivalent metals form tri-oxalato ions, $[M(C_2O_4)_3]^{3-}$, and such ions should be enantiomorphous. The compounds $K_3[Cr(C_2O_4)_3]$ and $K_3[Co(C_2O_4)_3]$ have in fact been resolved into their optical antimers, but the corresponding compounds containing Mn^{III}, Fe^{III}, and Al^{III} have not. The observed magnetic moments of these oxalato compounds apparently indicate that the latter are ionic and the cobalt compound covalent. Since the chromium compound behaves similarly to that of cobalt, it also probably contains covalent bonds from the metal to the oxygen atoms of the oxalate groups.

(b) The Configuration of certain Metallic Complexes

Four bonds formed by an atom are usually arranged tetrahedrally but a few elements form four coplanar bonds. In the case of copper and silver the arrangement of four bonds depends on the valency state of the metal, the univalent metal forming four tetrahedral and the divalent metal planar bonds. Magnetic measurements could not be used to confirm the planar configuration of complexes of these two metals in the divalent state because the number of unpaired electrons would be the same (one) for both types of bonds. In the case of divalent nickel, however, the formation of tetrahedral or planar bonds leaves different numbers of unpaired electrons, as may be seen from the following data:

	3d	4s	4p	*Number of unpaired electrons*
Ni^{II} forming sp^3 bonds (tetrahedral)	8	2	6	2
Ni^{II} forming dsp^2 bonds (planar)	8 +	2 2	4	0

In the former case the eight electrons in the 3*d* shell are distributed among the five orbitals, two of which contain single unpaired electrons. It is found that many complexes of divalent nickel are diamagnetic, including

the $[Ni(CN)_4]^{2-}$ ion, the glyoximes, and the dithio-oxalate ion. In these the bonds from the Ni atom are therefore coplanar. Certain other complex compounds of divalent Ni, on the other hand, are paramagnetic (μ from 2·6 to 3·2 Bohr magnetons), e.g. $[Ni(NH_3)_4]SO_3$, and these presumably contain tetrahedral nickel bonds. It should be noted that $Ni(CO)_4$, though tetrahedral, is not paramagnetic. This is a compound of neutral, not divalent, nickel, so that there are two more electrons than in the case of a derivative of Ni^{II} and a full complement of 10 electrons in the 3*d* shell. Assuming simple electron pair bonds (see, however, p. 453) we should have

	3*d*	4*s*	4*p*
Ni in $Ni(CO)_4$:	10	2	6

Similar considerations apply to complexes of Pd^{II} and Pt^{II}, all of which so far examined are diamagnetic and therefore planar. A more detailed account of the stereochemistry of the Group VIII elements, and also of some others, will be found in Chapter XVI.

Certain paramagnetic substances exhibit, at temperatures below a certain temperature θ characteristic of the substance, a type of magnetism called ferromagnetism. This magnetism, which can exist in the absence of an external field, is a property of certain metals and alloys—notably of iron, cobalt, nickel, and certain of the rare earths and alloys such as the Heussler and Mishima alloys, $(Cu,Mn)_3Al$ and Fe_2NiAl respectively. Since ferromagnetism is a property associated with the metallic state, being dependent on the presence of free electrons, we shall not have occasion to discuss it further. For other examples of the use of magnetic data see, for example, $H_4P_2O_6$ (p. 418), and $ON.(SO_3K)_2$ (p. 233).

ELECTRIC DIPOLE MOMENTS

An isolated atom is non-polar, i.e. the centre of action of the positive charges coincides with that of the negative charges. In a molecule this is not necessarily so, in which case the molecule is said to be polar and possesses a permanent dipole moment. The bond between two atoms of the same element or between two atoms of similar electronegativity is non-polar, and a molecule such as Cl_2 has no tendency to orient itself when placed in an external electric or magnetic field. A molecule like HCl, on the other hand, will orient itself in such a field because it behaves as a permanent dipole. However, a non-polar molecule may develop a dipole moment when placed in an external field owing to the alteration in the distribution of the positive and negative charges caused by the field, a phenomenon called polarization. This temporary dipole moment, which is in the direction of the field, arises from two causes:

(1) The electrons tend to be displaced with respect to the nuclei towards the positive pole of the field, giving rise to electron polarization, P_E.

(2) As a result of (1) the nuclei themselves may be displaced relative to one another, this effect usually being small compared with the electron polarization. It is termed atom polarization, P_A. We shall restrict this term to harmonic vibrations of small amplitude leading to polarization which is independent of temperature. (We shall see later that in some molecules there are vibrations of greater amplitude which in some cases are temperature dependent and in others temperature independent.)

These two effects are functions only of the field strength and of the structure of the molecule. For molecules possessing a permanent dipole moment there is a third effect.

(3) The field tends to orient the dipoles, resulting in orientation polarization, P_O.

The dipole moment of a bond is a vector quantity, i.e. it is directed along the length of the bond. A complex molecule may contain a number of polar bonds inclined at various angles. From the total polarization of the molecule we can determine only its resultant dipole moment, but if we know the moments of the individual bonds and assume that their moments are unaffected by others in the molecule (an assumption which is discussed below) it is possible to calculate the angles between the polar bonds. Considerable use has been made of dipole moments to find the relative orientations of bonds in molecules.

Experimentally we measure the total polarization of the molecule which is the sum of $P_E+P_A+P_O$. Our problem is to evaluate P_O, or in other words to separate P_O from (P_E+P_A). Dipole moments are usually derived from measurements of dielectric constants and we shall therefore deal with these first, but there are two other experimental methods of restricted applicability.

(1) Dipole Moments from Dielectric Constants

Since the electric field polarizes the molecule, the field in the polarizable medium is less than it would be in the absence of the medium, energy being used in polarizing the molecules. Thus if we have two charged plates, which constitute a condenser, *in vacuo* and insert the medium, the capacity of the condenser increases. The ratio of the capacity of the condenser filled with dielectric to the capacity of the condenser *in vacuo* is called the dielectric constant ϵ. The dielectric constant is related to the molecular polarization P of a substance of molecular weight M and density Δ by the Clausius-Mosotti law:

$$P = \frac{\epsilon-1}{\epsilon+2}\frac{M}{\Delta}.$$

(There is a similar relation between the molecular refractivity R and the refractive index n,

$$R = \frac{n^2-1}{n^2+2}\frac{M}{\Delta} \quad \text{(Lorentz-Lorenz law)}$$

to which we refer later.)

The Clausius-Mosotti law is subject to certain limitations. If we have a mixture of two compounds with polarizations P_1 and P_2 in the molecular proportions x and $1-x$ the mean polarization P_m should, according to this law, be the arithmetic sum of terms due to the two constituents: $P_m = xP_1+(1-x)P_2$. In other words, the value of P_1, e.g. the polarization of the solute in a solution, should be independent of its concentration. This is not the case, and since it is not possible to calculate the interaction between solute and solvent, we avoid this complication either by working with dilute solutions and extrapolating to infinite dilution or by using the vapour of a pure substance. Furthermore, according to the Clausius-Mosotti equation P should be independent of temperature. The orientation polarization P_O, however, is due to the effect of the field in trying to orient the dipoles, a process which is opposed by their thermal movement. For this reason P_O decreases as the temperature rises. Debye showed that the total molecular polarization

$$P = \frac{4\pi N}{3}\left(\alpha_0+\frac{\mu^2}{3kT}\right),$$

where α_0 is the sum of the electronic and atomic susceptibilities (which are independent of temperature), μ is the dipole moment, and the other symbols have their usual significance. Writing this equation in the form

$$P = A+\frac{B}{T} \quad \left(B = \frac{4\pi N}{9k}\mu^2\right),$$

we see that if P is determined at a series of temperatures and plotted against $1/T$ a straight line is obtained. If the compound is non-polar $\mu = 0$ and hence $B = 0$ and the line has zero slope, but if it is polar the dipole moment μ may be found from the slope of the line. This, the *temperature method*, is the most satisfactory way of separating the temperature dependent P_O, from which μ may be found, from the temperature independent P_E and P_A. In practice there is the difficulty that measurements should be made over a fairly large temperature range (100° if possible) in order to obtain accurate results and this is not always possible with unstable compounds. It may be applied to gases or to dilute solutions in non-polar solvents.

The second method makes use of the differences between the times required to set up the three types of polarization in the molecule. The inertia of the electrons is very small and the distortion of their orbits follows the oscillations of the applied electric field up to very high frequencies, far in the ultra-violet. Atomic polarization is a slower process, owing to the greater masses of the nuclei, and it follows the oscillations of the field only up to the infra-red frequencies. Finally the orientation polarization is slower still, so that if we plot the polarization or refractive index of a polar substance against frequency we obtain a curve of the form shown in Fig. 56. We may therefore determine the total polarization P

from the dielectric constant measured with wireless waves (e.g. $\lambda = 100$ m.):

$$P = \frac{\epsilon-1}{\epsilon+2}\frac{M}{\Delta} = P_E+P_A+P_O .$$

and determine P_E+P_A from the refractive index measured with light in the visible region:

$$P_E+P_A = \frac{n^2-1}{n^2+2}\frac{M}{\Delta}.$$

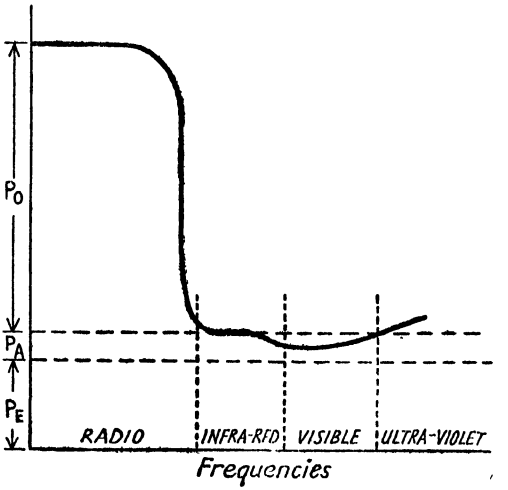


FIG. 56. The variation of polarization with wavelength of radiation (after Sidgwick).

In the case of a dilute solution in a non-polar solvent a number of measurements are made at different concentrations followed by extrapolation to infinite dilution. Since, however, atom polarization is first manifested in the infra-red, it is not sufficient to make measurements of refractive index only in the visible region and then to extrapolate to infinite wavelength. This would amount to neglecting P_A and may lead to serious errors. It is necessary to extend the refractivity measurements into the infra-red (or, of course, to use the temperature method described above), which is a matter of some difficulty experimentally, or to assess P_A as some 5–15 per cent. of P_E. This latter alternative is unsound for 'flexible' molecules (see below), and the soundest method is to calculate P_A approximately as

$$P_A = \frac{4\pi N\mu_1^2}{9V_0}$$

for each one-dimensional oscillation in the molecule, μ_1 being the vibrating moment and V_0 the force constant of the bond. If the component moments are less than 2·5 D, then the 5–15 per cent. P_E rule is a sufficiently good approximation. (The unit of electric dipole moment, 1 D = 10^{-18} e.s.u.)

(2) Dipole Moments by the Molecular Beam Method

This method is not of general application and has been comparatively little used. The theoretical importance of the Stern-Gerlach experiment was mentioned in Chapter I. The substance is heated in a small oven to a temperature at which it has a perceptible though very low vapour pressure. A stream of molecules, sufficiently far apart that there is no appreciable interaction between them, emerges from the oven through a narrow slit into a high vacuum. The beam is cut down to a very narrow ribbon by a second slit and then passes through a high inhomogeneous electric field, one pole being a knife-edge parallel to the direction of the beam and the other a half-cylinder enclosing it. The molecules are either received on a brass plate cooled by liquid air and the resulting trace observed through a microscope or they may be allowed to fall on a photographic plate. With the field off, the molecules pass straight through and condense in a narrow vertical line. If the molecules are non-polar, application of the electric field produces a movement of the molecules towards the stronger part of the field so that the trace shifts. Since the direction of the induced dipoles is determined only by that of the field, all the molecules are affected similarly and the trace moves as a whole. If, however, the molecules are polar, the displacement of any one of them depends on the orientation of the dipole in the field and as the molecules are randomly oriented the result is to broaden the trace. The extent of the broadening is a measure of the dipole moment. It is clear that the method could be of value for substances which are, for example, not sufficiently soluble in non-polar solvents or sufficiently volatile (without decomposition) to give vapours dense enough for measurements of dielectric constant and refractivity. The approximate moments of the following salts have been determined by the molecular beam method: NaI, KI, TlI, RbBr, and CsCl. It has also the advantage that, owing to the considerable separation of the molecules in the beam, their mutual interactions can be neglected.

(3) Dipole Moments from Spectroscopic Data

Finally we may mention an independent method of finding the dipole moments of certain individual bonds. For a diatomic molecule (e.g. HCl) it is possible to calculate the moment of the bond from the absorption coefficients for its fine rotational lines in the far infra-red, and it is also possible to determine the moment of the bonds in a symmetrical molecule like CH_4 from spectroscopic data. The experimental difficulties are very great and very few bonds have been studied in this way. It is, however, of considerable importance to obtain the absolute value of the moment of a bond like C—H which otherwise has to be calculated indirectly from the moments of molecules such as $CHCl_3$ or CH_2Cl_2, making assumptions about interbond angles or using values of these angles obtained by other methods.

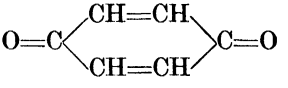
Miscellaneous Remarks

There are a number of points worth noting in amplification of the above remarks.

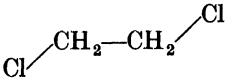
(*a*) *Solutions.* Measurements on solutions are complicated by a number of factors, and the methods of interpreting the experimental results are semi-empirical. For example, the polarization of the solute frequently depends on the dielectric constant of the medium which itself changes with temperature, so that the temperature method is not applicable to solutions. Also, there may be induced polarization and consequent orientation of the solvent molecules due to their own anisotropy. For non-polar solvents satisfactory data are usually obtainable, but for polar solvents only a qualitative treatment is possible. In some cases there are abnormal 'solvent effects'. For example, the moments of the halogen acids HX are greater in solution than in the vapour state, possibly owing to the increased ionic character of the bonds in solution.

(*b*) *Induced Moments.* A polar bond or group may induce relatively large moments in other parts of a molecule. There is no exact treatment so far for all cases. If the induced dipole moment is only of the order of one-tenth of the primary moment, being say 5–6 A. distant, it can be accurately calculated, but if it is one-half or more of the primary moment (say, 1–2 A. distant) it cannot.

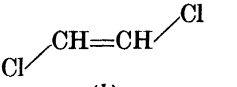
(*c*) *Flexible Molecules.* Some molecules which one would expect to be non-polar were found to possess different polarizations for radio and visible frequencies, the difference being some 20–40 per cent. P_E. This could not be attributed to any solvent effect, for the discrepancy was just as great for the vapours. Being temperature independent they appeared to be cases of abnormally large atom polarizations. The *p*-benzoquinone molecule is an example of this phenomenon and the additional polariza-



tion is now known to arise from the vibrations of the C=O bonds perpendicular to the plane of the ring. Ethylene chloride presents an example of another type of anomaly. If the molecule has the trans configuration (*a*) it should be non-polar and exhibit only atom and electron polarization



(*a*)



(*b*)

like, for example, trans dichloroethylene (*b*). Actually the molecule possesses a dipole moment, and this is due to rotation of the two 'halves' of the molecule relative to one another. The molecule spins as nearly as possible about the line joining the heaviest atoms (chlorine), so that the trans configuration is favoured. Owing to thermal agitation some displacement from this symmetrical arrangement occurs, the extent of which

(and therefore the dipole moment) depends on the temperature. Polarization of this sort may therefore be temperature dependent, according to the nature and amplitude of the vibrations of the flexible molecule.

Some Applications of Dipole Moments

In the case of the hydrogen halides the dipole moments of the molecules are the moments of single bonds. The moments of other bonds have to be determined indirectly, e.g. N—H from that of NH_3, O—H from H_2O or other molecules, utilizing values of interbond angles determined by other methods. As regards the direction of a dipole moment the more electropositive atom forms the positive end of the dipole. Thus in all bonds from hydrogen to other elements the H atom is the positive member, and in all bonds C—X (except C—H) the C atom is the positive member. The direction of a number of moments, mostly of bonds C—X, can be derived from the moments of para-di-substituted benzenes, assuming the direction of one moment.

The most obvious application of dipole moment measurements is to confirm the general shape of simple molecules. Thus molecules AB_2 are polar if non-linear (H_2O, H_2S), but non-polar if linear (CO_2, CS_2), and molecules AB_3 are pyramidal if polar (NH_3, PCl_3, etc.). A molecule AB_4 would be non-polar whether planar or tetrahedral and only one molecule of this type has been found to be polar ($TeCl_4$), showing that it has a less symmetrical configuration.

In the case of compounds MA_2B_2 which form planar molecules the dipole moments enable us to distinguish between cis and trans isomers (see Chapter XVI). The latter has the smaller moment, which should be zero for a centro-symmetrical planar molecule. Actually in a number of cases the trans isomer has a small moment, as also has the trans molecule $[(C_2H_5)_2AuBr]_2$ (see p. 508), and these abnormal moments are due to the same causes as that of *p*-benzoquinone (see above). Knowledge of dipole moments is important when assessing the contributions of the various possible structures in resonating systems. For example, there are two reasonable structures for the nitrous oxide molecule:

$$^{-}:\ddot{N}=\overset{+}{N}=\ddot{O}: \quad \text{and} \quad :N\equiv\overset{+}{N}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:^{-}$$

between which resonance is possible. The fact that the dipole moment is nearly zero shows that the molecule resonates between these two forms. See also the discussion of the CO molecule in Chapter XIII.

Numerous other applications of dipole moment measurements are concerned with the structures of organic molecules, but discussion of these is outside the scope of this book.

THE METHODS OF CLASSICAL STEREOCHEMISTRY

At the beginning of this chapter we classified structural methods into three groups, the last of which included the study of properties dependent

on shape and symmetry, properties of a group of atoms which cannot be expressed as the scalar or vector sum of those of the constituent atoms or bonds. Before the development of the methods we have just been describing, the evidence for the structure of an inorganic molecule or complex ion came from

(*a*) the number of stereoisomers,

(*b*) the presence or absence of optical activity.

A subsidiary method, directly dependent on (*a*) or (*b*), consisted in the deduction of the configuration of a particular molecule or ion from that of a compound from which it could be formed or into which it could be converted. We shall consider this method later; such deductions involve assumptions about the mechanism of chemical reactions which in many cases cannot be justified. We shall also mention in this section the optical and magnetic anisotropy of molecules in connexion with structural studies.

Stereoisomerism

The problem of finding the configuration of a metallic complex which consists of a central metal atom surrounded by a number of atoms or groups may be resolved into two parts:

(1) The arrangement of the atoms or groups around the central atom, without regard to their arrangement relative to one another, i.e. the configuration of the bonds from the metal atom.

(2) The arrangement of the atoms relative to one another, if there are several possibilities.

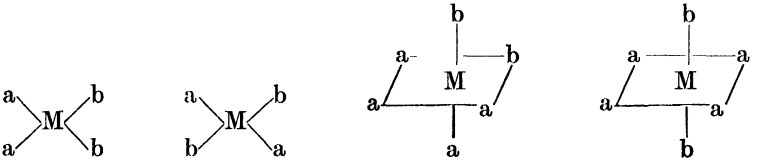
(1) We may assume that we are dealing only with cases in which all the coordination positions are equivalent. Then a complex of the type Ma_3b or Ma_5b can obviously exist in only one form, but the number of isomers of Ma_2b_2 or Ma_4b_2 will be different for different configurations. For 4-coordinated complexes the only bond arrangements found are the planar and tetrahedral, and for 6-coordinated the octahedral arrangement. For the latter the other two most symmetrical arrangements would be the hexagon and trigonal prism. The numbers of isomers of Ma_2b_2 and Ma_4b_2 for these various configurations are set out below:

	Planar	*Tetrahedral*		*Octahedral*	*Hexagonal*	*Trigonal prism*
Ma_2b_2	2	1	Ma_4b_2	2	3	3

It is clear that an exhaustive study of the numbers of isomers of various types of complex should, in principle, enable us to determine the arrangement of the bonds formed by the metal atom, and evidence of this kind was in fact adduced by Werner in support of his theory of the octahedral coordination of cobalt in its ammines. Two points may be noted. First, it is important to be sure that all the supposed isomers have the same molecular weight. For example, the compound $Pd(NH_3)_2Cl_2$ exists in two crystalline forms. Both the pink and yellow forms apparently had simple molecular weights as determined by the depression of the freezing-

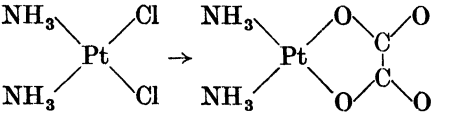
point of phenol. It is now known, however, that while the yellow form is, in fact, $Pd(NH_3)_2Cl_2$, the pink form is a salt $[Pd(NH_3)_4][PdCl_4]$, and this particular piece of evidence for the planar arrangement of the four bonds of Pd^{II} was invalidated. (This point is no longer of importance as the planar arrangement of Pd^{II} bonds has been established in other ways.) The second point is that only the isolation of the maximum number of isomers is satisfactory evidence in the argument used above. The isolation of only two forms of Ma_4b_2, for example, is not conclusive proof that the arrangement of the bonds is octahedral since a third isomer might have been missed owing to its much smaller stability or much greater solubility. For example, only the trans forms of a number of palladium compounds are known (p. 528). However, these difficulties may usually be overcome by a survey of the numbers of isomers of a sufficiently large number of different complexes.

(2) Having established that a complex of the type Ma_2b_2 is planar, or Ma_4b_2 octahedral, we have to discover which isomer has the configuration (*a*) or (*b*) in the first case or (*c*) or (*d*) in the second.

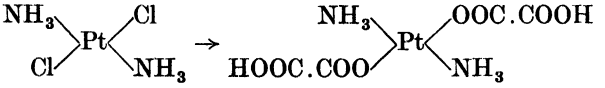


Apart from the use of generalizations, of doubtful value, such as the cis compounds having greater solubility and deeper colour, the decision between cis and trans was made by deriving one or both of the isomers from a complex of known configuration or by converting one or both into such a compound. The following examples are typical of the arguments used.

α-$Pt(NH_3)_2Cl_2$ readily forms the oxalato complex, $Pt(NH_3)_2C_2O_4$, whereas β-$Pt(NH_3)_2Cl_2$ yields an acid oxalate, $Pt(NH_3)_2(C_2O_4H)_2$. Hence the former isomer has the two chlorine atoms adjacent to one another since they are replaceable by the oxalato group which occupies two adjacent coordination positions:



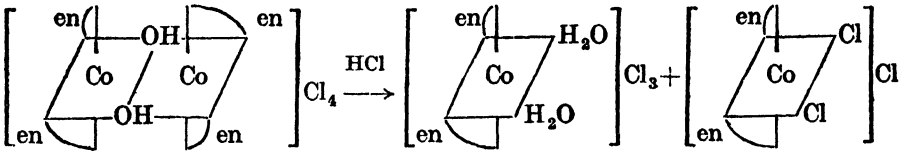
but



Similarly in 6-coordinated cobaltammines, atoms easily replaced by such a group as C_2O_4 were assumed to be adjacent and the complexes formed by the replacement of an oxalato or carbonato group by two chlorine

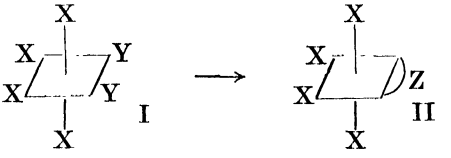
atoms, for example, were assumed to be the cis isomers. (The dimensions of the C_2O_4 group are such that it would be impossible for it to occupy trans positions.)

In addition to the simple mononuclear cobaltammines there are the bridged compounds. The products of rupture of a complex ion such as that shown below were supposed to be the cis compounds:



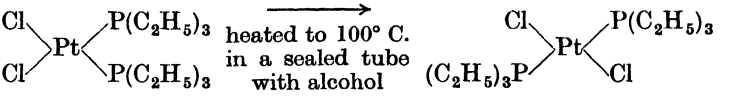
The configuration of a particular complex may follow from the fact that it is optically active. For example, of the two possible isomers of $[Co(NH_3)_2(C_2O_4)_2]^-$ one is active and the other not. Since the optically active isomer is obtained from $[Co(NH_3)_2(NO_2)_4]^-$ it should follow that the latter is the cis isomer. This particular case is discussed in more detail in Chapter XVI.

All the above arguments assume that there is no change of configuration during a chemical reaction, e.g. that if I is converted into II then the incoming group takes up the positions occupied by the atoms it replaces.



When, however, we remember that atoms possess size it would seem that this is very unlikely to happen. Not only would the atoms Y obstruct the entry of Z, but it is also unlikely that both Y atoms come away instantaneously and in the meantime rearrangement of the remaining atoms may take place. There is now a considerable amount of evidence that rearrangements of this sort do take place. On the one hand, there are the reactions of, say, a trans isomer in solution (the cis isomer being unknown) which would appear to be in some cases those expected of a cis isomer, and on the other the numerous well-established examples of change of configuration during chemical reactions. Of these we may quote the following:

(1) *Cis-trans conversions*



trans $[Co\ en_2\ Cl_2]Cl$ $\xrightarrow{KOH}$ cis $[Co\ en_2(H_2O)OH]Cl_2$

trans $[Co\ en_2(NH_3)Cl]^{2+}$ $\xrightarrow{NH_4OH}$ cis $[Co\ en_2(NH_3)OH]^{2+}$

(2) *Dextro-laevo conversions.* The reaction

$$\text{cis-[Co en}_2\text{Cl}_2\text{]Cl} \rightarrow \text{cis-[Co en}_2(\text{NH}_3)_2\text{]Cl}_3$$

is typical. At and below the boiling-point of liquid ammonia the product has the same sign of rotation as the starting material. At higher temperatures the product is predominantly the other enantiomorphic form. Moreover, a small quantity of the trans isomer is formed in all cases.

Optical Activity

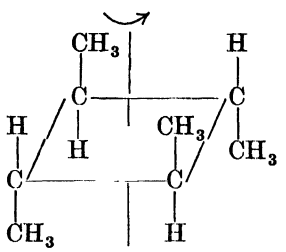
Optical activity, the property of rotating the plane of polarization of plane-polarized light, may be exhibited by matter in all states of aggregation. If the symmetry of a group of atoms, whether a finite group (molecule or complex ion) or an extended array forming a crystal, is such that the grouping cannot be superposed on its mirror image, then the arrangement is said to be enantiomorphous. It exhibits optical activity.

(There are apparently one or two examples of enantiomorphous crystals—as judged by the arrangement of their faces—which are not optically active, so that there may possibly be exceptions to the above statement. There are, however, no known exceptions to the converse, that optical activity implies enantiomorphism.)

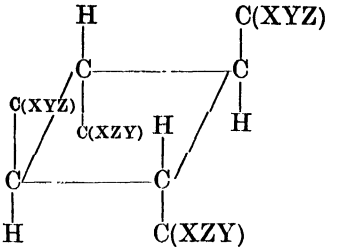
Such an arrangement of atoms exists in two forms, identical as regards composition and mode of linking of the atoms, and related to one another as object and mirror image. They differ in rotating the plane of polarization in opposite senses and are described as the dextro- and laevo-rotatory forms—*d*- and *l*- or right- and left-handed forms.

The optical activity of a crystal may be due to the fact that it consists of enantiomorphous molecules or to an enantiomorphous arrangement of atoms—as in $NaClO_3$, HgS, or quartz (SiO_2). In the former case the activity persists in solution, but in the latter it is characteristic of the solid state alone, and disappears when the crystal is dissolved or fused. Of the thirty-two classes of point-symmetry (p. 158) eleven are enantiomorphous. The criterion is the absence of an axis of rotatory inversion. Of these axes, $\bar{1}$ is synonymous with a centre of symmetry, $\bar{2}$ with a plane of symmetry, $\bar{3}$ implies the presence of a centre of symmetry, and $\bar{6}$ the presence of a plane of symmetry. Since an axis of 4-fold rotatory inversion ($\bar{4}$) is likely to occur very rarely in molecules, we may for practical purposes take as the criterion for optical activity in a molecule (or complex ion) the absence of a *centre* or *plane of symmetry.*

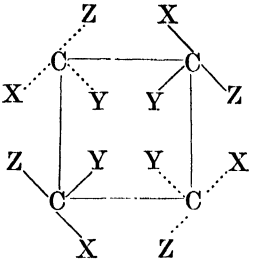
(Certain substituted cyclobutanes possess this unusual symmetry axis, e.g. that shown below (I). This molecule also, however, possesses diagonal planes of symmetry parallel to the $\bar{4}$ axis, so that its lack of enantiomorphism cannot be attributed to the presence of that axis. These planes of symmetry would disappear if groups C(XYZ) were substituted for the methyl groups, giving the molecule II *a*. In the plan at II *b* only these C(XYZ) groups are shown to illustrate the absence of diagonal symmetry planes. This molecule would not be optically active since it is superposable on its mirror image, though it contains no less than eight asymmetric carbon atoms.)



I



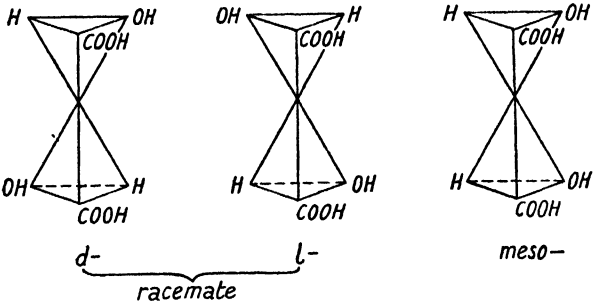
II *a*



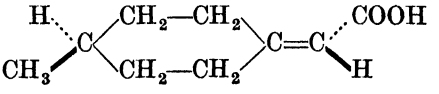
II *b*

Optical activity was first studied in compounds of carbon. In 1874 van 't Hoff showed how optical activity could arise if the four bonds from a carbon atom were arranged tetrahedrally. Le Bel independently, and almost simultaneously, put forward somewhat similar views. A molecule Cabcd in which a C atom is attached to four different atoms or groups should exist in two forms related as object and mirror image. The central C atom was described as an asymmetric C atom. A simple molecule of this sort is that of lactic acid, $CH(CH_3)(OH)COOH$, which exists in *d*- and *l*-forms. There is a third form of such a compound, the racemic form, consisting of equal numbers of *d*- and *l*-molecules. A crystal of the racemic form is optically inactive.

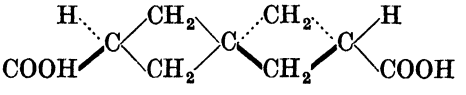
A molecule containing two similar asymmetric C atoms, cbaC—Cabc, exists not only in *d*- and *l*-forms (which combine to form a racemate) but also in an inactive meso- or 'internally compensated' form. The racemate is described as 'externally compensated'. For tartaric acid the *d*-, *l*-, and meso-forms may be represented:



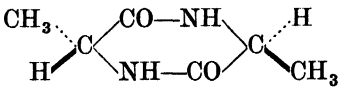
We now know that (1) optical activity may arise without the presence of asymmetric carbon atoms, and (2) the presence of asymmetric carbon atoms does not necessarily lead to optical activity. In other words, the criterion is the symmetry of the molecule as a whole. The following molecules are examples of (1):



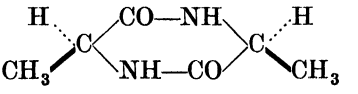
and



bonds shown as dotted and heavy lines lying in a plane perpendicular to and respectively behind and in front of the plane of the paper. The compound dimethyl-diketopiperazine provides an interesting example of (2). It exists in cis and trans forms, each containing two asymmetric carbon atoms. The trans form possesses a centre of symmetry and is therefore not optically active, while the cis form is resolvable into optical antimers (*d*- and *l*-forms).



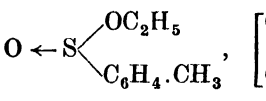
trans



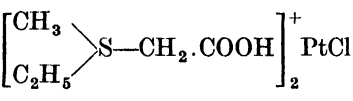
cis

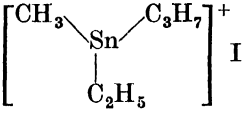
We shall conclude these remarks on optical activity by giving a few examples of molecules or ions the resolution of which into their optical antimers demonstrates the general arrangement of the bonds formed by the central atom.

Three pyramidal bonds

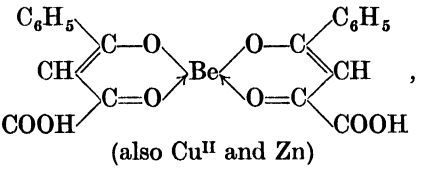


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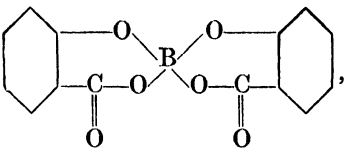


Four tetrahedral bonds

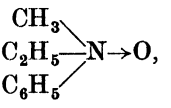


(also Cu^{II} and Zn)

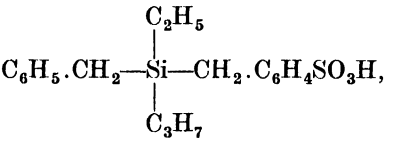
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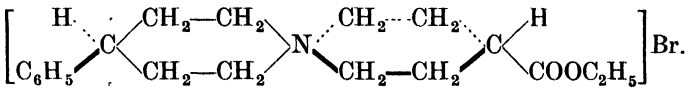


,



(also P)

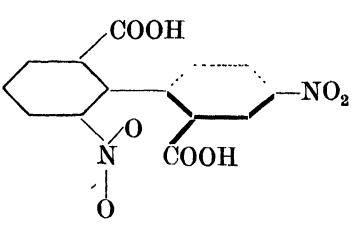




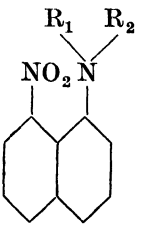
The last compound is of some interest historically. It was at one time suggested that the resolution of tetra-substituted ammonium salts $[Nabcd]^+X^-$ was possible owing to the arrangement of five atoms around N at the apices of a square pyramid. If in the above molecule the four carbon atoms were arranged at the corners of the base of a square pyramid, the molecule would possess a plane of symmetry. The resolution of this compound confirmed that the ion $[Nabcd]^+$ is, as regards its stereochemistry, similar to a carbon compound Cabcd, the negative X ion not being directly attached to the N atom.

Examples of optically active metallic coordination compounds are given in Chapter XVI.

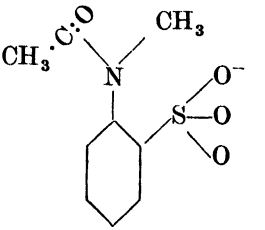
As a matter of interest we may mention a type of molecule, examples of which are shown below, the optical activity of which is due to the restricted rotation around a single C—C bond. The molecule is unable to adopt the most symmetrical form owing to the presence of groups projecting from the aromatic rings, and enantiomorphous forms result.



(1)



(2)



(3)

In the case of (3) the replacement of SO_3^- by the smaller COO^- group destroys the optical activity.

OPTICAL AND MAGNETIC ANISOTROPY

For the simple ionic structures with cubic symmetry the molar refractivity is the sum of the refractivities of the individual ions, and the diamagnetic susceptibility is similarly an additive function of the individual susceptibilities. These structures are composed of simple ions with spherical symmetry and the refractive index is independent of the direction in which light travels through the crystal. Such crystals are described as isotropic. Crystals of lower symmetry are birefringent (doubly refracting), i.e. the refractive index is different for light travelling in different directions. This anisotropy is also exhibited in the diamagnetic susceptibility. A group of atoms forming a molecule or complex ion may be described as anisotropic if its shape is far from spherical. Ions such as the planar NO_3^- or CO_3^{2-} ions have very different refractive indices for light polarized in different directions. For light polarized in the plane of the group the refractive index is high, but for vibrations perpendicular to this plane the refractive index is much lower. This is described as negative birefringence and is characteristic of many planar molecules in which there is resonance between single and multiple bond structures (e.g. urea and aromatic compounds) and also of layer structures. The other extreme type of anisotropy is that of long rod-shaped groups of atoms—linear molecules or ions or the infinite chains in chain structures. For these there is one large refractive index (for vibrations along the length of the chain), and the refractive index is small for vibrations perpendicular to the chain axis (positive birefringence). The diamagnetic anisotropy of these atomic groupings is equally marked. For long-chain aliphatic carbon compounds (containing few or no multiple bonds) the

chain axis is the direction of maximum diamagnetic susceptibility and maximum refractivity, and for layer structures the maximum diamagnetic susceptibility and refractivity both lie in the plane of the layer. Planar ions or molecules, in which there is resonance between single and double bonds (e.g. the acetate ion and aromatic nuclei), show magnetic anisotropy opposite in sign to that of the optical birefringence, the magnetic birefringence being positive.

The determination of the relative orientations of anisotropic molecules in crystals, utilizing optical and magnetic data, is quite similar in principle to the calculation of interbond angles from a knowledge of the resultant dipole moment of a molecule and the moments of the individual bonds. Many molecules of extreme shape or molecules containing particular types of bonds are markedly anisotropic. When such molecules are packed together in a crystal the resulting anisotropy is a function both of the anisotropy of the individual molecules and of their relative orientations. The anisotropy of the crystal will obviously be most marked when the molecules are packed with their optical or magnetic axes parallel, but this is rarely the case because of the difficulty of packing, and the relation of the anisotropy of the crystal as a whole to that of the individual molecules

TABLE 14

Optical Properties of Crystals

Shape and arrangement of structural units	*Optical properties*	*Conclusions*	*Examples*
Rod-shaped			
(*a*) All parallel to one direction	Large positive birefringence	Units parallel to direction of maximum refractive index	1. Chain structures, e.g. Se 2. Long-chain hydrocarbons
(*b*) All parallel to a plane but not to each other	Large negative birefringence	Molecules lie in planes normal to direction of least refractive index	
(*c*) Inclined in all directions	Isotropic or approximately so	Units not arranged as in (*a*) or (*b*)	
Planar			
(*a*) Planes parallel	Large negative birefringence	Planes of molecules normal to direction of minimum refractive index	1. Layer structures, e.g. mica 2. Calcite
(*b*) Planes all parallel to a line but not to each other	Large positive birefringence	Planes of molecules parallel to direction of maximum refractive index	Urea
(*c*) Planes inclined in all directions	Isotropic or approximately so	Units not arranged as in (*a*) or (*b*)	$Pb(NO_3)_2$, resorcinol

(or other structural units) is not simple. For example, the NO_3^- ion possesses strong negative birefringence, as does a crystal of $NaNO_3$, in which the planes of all the NO_3^- ions are parallel. In lead nitrate, on the other hand, the planes of the NO_3^- ions are inclined to one another in accordance with the cubic symmetry of the crystal, which is isotropic.

The relations between the optical properties of individual molecules and those of the crystal are summarized in Table 14.

It will be apparent that only in certain cases can information be obtained from a comparison of the anisotropy of the crystal with that of the individual units of structure. In favourable cases, however, a knowledge of the optical and magnetic properties of crystals, particularly of organic compounds, can be of considerable assistance in estimating the relative orientations of the molecules.

COLOUR

These remarks on the colours of certain compounds are included simply to draw attention to one type of coloured compound of peculiar interest from the point of view of structural chemistry. We use the term colour to refer to the property of preferential absorption of light of one or more wavelengths or ranges of wavelength in the visible spectrum. Clearly this is an arbitrary use of the term; the intense absorption of light of wavelengths outside the visible spectrum is equally important from the physical standpoint. The absorption of light, including the preferential absorption of particular wavelengths which gives rise to colour, is due to electronic transitions within the atoms. We have remarked that ions such as those of the alkali metals with completed outer shells of electrons are colourless, whereas those of the transition metals are coloured. In these ions the penultimate shell is incomplete. In the rare earth ions the incompleteness of the $4f$ sub-shell gives rise to characteristic absorption, though not always in the visible region. To absorb in this region an ion must be capable of an electronic transition corresponding to the absorption of a quantum of visible light (40–70 k.cals./gram atom). In Na^+ the transfer of an electron from one completed shell to another requires far more energy and leads to absorption in the ultra-violet, but in the Na atom the transfer of the single electron in the outer shell from an s to a p orbit requires less energy and accordingly sodium vapour absorbs in the visible region of the spectrum (the sodium D lines). We shall not be concerned with colour arising in this way in simple ions or in complexes containing such metals, as for example in the yellow CrO_4^{2-} or the purple MnO_4^- ions or the cobaltammines with their striking colours ranging from one end of the spectrum to the other.

From time to time compounds have been prepared which possess intense colour not exhibited by other compounds of the particular element, and many of them appeared to contain an atom in an unusual valency state. It is now known that some, at least, of these compounds owe their colours

to the fact that an element is present in two different valency states. If the compound contains equal numbers of atoms exhibiting valencies differing by two units, the empirical formula may indicate an intermediate valency, but this depends on the valency of the negative ion. For example, $M^{I}M^{III}X_2^{II}$ reduces to $M^{II}X^{II}$, apparently containing M^{II}, but $M^{II}M^{IV}X_3^{II}$ does not reduce to a simpler form with integral numbers of atoms.

The following are some examples, chosen at random, of compounds containing atoms of the same element in two different valency states. We shall not have any more to say about these compounds here, but references to other chapters are given in cases where their structures have been studied.

Gold. The double halide with empirical formula $CsAuCl_3$ forms jet-black crystals. It is now known to contain aurous and auric atoms and to be more correctly formulated $Cs_2Au^{I}Au^{III}Cl_6$. The analogous silver salt $Cs_2AgAu^{III}Cl_6$ is also known (see p. 290).

Cerium. In the oxidation of white $Ce(OH)_3$ to yellow $Ce(OH)_4$ an intermediate cero-ceric hydroxide of composition approximating to $Ce(OH)_3.Ce(OH)_4$ is formed. This is violet to blue-black in colour. The deep red cero-ceric acid sulphate may be crystallized from a solution of cerous sulphate (colourless) and excess of ceric sulphate (deep yellow) in moderately concentrated sulphuric acid. Various formulae have been assigned to this compound, e.g. $HCe^{III}Ce^{IV}(SO_4)_4.12H_2O$. The trivalent cerium is replaceable by La^{III}, Pr^{III}, or Nd^{III}. Also of interest in this connexion is the deep blue compound, of approximate composition $UO_2.2CeO_2$, formed by precipitating a solution of uranyl and cerous nitrates with excess ammonia. The precipitate at first formed is yellow, but it rapidly turns deep blue.

Antimony. Violet-black salts $(NH_4)_2SbBr_6$ and Rb_2SbBr_6 may be crystallized from solutions, which are only slightly coloured, containing Sb^{III}, Sb^{V}, and the appropriate alkali halide. The diamagnetism of these salts shows that they do not contain $SbBr_6^{2-}$ ions with tetravalent antimony, for the latter would have one unpaired electron. They crystallize with the K_2PtCl_6 structure (p. 289) and must contain equal numbers of $[Sb^{III}Br_6]^{3-}$ and $[Sb^{V}Br_6]^{-}$ ions. The structures of the brownish-black Bi_2Cl_4 and Bi_2Br_4 (compare $BiBr_3$ orange) are not known.

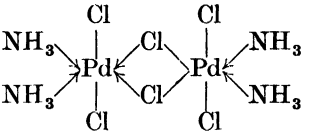
Molybdenum. 'Molybdenum blue' is formed as a colloidal solution by the partial reduction of molybdic acid or molybdates or by the careful oxidation of compounds of molybdenum in lower valency states. Evaporation of this sol gives a black residue and coagulation by electrolytes a dark blue powder. Its composition is reported to be $Mo_8O_{23}.xH_2O$.

Tungsten. The blue oxide formed by reducing WO_3 in a stream of dry hydrogen has a composition intermediate between WO_2 and WO_3 and is presumably related to molybdenum blue. The tungsten bronzes result from the reduction of alkali or alkaline-earth tungstates by hydrogen or molten zinc. They show a range of colours and are notable for their

metallic lustre. The sodium-containing bronzes have been studied by the X-ray method (see p. 331). They contain some W^{VI} reduced to W^{V}, a sodium atom being taken up for every such atom, giving the general formula $Na_xW^{V}_xW^{VI}_{1-x}O_3$.

Iron. For the structure of Prussian blue and other complex ferrocyanides see p. 449.

Palladium. Black crystals of empirical formula $(NH_3)_2PdCl_3$ result from the action of HCl and H_2O_2 on $(NH_3)_2PdCl_2$. They probably contain molecules in which palladium is present in both the di- and tetra-valent states. The dark red NH_3(pyridine)$PtCl_3$ and the black $(NH_3)_2Pd(OH)Cl_2$ probably owe their intense colours to the same cause.



Differences in colour between a solid and its solution are important as indications of structural changes. We have already referred to the dissolution of blue crystals of Cs_2CoCl_4 and Cs_3CoCl_5 to form pink solutions, a colour change indicating the breakdown of the $CoCl_4^{2-}$ complexes to aquo-complexes. The numerous examples of this type of colour change include the salt $(NH_4)_2SbBr_6$ mentioned above and $K_4Mn(CN)_6$, which crystallizes as deep-blue crystals from a pale yellow solution. As an example of a structural change which results in the formation of a deeply coloured solution from nearly colourless crystals we may quote the salt $ON(SO_3K)_2$. The oxidation in alkaline solution of potassium hydroxylamine disulphonate, $OH.N(SO_3K)_2$, produces a purple solution which on evaporation deposits yellow crystals of empirical formula $ON(SO_3K)_2$. These redissolve to give the purple solution. The solid is very feebly paramagnetic, but the paramagnetism of the aqueous solution corresponds to the theoretical value for a molecule with an odd unpaired electron. It is probable that the crystal contains double molecules,

$$\underset{\text{Solution}}{2[ON(SO_3K)_2]} \rightleftharpoons \underset{\text{Crystal}}{[ON(SO_3K)_2]_2}.$$

PART II

CHAPTER VII

HYDROGEN

THE hydrogen atom has the simplest electronic structure of all the elements. For this reason theoretical studies of the relation of spectra to the intra-atomic electronic transitions and of the forces between atoms have naturally started with hydrogen. The atom has one valency electron, the loss of which leaves the singly charged H^+ ion or proton. Owing to its exceedingly small size this ion has very great polarizing power: the behaviour of the hydroxyl (OH) group illustrates the effect of the proton on the oxygen atom. Hydrogen is an essential constituent of acids, the ionization of which consists in the liberation of H^+ ions. The hydrogen atom has only one stable orbital, the 1*s* orbital. It can therefore acquire the stable helium configuration either by forming one covalent bond or by acquiring an extra electron to form the H^- ion. This ion is much less stable than the H^+ ion, as is seen by comparing the electron affinity and ionization energy of hydrogen:

$$H + e \rightarrow H^- + 16{\cdot}4 \text{ k.cals./mole (electron affinity)}$$
$$H^+ + e \rightarrow H + 312 \text{ k.cals./mole (ionization energy).}$$

The H^- ion cannot exist in aqueous solution since it immediately unites with H^+ forming H_2 molecules and leaving OH^- ions in solution. There are, however, a number of crystalline hydrides containing this ion.

We have said that the H atom has only one stable orbital and can therefore form only one covalent bond. In the past, structural formulae involving 2-covalent hydrogen have been assigned to many compounds, but the modern view is that where the H atom is genuinely attached to more than one atom the bonds are not covalent. Such bonds are called 'hydrogen bonds' and will be discussed later. The covalent bonds formed by H are normally electron-pair bonds, but, as was pointed out in Chapter II, there may be 1-electron bonds in the boron hydrides. In the H_2^+ molecule-ion there is necessarily a 1-electron bond as there is only one electron available for bond formation. The structures of H_2^+ and of the H_2 molecule have been mentioned in connexion with the formation of 1- and 2-electron bonds in Chapter II.

We may summarize the chemistry of hydrogen under four heads:

(*a*) The H^+ ion and the structure of acids.

(*b*) The H^- ion and the hydrides of the alkali and alkaline-earth metals.

(*c*) Hydrogen forming one covalent bond, either 1- or 2-electron.

(*d*) The hydrogen bond, X—H—X.

Before outlining the structural chemistry of hydrogen two points of interest in connexion with the element will be mentioned.

When discussing the structure of the atom it was mentioned that the atoms of an element do not, in general, all possess the same nuclear mass, atoms with the same outer electronic structure but different nuclear masses being termed isotopes. Any differences between the properties of isotopes of a given element arise from the difference between the masses of the nuclei, and the relative difference in properties between isotopes of mass m and $m+1$ depends on the value of m. The moments of inertia, for example, of diatomic molecules $M_m M_m$, $M_m M_{m+1}$, and $M_{m+1} M_{m+1}$ are functions of the products of the masses, i.e. of m^2, m^2+m, and m^2+2m+1, and the ratio of the two extremes $(m+1)^2/m^2$ is clearly greater the smaller the value of m. Ordinary hydrogen consists of a mixture of two isotopes,* of masses 1 and 2, and there are considerable differences between the physical properties of compounds containing these isotopes. In spite of this fact the second isotope, called deuterium, was not isolated until 1932. Its presence was first suspected from the discrepancy between the chemical value of the atomic weight of hydrogen (1·00799, referred to O = 16) and the value $1{\cdot}00778 \pm 0{\cdot}00015$ obtained by Aston in 1927 from mass spectrographic measurements. It was later separated by electrolytic methods. To illustrate the effect on the physical properties of the difference in nuclear mass we may compare some of the physical constants of H_2O and D_2O:

	H_2O	D_2O
Boiling point	100	101·42° C.
Melting point	0	3·82° C.
Density (20°)	0·9982	1·1059 g./c.c.
Temperature of maximum density .	4	11·6° C.

There is evidence that in the H_2 molecule the two nuclei are spinning so that there are two forms of the molecule according to whether the spins are in the same or in opposite senses:



ortho para

The two forms differ in intramolecular energy, that of the ortho form being greater than that of para hydrogen. The equilibrium proportions of the two forms therefore vary with temperature, the theoretical values ranging from 100 per cent. para at 0° K. to 25 per cent. para at high temperatures. Equilibrium concentrations of the two forms are soon reached in the presence of certain catalysts. For example, if ordinary hydrogen is placed in contact with active carbon at 20° K. it is soon converted into 99·7 per cent. para and 0·3 per cent. ortho.

* A third (radioactive) isotope H^3 has been produced artificially by bombarding deuterium with deuterons (the deuteron being the analogue of the proton): $D^2+D^2 \rightarrow H^1+H^3$.

ACIDS AND BASES

The terms acid and base were originally defined by the relation: acid + base → salt + water. Later, with the advent of the theory of electrolytic dissociation, the term acid was applied to any compound which on solution provided H^+ ions, and a source of OH^- ions was termed a base. In the investigation of the effects of acids, bases, and salts on the speeds of certain chemical reactions it was found that many ions and also apparently undissociated molecules of weak acids and bases had catalytic effects quite analogous to those of H^+ and OH^- ions. For this reason the meaning of the term base was extended to cover any substance which unites with protons, an acid still being defined as a source of protons. Thus the relation between acid and base becomes

$$\underset{\text{acid}}{A} \rightleftharpoons H^+ + \underset{\text{base}}{B}.$$

Clearly the original definition of base as a source of OH^- ions is unsatisfactory since it did not include such compounds as NH_3 and its substituted derivatives, although it included an aqueous solution of ammonia ($NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$). On the above Brønsted-Lowry definition the NH_4^+ ion is regarded as an acid since

$$\underset{\text{acid}}{NH_4^+} \rightleftharpoons \underset{\text{base}}{NH_3} + H^+$$

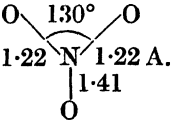
and water as both acid and base since

$$\underset{\text{acid}}{H_2O} \rightleftharpoons H^+ + \underset{\text{base}}{OH^-} \quad \text{and} \quad \underset{\text{base}}{H^+ + H_2O} \rightleftharpoons \underset{\text{acid}}{H_3O^+},$$

assuming the existence of hydrated rather than simple protons in aqueous solution.

The Structures of Acids

Some of the inorganic acids, such as sulphuric acid H_2SO_4, were among the compounds known to the earliest chemists, but little is known even to-day of the structures of the inorganic acids as a class. This is largely due to the fact that many are liquid at ordinary temperatures or are known only as aqueous solutions, and the investigation of the structures of liquids is still in its infancy. A few of the simpler organic acids have been studied in the solid and/or vapour states, and examples of these will be described later in our discussion of the hydrogen bond. The structure of the molecule of nitric acid has been studied in the vapour state by the electron diffraction method. The three O atoms are coplanar with the N atom, one (presumably that of the OH group) being at a much greater distance from that atom than the other two. We shall denote an acid



by the general formula H_nA, where A may be a single atom or a group of atoms. This group A is known to have a separate existence in the crystalline salts and also in the dilute solutions of many acids. We may conveniently consider the determination of the structure of an acid as consisting of two problems. The first is to find the structure of the complex A, and this may be determined by a study of the salts. The second is to discover the relation of the hydrogen atom(s) to the A groups in the pure acid, assuming that the form of these groups is not greatly different in salt and acid. We shall confine our attention here to the second point; the structures of the groups A will be dealt with elsewhere.

A characteristic property of acids is that in solution they dissociate, to varying extents, yielding H^+ ions. If, in the formula H_nA, $n > 1$ we may imagine the process of ionization to take place in stages, viz.

$$H_nA \rightleftharpoons H^+ + [H_{n-1}A]^{-1} \text{ and so on.}$$

The conductivities of solutions of weak dibasic acids such as oxalic and tartaric acids can be explained if it is assumed that ionization takes place in two stages, the second process

$$\begin{bmatrix} COOH \\ | \\ COO \end{bmatrix}^- \rightleftharpoons \begin{bmatrix} COO \\ | \\ COO \end{bmatrix}^{2-} + H^+$$

in the case of oxalic acid becoming important only in very dilute solution. In the case of inorganic salts containing more than one H atom per molecule, e.g. H_2SO_4, H_2CO_3, the existence of acid salts such as $NaHSO_4$ and $NaHCO_3$ is not necessarily to be regarded as evidence for the existence of the intermediate ions $[HSO_4]^-$ or $[HCO_3]^-$ in solution, since in the crystals of 'acid salts' there are no finite ions with these formulae. Instead we find in $NaHCO_3$ crystals an infinite array of CO_3 groups joined by hydrogen bonds. This is merely another example of the general rule that the constitution of a compound in solution cannot be deduced from the empirical formula of the solid. Similarly, from the existence of solid compounds we may not infer the existence of the corresponding acids. For example, there is no acid corresponding to the solid $MgSiO_3$, for this particular Si:O ratio arises from the arrangement of the Si and O atoms to form infinite ions which can exist only in the solid state. Again, an ion may be stable in a crystal but not in the presence of H^+ ions, as in the case of the thiosulphate ion. The properties of acids should not be confused with those of the ions A^{n-}.

Table 15 shows the forms in which a number of the simpler inorganic acids are obtained. The poly-acids derived from the more metallic elements are omitted from this table as they are more conveniently described under the chemistry of oxygen.

In oxy-acids in the condensed states the H atoms join neighbouring oxy-ions together by means of hydrogen bonds; see, for example, the structure of boric acid, below. The liquid or solid acid consists of groups

TABLE 15

Class	Pure acids known at ordinary temperature as: Solid	Liquid	Vapour	Acid known only in aqueous solution
(*a*)		HN_3 H_2O_2 H_2S_2, H_2S_3 H_2S_5	H_2S HF, HCl, HBr, HI	
(*b*) Simple oxy-acids (i)	H_3BO_3 H_6TeO_6			
(ii)	HBO_2*			H_2CO_3
		HNO_3		HNO_2
	H_3PO_2			
	H_3PO_3			
	H_3PO_4			
	HPO_3†			
	H_2SeO_3	H_2SO_4		H_2SO_3
	H_2SeO_4	HSO_3F		
	H_2SO_5	HSO_3Cl		H_2TeO_3‡
				HClO, HBrO, HIO
				$HClO_2$
				$HClO_3$
	HIO_3			$HBrO_3$
	HIO_4	$HClO_4$		
	H_5IO_6			
Per- and Pyro-acids	$H_2B_4O_7$*			
	$H_4P_2O_6$			
	$H_4P_2O_7$§	$H_2S_2O_7$		
	$H_2S_2O_8$			
Poly-acids	$H_2N_2O_2$			$H_2S_2O_3$‖
				Polythionic acids ($H_2S_nO_6$, $n = 3, 4, 5, 6$)

* HBO_2 and $H_2B_4O_7$ are said to be intermediate phases, formed at 100° and 140° respectively in the dehydration of H_3BO_3.

† Usually obtained as a syrup or glass.

‡ Existence doubtful, since TeO_2 is practically insoluble in water.

§ Often glassy.

‖ Existence doubtful.

of atoms (A) joined by hydrogen bonds, and the structure of the crystalline acid will depend on a number of factors, e.g. the ratio of the number of H atoms available to the number of O, N, etc., in the groups A between which the hydrogen bonds are to be formed. This will be a more important

factor than the shape of the group A. The SO_4 group, for example, is very roughly spherical, but in H_2SO_4 there are twice as many H^+ ions as SO_4^{2-} ions. It would therefore be possible for each SO_4 ion to be surrounded by four others, to each of which it is linked by a hydrogen bond between one of its own O atoms and an O atom of a neighbouring ion. The SO_4 ions could therefore be arranged like the carbon atoms in diamond. In the liquid a similar average coordination would be found, but the neighbours of a given ion would be constantly changing owing to the greater thermal motion in liquids compared with that in solids. It will be seen later that this picture of a solid acid is very similar to that of certain acid salts (e.g. KH_2PO_4) in which also there is an extended network of ions linked by hydrogen bonds, with metal ions in the interstices.

When the acid is dissolved in water the lattice of SO_4 groups breaks down and there is often very considerable interaction between the ions produced and the water, as is seen from the heat evolved in diluting H_2SO_4 and also, in the case of many acids, from the formation of well-defined hydrates ($HClO_4.H_2O$, $HNO_3.H_2O$, etc.) and constant-boiling mixtures. This interaction is to be expected since the structure of water itself is determined by hydrogen bonds which may now be formed between the groups A and the O atoms of the water molecules. In dilute solution there will be little interaction between one A group and another or between A groups and H^+ ions, as each kind of ion will be surrounded, and therefore separated, by many water molecules. We may therefore expect considerable differences between the properties of pure liquid acids or their concentrated aqueous solutions and their dilute solutions. We must, however, be sure that the property we are discussing is a property of the pure acid and not of some decomposition product. For example, the oxidizing properties of concentrated HNO_3 or $HClO_4$ are apparently associated with the presence of NO_2 or Cl_2O_7 respectively. Pure colourless HNO_3 has very little or no oxidizing action on metals, sulphur, etc., and concentrated HNO_3 mixed with urea (which reacts with the oxides of nitrogen) behaves similarly. One important property of concentrated HNO_3 is that of nitrating organic compounds. Water is liberated in the process, e.g.

$$C_6H_6+HNO_3 \rightarrow C_6H_5NO_2+H_2O,$$

so that the reaction would slow down if the water were not removed. For this reason concentrated H_2SO_4 is added, thus making use of the great attraction for water of this acid, a property already mentioned. The difference between the structures of concentrated and dilute acids is shown by the ultra-violet absorption spectra. That of dilute HNO_3, for example, is similar to that of a solution of an alkali nitrate, but quite different from that of the concentrated acid.

The extent to which an acid can be concentrated in aqueous solution varies widely. Solutions of boric acid and of a number of others (see Table 15) may be concentrated until all the water is removed and the solid acid is left. If, on the other hand, we attempt to concentrate by

evaporation a solution of H_2SO_4 or HNO_3, the concentration of the acid increases to a certain value (which for a given acid depends on the pressure above the solution) and the concentration thereafter remains constant (constant-boiling mixture). The pure acids may be obtained by freezing such solutions or by adding the calculated quantity of SO_3 or N_2O_5 respectively, but they are not stable under ordinary conditions. The 100 per cent. H_2SO_4, for example, loses SO_3 until it reaches a concentration of 98·3 per cent. (constant-boiling mixture), and this solution then takes up water until its vapour pressure equals that of the water in the surrounding atmosphere. The behaviour of carbonic acid is representative of that of a number of unstable acids. Water dissolves only about its own volume of carbon dioxide at 15° C. and the solubility decreases rapidly with rise in temperature. Only a very small concentration of CO_3^{2-} (or HCO_3^-) ions can therefore be obtained in the acid solution, the reaction $CO_3^{2-} + H^+ \rightarrow CO_2 + OH^-$ or $HCO_3^- \rightarrow CO_2 + OH^-$ taking place very readily. The alkali carbonates, however, are quite soluble in water, that of potassium dissolving in its own weight of water. There is some hydrolysis in such solutions ($CO_3^{2-} + H^+ \rightarrow HCO_3^-$), leaving excess OH^- ions, but no CO_2 is evolved unless the solution is boiled. Thus a considerable concentration of CO_3^{2-} or HCO_3^- ions is possible in alkaline solution, so that the instability of solutions of carbonic acid does not mean that these ions are unstable in aqueous solution. The thiosulphate ion, $S_2O_3^{2-}$, appears to be even more unstable in the absence of metal ions and it is doubtful if thiosulphuric acid exists at all in aqueous solution.

The Types of Inorganic Acids

For descriptive purposes we may divide the inorganic acids into the following groups:

(*a*) *Simple acids*—H_mX_n—e.g. the hydrogen halides, H_2S and the higher acids H_2S_n, HN_3. Hydrogen peroxide, H_2O_2, may be included here or in (*b*).

Little need be said here about the structures of the hydrogen halides, which are all gases under ordinary conditions. The natures of the bonds in the molecules of these acids have already been mentioned in Chapter II. In aqueous solution ionization of the molecules takes place. Hydrofluoric acid differs from HCl, HBr, and HI in forming complex molecules in the vapour and also in forming acid salts containing the F—H—F ions (see the section on the 'Hydrogen Bond', p. 249). The structure of the H_2S molecule has been determined by electron diffraction experiments on the gas (p. 78), but in the case of other acids in this group only the structures of the complex ions X_n are known, and these will be described under the chemistry of the appropriate elements.

(*b*) *Oxy-acids*—$H_mA_nO_p$. These may be further subdivided as follows:

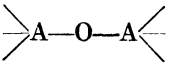
Simple oxy-acids ($n = 1$)

(i) Certain hydroxy-acids $A(OH)_m$, such as H_3BO_3, H_6TeO_6, may be differentiated from the rest on structural grounds. Their structures are discussed under hydroxides in Chapter X, p. 355.

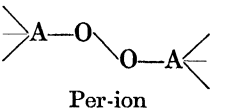
(ii) Other simple oxy-acids, H_2SO_4, HNO_3, etc.

Per- and pyro-acids ($n = 2$)

These important types arise from the condensation of simple AO_x groups, the two A atoms being joined through one or two O atoms respectively, viz.



Pyro-ion



Per-ion

The pyro-ions are not necessarily symmetrical—see the structure of the metabisulphite ion, $S_2O_5^{2-}$, p. 305. The per-acids may be regarded as derivatives of hydrogen peroxide. Nothing is known of the structures of per-acids; for the structures of per-acid ions see under the element A and for the sulphur per-acids, p. 303.

Poly-acids

These are differentiated from the per- and pyro-acids since in these poly-acids the A atoms are directly joined. Among the simpler examples are the polythionic acids, $H_2S_3O_6$, to $H_2S_6O_6$, and $H_2N_2O_2$.

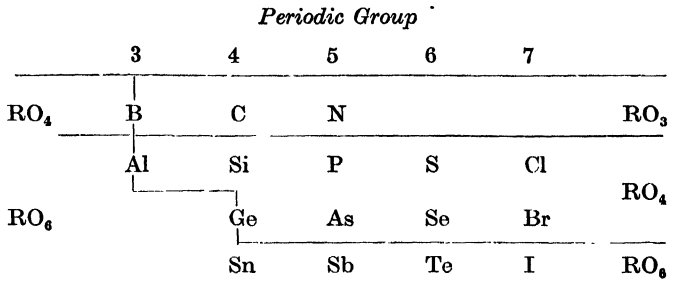
The so-called iso- and hetero-poly acids formed by a number of metals such as Mo and W should really be described as pyro-acids since their complex structures involve the linking of metal atoms through single O atoms. These acids and their salts and in general all acids containing metallic, as opposed to non-metallic, atoms are described in Chapter X.

The Stability of the Simple Oxy-acids

It is worth while to review briefly some of the evidence for the existence of the simple oxy-acids of the commoner elements. The more general question as to whether compounds $A_mB_nO_p$ should be regarded as salts of acids or as mixed oxides will be deferred until later, when the structures of such solids will be treated systematically. It is relevant to inquire first whether the acids can be isolated. Some preliminary information on this point is given in Table 15 for the oxy-acids of the non-metals, but we must now include in our discussion some of the more electropositive elements of the later Periodic Groups. It will be convenient to discuss first the typical and B sub-group elements and then some of the elements of the later A sub-groups.

(*a*) *Oxy-acids of the Typical and B Sub-group Elements*

The elements are set out below divided into groups according to their oxygen coordination numbers. These are the maximum numbers of O atoms which are found surrounding the particular atom in its compounds.



The element may, of course, exhibit a smaller coordination number, as in the case of SO_3^-, ClO_3^-, and BrO_3^-. A line passing through the symbol of an element indicates that it is found with two coordination numbers. We shall consider the columns in turn. Boric, carbonic, and nitric acids have already been mentioned (Table 15). The acidic properties of $Al(OH)_3$ and other 'amphoteric' hydroxides are supposed to be shown by (1) the solubility of the hydroxides in alkali, and (2) the existence of aluminates and similar salts. The solubility of many hydroxides in, for example, NaOH solution ($Al(OH)_3$, $Pb(OH)_2$, $Sn(OH)_2$, $In(OH)_3$, $Cu(OH)_2$, $Zn(OH)_2$, etc.) is probably due to colloid formation—there is no evidence for the existence of ions containing the metal. The 'aluminates' exist only in the solid state. In solution they hydrolyse, though the hydrolysis is not always apparent as the hydroxide remains in colloidal suspension instead of being immediately precipitated. The behaviour of the 'acids' of Si, Ge, Sn, Ti, Zr, and Th is similar. The action of strong acids on a solution of Na_2SiO_3 followed by dialysis yields a clear colloidal solution, and 'silicic acid' can be obtained in all forms from a clear colloidal solution to gels which can be cut with a knife ($30H_2O:SiO_2$) or gels which can be finely powdered ($6H_2O:SiO_2$). The hydrated forms of Sb_2O_3 and Sb_2O_5 are also colloidal. There is no good evidence for the existence of acids H_3SbO_3 or H_3SbO_4 in solution and little for H_3AsO_3, though As_2O_3 certainly dissolves in water to give a very weakly acid solution. Arsenites, M_3AsO_3, are almost completely, if not completely, hydrolysed in solution. Arsenic acid, however, can be obtained crystalline by evaporating at 100° C. the solution resulting from the oxidation of As or As_2O_3 by nitric acid. The crystals have the composition H_3AsO_4. Crystallization at a lower temperature gives a crystalline hydrate, $2H_3AsO_4.H_2O$, isomorphous with the corresponding hydrate of orthophosphoric acid. The acids of phosphorus are remarkable in that they are mostly well-crystallized compounds at ordinary temperatures. Their structures are discussed in Chapter XII.

When we come to the 6th and 7th Periodic Groups we find an interesting difference between the properties of the heaviest members, Te and I, and the pairs of lighter elements S and Se, and Cl and Br, respectively. This difference is due to the fact that the oxygen coordination number of these lighter elements is restricted to 4, whereas that of Te and I may rise to 6. The acids HXO_3 are included in Table 15. Of S, Se, and Te only Se forms

a stable well-defined crystalline acid of the type H_2XO_3, and H_2TeO_3 is probably non-existent. The acids sulphuric, selenic, and telluric have a number of points of interest. As already remarked, pure H_2SO_4 is not stable and loses SO_3. It will also dissolve excess SO_3. If we plot the physical properties of mixtures of H_2O and SO_3 for all proportions from pure H_2O to pure SO_3 we find in some cases no discontinuity at the points corresponding to H_2SO_4 and $H_2S_2O_7$. The freezing-point curve shows maxima at these points (and also at points corresponding to a number of hydrates, e.g. $H_2SO_4.4H_2O$, $H_2SO_4.H_2O$), but the specific heat curve is continuous from H_2O to SO_3. The acid H_2SeO_4 forms a crystalline solid, but evaporation at room temperature of a solution of telluric acid yields H_6TeO_6. This is not a hydrate but a hydroxy-acid, $Te(OH)_6$, though the fact that it does not lose water at 100° C. is no proof that it is not a hydrate. Other metastable forms of telluric acid may be obtained by evaporating a hot solution of the ordinary form—these are syrups or glassy solids insoluble in water. Such forms may be colloidal, but certain of the properties of the syrupy 'allotelluric acid' suggest that it may consist of one or more complex isopolyacids. For example, it precipitates albumen and with alkalis gives sparingly soluble salts in contrast to the soluble salts of H_6TeO_6. The formulae of the soluble salts $M_2H_4TeO_6$ may be compared with those of the periodates, and salts of more complex types have also been described.

Some remarks on the oxy-acids of the halogens will be found in Chapter VIII. We need only note here that iodic acid differs greatly from $HClO_3$ and $HBrO_3$ in stability, that the structures of iodates are not similar to those of chlorates and bromates, and that periodic acid and its salts have formulae quite different from perchloric acid and perchlorates. The latter contain simple ClO_4^- ions and are often isomorphous with sulphates, whereas many periodates are derived from H_5IO_6, which is the normal form in which the acid is obtained. (HIO_4 is apparently formed by heating H_5IO_6 at 100° C. *in vacuo*—compare H_2TeO_4 which is said to be obtained by heating H_6TeO_6.) Some simple periodates exist, e.g. $NaIO_4$, but the addition of a solution of this salt to one of silver nitrate produces Ag_5IO_6, and other types of periodates include K_3IO_5, $K_4I_2O_9$, and $(NH_4)_2H_3IO_6$. (See also pp. 260 and 273.)

(*b*) *Oxy-Acids of the A Sub-group Elements*

The metals under consideration are set out in the accompanying table, which also indicates their oxygen coordination numbers. By fusing the highest oxide of the metal with alkali or a lower oxide with alkali and a suitable oxidizing agent, solid compounds of the type $A_xB_yO_z$ are obtained. Solutions of some of these compounds may also be prepared by chemical or electrolytic oxidation of a suitable compound of the metal in alkaline solution. Many such compounds have characteristic colours, e.g. green manganates (Na_2MnO_4) and purple permanganates ($NaMnO_4$), and dissolve in water to form coloured solutions. Iron gives red 'ferrates'

and for this reason is included in the table. Although many of these compounds are quite stable in neutral or alkaline solution, the result of

	V	VI	VII	VIII
RO_4	V	Cr	Mn	(Fe[3])
	Nb	Mo		
RO_6	Ta	W		
		U		

acidifying such solutions is very different in different cases. The hypothetical acids H_2MnO_4 and H_2FeO_4 cannot be obtained even in solution, for acidification of solutions of manganates and ferrates leads only to precipitation of an oxide of the transition metal. The acids H_2CrO_4 and $HMnO_4$, on the other hand, can be obtained in concentrated solution, but the anhydrous acids have not been isolated. Chromium has some tendency to form more complex ions—the dichromates $M_2Cr_2O_7$ are well known and more complex salts have been described—and resembles in this respect the later members of the group, Mo, W, and U, the oxygen chemistry of which is described later. The elements V, Nb, Ta, Mo, W, and U are notable for forming many complex salts by fusion of their higher oxides with alkalis. In the case of V, Nb, and Ta, acidification of the solutions of these salts gives precipitates of the so-called vanadic, niobic, and tantalic acids, but these are probably colloidal oxides and on heating are converted into the pentoxides (compare Sb).

Of the last three elements we are considering here, Mo, W, and U, many more complex compounds are known of the first two than of U. The so-called uranic acids are probably hydrogels of UO_3 into which they are converted on complete dehydration. This oxide is of some interest since it dissolves in excess of nitric acid to form uranyl nitrate which crystallizes as the hydrate, $UO_2(NO_3)_2.6H_2O$. A number of other salts containing the uranyl ion UO_2^{2+} are known. The action of acids on molybdates and tungstates usually produces colloidal molybdic and tungstic acids. A crystalline compound $MoO_3.2H_2O$ separates slowly from a solution of ammonium molybdate acidified with excess nitric acid, and there is a well-crystallized metatungstic acid; see p. 339.

To summarize: no simple oxy-acid H_mMO_n of any of these A sub-group elements is known in the pure state. In the case of the last six elements the so-called acids are colloidal hydrated oxides, using the term hydrated merely as meaning associated with water. The metatungstic acid, as will be seen later, is probably a complex pyro-acid.

HYDRIDES

The compounds of the elements with hydrogen fall naturally into three classes:

(1) The molecular hydrides.
(2) The salt-like hydrides of the alkali and alkaline-earth metals.
(3) The interstitial hydrides of the transition metals.

(1) The Molecular Hydrides

In this group we have to consider the hydrides of the following elements of the first two short periods and of the B sub-groups:

	Periodic Group			
3	4	5	6	7
B	C	N	O	F
	Si	P	S	Cl
	Ge	As	Se	Br
	Sn	Sb	Te	I
	Pb	Bi	Po	

The formulae of the simplest molecular hydrides, apart from those of B, which are exceptional, are of the type AH_{8-N}, where N is the number of the Periodic Family. The formation of $8-N$ bonds leads to a group of eight electrons which, for the elements of the first short row, completes the second quantum group. The structures of the simplest halides of these elements are determined in the same way—CCl_4, NCl_3, OCl_2, FCl. In addition to forming the neutral molecule NH_3 nitrogen can attain the same electronic structure in the ammonium ion, NH_4^+, and in the amino ion, NH_2^-. The latter ion is not stable in aqueous solution (because $NH_2^- + H^+ \rightarrow NH_3$) but it exists in the crystalline amides of the alkali metals (e.g. $NaNH_2$), and many reactions between salts in liquid ammonia suggest the existence of the ion in such solutions, e.g.

$$KNH_2 + AgNO_3 \rightarrow AgNH_2\downarrow + KNO_3.$$

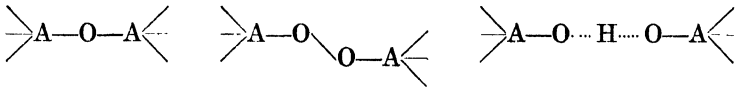
The isoelectronic hydroxyl ion, OH^-, is discussed in detail in Chapter X.

As we pass down a given periodic column we find that the hydrides of the elements are of the same type as that of the lightest element; compare NH_3, PH_3, AsH_3, SbH_3, BiH_3, and OH_2, SH_2, SeH_2, and TeH_2. This is in marked contrast to the halides in the 5th and 6th groups, P and the heavier elements forming pentahalides and in the 6th group the heavier elements form tetra- and hexa-halides in addition to halides AX_3 and AX_2 respectively. In general the stability of the hydrides decreases steadily down a particular column of the Periodic Table.

These hydrides exist in the same molecular form in all states of aggregation. When solid methane is transformed successively into liquid and gas there is no rearrangement of the C and H atoms relative to one another, the CH_4 molecule retaining its structure throughout. There are only the weak van der Waals forces acting between the molecules, and this is true of all molecular hydrides except those of the most electronegative elements of the first short period, N, O, and F. The physical properties of NH_3, OH_2, and FH are abnormal in many respects, more particularly in the liquid and solid states, owing to the formation of intermolecular hydrogen bonds. We shall return to this aspect of these hydrides in a later section. In many cases the solids form close-packed structures in which the mole-

cules are rotating (compare the cubic close-packed structures of CH_4, PH_3, AsH_3, SH_2, SeH_2, etc.)

We have so far mentioned only the mononuclear compounds AH_n. There are also some more complex hydrides. In a previous section we saw that structures of considerable complexity can be built from groups AO_n since the A atoms can be linked up in a number of ways, e.g.



in addition to the simplest way, —A—A—A—, etc. These complications do not arise in the hydrides since H is restricted to a covalency of one. The higher hydrides therefore correspond only to the true poly-acids and involve direct linking of the A atoms as in

$$H_3C—CH_3, \quad H_2N—NH_2, \quad \text{and} \quad HO—OH.$$

More complex hydrides are formed by S to a limited extent—they are necessarily of the type H—S_n—H (see the H_2S_n acids, p. 305)—and also by B, Si, and Ge. By far the most extensive series of hydrides, however, is that of carbon. We restrict ourselves here to a few general remarks about molecular hydrides. Any detailed discussion of particular hydrides will be found under the chemistry of the element concerned.

Group III. The hydrides of boron are of exceptional interest because they do not contain sufficient valency electrons for the formation of electron-pair bonds between the atoms. They are discussed in Chapter XV.

Group IV. The simplest hydrides, of the type AH_4, form tetrahedral molecules. Carbon forms extensive series of hydrides (hydrocarbons) which fall naturally into two main groups:

(*a*) Aliphatic: chains (simple or branched) or rings of C atoms joined by single or multiple bonds.

(*b*) Aromatic: based on rings of six C atoms which acquire exceptional stability and chemical properties owing to resonance between forms involving different arrangements of single and double bonds.

A limited number of hydrides of Si and Ge are known of type (*a*), e.g. Si_nH_{2n+2} up to Si_6H_{14} and Ge_2H_6 and Ge_3H_8. In the case of Sn only SnH_4 is known. The existence of PbH_4 was detected by the 'radioactive indicator' method using the isotope ThB.

Group V. The 'typical' hydride in this group is of the type AH_3. All the elements N, P, As, Sb, and Bi form such a hydride. Ammonia has weak basic properties and forms a large number of salts, but the basic properties of the other hydrides fall off very rapidly with increasing metallic character of the elements. The existence of BiH_3 was first proved by the radioactive indicator method. An alloy of Mg and ThC, a radioactive isotope of Bi, was dissolved in dilute acid. From the hydrogen produced a gas was condensed which had the radioactive characteristics of ThC.

The evidence for the existence of more complex hydrides of P is unsatisfactory. Nitrogen, however, forms hydrazine, N_2H_4, which possesses basic properties, and hydrazoic acid, HN_3. The latter forms salts with a number of metals and also with NH_3 and N_2H_4—$(NH_4)N_3$ and $(N_2H_5)N_3$ respectively.

Group VI. The following hydrides are known: H_2O, H_2S, H_2Se, and H_2Te. The properties of H_2O are abnormal and are described elsewhere (p. 362). The S, Se, and Te compounds are oxidized with varying ease, e.g. all are oxidized to the element by ferric salts, and H_2Se and H_2Te also by mercuric salts. In contrast to these compounds water has no reducing properties. The only other hydride of oxygen is H_2O_2, but S forms a number of other hydrides. In the higher hydrides of carbon and silicon the atoms of these elements form chains or rings, utilizing in the process two bonds per atom and leaving two bonds which are satisfied by the hydrogen atoms. Sulphur, however, forms only two bonds in its hydrides, so that the hydrogen atoms are attached only to the terminal atoms:

compare	$CH_3—CH_2—CH_2—CH_2—CH_3$	general formula	C_nH_{2n+2}
with	$HS—S—S—S—SH$	—	S_nH_2.

The compounds H_2S_2, H_2S_3, and H_2S_5 are all rather unstable yellow liquids, extremely sensitive to alkali, which converts them into H_2S and S. They are, however, stable in benzene and other organic solvents, and cryoscopic measurements on such solutions confirm their formulae (see also p. 305).

Group VII. The only hydrides are of the type HX (see p. 271).

(2) The Salt-like Hydrides

These are ionized compounds containing H^- ions. They include the following:

LiH	CaH_2	LaH_3
NaH	SrH_2	
KH	BaH_2	
RbH		
CsH		

They are readily formed by heating the metal in hydrogen, and they form colourless crystals. The alkali metal compounds have the rock-salt structure, and they resemble in many ways the alkali halides. Electrolysis of molten LiH at a temperature a little below the melting-point (680° C.) with steel electrodes yields Li at the cathode, hydrogen being evolved at the anode. These ionic hydrides have much higher melting-points than the molecular hydrides discussed in the previous section. They all react readily with water evolving hydrogen, a solution of the metallic hydroxide remaining. There is an interesting reaction between heated solid NaH and CO_2 leading to the formate: $H^- + CO_2 \rightarrow (COOH)^-$.

(3) Interstitial Hydrides

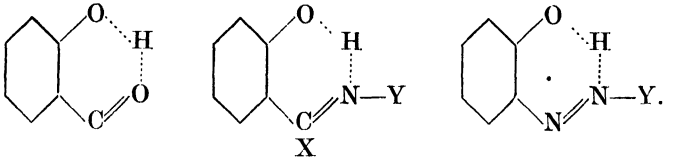
The compounds of hydrogen with the transition metals differ greatly from those with the alkali and alkaline earth metals. The former metals absorb hydrogen without any fundamental change in the metal lattice and there is often considerable variation in composition. Structural investigations of these compounds show that the small H atoms enter the holes between the metal atoms, and these interstitial compounds are accordingly most conveniently discussed in connexion with metal and alloy structures. Certain borides, carbides, and nitrides have similar structures; see Chapter XVII.

THE HYDROGEN BOND

When we were discussing the classification of crystals in Chapter IV we saw that in some crystals the atoms are arranged in an infinite 3-dimensional array with forces of the same type acting between all the atoms. In other crystals atoms are bound together to form layers or chains, and in a fourth class were crystals in which finite groups of atoms could be distinguished. The binding forces within these various types of complex are different from those between one complex and another, as shown by the interatomic distances and generally by the chemical and physical properties of the crystals. In the classification allowance was made for three types of binding between the layers, chains, or finite complexes (molecules or complex ions): electrostatic, van der Waals, and H bonds. (In distinguishing the H bond from electrostatic bonds we do not imply that it is not electrostatic in nature—the distinction is made because the presence of H bonds in crystals leads to structures quite different from those in which simple ionic bonds operate.) We have already met examples of crystals in which complex groups of atoms are held together by electrostatic or van der Waals forces. Many of the hydrides, e.g. CH_4, form typical molecular crystals in which the cohesion of the molecules is due to van der Waals forces, and we have seen that a characteristic of such crystals is that the molecule retains its identity in the liquid and vapour states. A considerable number of organic crystals, however, particularly those of hydroxy compounds, behave rather differently from the simple molecular crystals. For example, the latter are soft and have rather low melting- and boiling-points, but the sugars, on the other hand, are much harder and more brittle and melt at higher temperatures. Again, many carboxylic acids show a pronounced tendency to form double molecules—this is so with formic and acetic acids even at their boiling-points.

The study of pure liquids and of solubility relationships has shown that we must distinguish between associated and non-associated solvents. The molecules of associated solvents can form H bonds with one another and naturally also with suitable solute molecules. If we dissolve acetic acid,

for example, in an associated solvent H bonds are formed between the acetic acid molecules and the solvent molecules, but if it is dissolved in a non-associated solvent like benzene, then H bond formation is possible only between pairs of solute molecules since benzene cannot form H bonds. It will be seen that the formation of H bonds will have a considerable effect on the solubilities of such compounds in different solvents, and also that abnormal values of molecular weights will be deduced from the freezing- or boiling-points of solutions in associated solvents. The study of such abnormalities of molecules containing —OH and —COOH groups led to another interesting discovery. Some compounds of this type show very little or no association, and in these cases it is found that H bond formation is possible within the molecule itself. This had been suggested by Pfeifer and co-workers in 1913 to account for the chemical inactivity of adjacent —OH and —CO groups in certain aromatic molecules. Examples of such intramolecular H bonds are:



With a few important exceptions the examples of H bond formation were for many years confined to organic compounds. Apart from such liquids as H_2O and HCN, the gas HF, and many liquid acids, the majority of inorganic compounds containing H bonds are solids at ordinary temperatures. Early work on $NaHF_2$ (1922) suggested that the F atoms in the crystals were joined together in pairs by H bonds, and the tetrahedral arrangement of the oxygen atoms in ice could be accounted for on the assumption that a H atom lay between each pair of O atoms (1923). However, detailed knowledge of the stereochemistry of the H bond could not be obtained until it became possible to work out the comparatively complex structures of these inorganic crystals.

Evidence for the Formation of Hydrogen Bonds

We shall say that a H bond is formed between two atoms whenever there is evidence that a H atom is situated between them and is in some way involved in the interaction between the atoms. The experimental evidence for the formation of such bonds may be summarized under four heads:

(1) Determination of the relative positions of atoms by X-ray or electron diffraction. It must be emphasized that the H atom cannot be directly located by X-ray diffraction studies on account of its small scattering power. The most we can do is to say that the H atoms presumably lie between certain pairs of atoms, these pairs of atoms being generally chosen in the following way. It is found that the distances

between various pairs of atoms are abnormally short and that we can account for the number and distribution of these short distances by placing H atoms between such pairs of atoms. The shortening of the distances between certain atoms of different molecules in the crystals of many organic hydroxy compounds as compared with the intermolecular distances for ordinary van der Waals interaction is so striking that there is no doubt about the positions of the H bonds, and the close approach of certain atoms in acid salts is equally good evidence of H bond formation.

(2) Less precise evidence comes from studies of solubility, freezing-point, and boiling-point determinations, and in general from all the phenomena involving association. Experiments of these kinds indicate merely that there is unusually strong interaction between molecules of solute or between molecules of solute and solvent. From the chemical nature of the molecules it is clear that the association is connected with the presence of hydrogen, usually as part of OH, COOH, NH_2, etc., groups. If the H is replaced by other groups (e.g. alkyl groups) there is no association, showing that the H plays an essential part when it is attached to an electronegative atom like O or N in the molecule. Such specific interaction between particular atoms of the solute and solvent molecules explains, for example, the much greater solubility of aniline and phenol in water than in nitrobenzene in spite of the much larger dipole moment of the latter ($4{\cdot}19\times10^{-18}$ e.s.u.) as compared with water ($1{\cdot}85\times10^{-18}$ e.s.u.).

(3) Spectroscopic evidence depends on the fact that a group like the OH group absorbs light of particular frequencies and that its characteristic absorption is largely independent of the nature of the rest of the molecule unless the H atom takes part in H bond formation. Then the absorption due to the OH group is altered, and instead of strong absorption of light of one frequency there is only weak absorption over a comparatively wide range of frequencies. The formation of intramolecular H bonds in many organic molecules has been shown by studying their infra-red absorption spectra in carbon tetrachloride solution.

(4) Comparison of H compounds with their deuterium analogues. Discussion of this point is best deferred until later.

The Nature and Stability of the Hydrogen Bond

The fact that H could in some way act as a bond between two atoms was first interpreted as implying that the H atom formed two covalent bonds, as e.g. $(F{:}H{:}F)^-$, and Sidgwick represented the bond as a co-ordinate link. The association of water and alcohols was represented

$$\begin{matrix} R & R & R \\ OH \leftarrow & OH \leftarrow & OH. \end{matrix}$$

Hydrogen has, however, only one stable orbital (1*s*) and is limited to a covalency of one. Furthermore, H bonds are formed only between the most electronegative atoms. Fluorine forms very strong H bonds, O rather

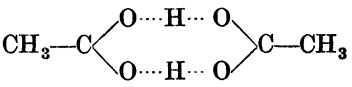
weaker, and N still weaker H bonds. H bonds between N and O are also known. The lengths of some H bonds are shown in Table 16 below.

TABLE 16

	Length (A.)	*Compound*
F—H—F	2·26	KHF_2
	2·32	NH_4HF_2
O—H—O	2·54±0·05	KH_2PO_4
	2·60±0·05	$(NH_4)_2H_3IO_6$
	2·63	$CO(NH_2)_2.H_2O_2$
	2·71±0·05	H_3BO_3
	2·71	$AlHO_2$
	2·70	FeO(OH)
	2·70	$C(CH_2OH)_4$
	2·76	Ice
N—H—F	2·76±0·06	NH_4HF_2
	2·68	NH_4F
	2·62	$N_2H_6F_2$
N—H—O	2·85	Diketopiperazine ($C_4N_2O_2H_6$)
	2·86 (mean)	Acetamide (CH_3CONH_2)
	2·94, 3·04	$CO(NH_2)_2.H_2O_2$
N—H—N	3·38	NH_3
	2·94, 2·99	NH_4N_3
	2·94—3·15	Dicyandiamide ($(NH_2)_2CNCN$)
	3·00—3·10	Melamine ($C_3N_6H_6$)

There is little evidence of H bond formation between atoms other than these, and this would suggest that the bond is largely ionic. This raises the question: Is the bond symmetrical, i.e. are the two links of the system O—H—O, for example, of equal strength? Since we cannot establish the position of the H atom by X-ray methods (and the most precise knowledge of the H bond comes from studies on solids) we must use other arguments to attempt to settle this point. Now there is considerable variation in the distances observed in different structures between atoms joined by H bonds. For example, in a number of acid salts, O—H—O bond lengths from about 2·55 A. to 2·60 A. are found, but in hydroxy compounds the distance is usually 2·70 A. or more. In the former cases there is a ratio of one H atom to every two O atoms (counting only those atoms involved in the O—H—O bridges), as in $(NH_4)_2H_3IO_6$ and KH_2PO_4, whereas in the hydroxy compounds there is one H for every O atom, as in H_3BO_3. It appears probable that there is a physical difference between the long and short bonds, the former being unsymmetrical and the short bonds symmetrical. For example, the distance O—H—O is 2·76 A. in ice, and in the H_2O molecule in the gas O—H is 0·96 A. For a symmetrical bond O—H would be 1·38 A., but the small difference between the vibrational frequencies associated with the stretching of the O—H bonds for ice and water vapour is not enough to indicate a change in the O—H distance

from 0·96 to 1·38 A. From studies of the infra-red absorption spectra of CH_3COOH and CH_3COOD the distance O—H in the dimer



is given as 1·075 A. Pauling's calculation of the residual entropy of ice assumes an unsymmetrical O—H—O bridge and gives a result agreeing well with the experimental value. Bernal and Megaw distinguish the long bonds as 'hydroxyl' bonds since they are formed by OH groups. We shall adopt their treatment of hydroxides in Chapter X, since it brings some sort of order into the description of the structures of these compounds. The structure of water and of hydrates will be considered in more detail in Chapter XI.

In the shorter O—H—O bridges there may be resonance between two or more configurations, e.g. O H ····· O and O ····· H ··· O, in which the H is about 1 A. from an O atom. An alternative view is that a hydrogen bond X ·· H· ·Y is due to the electrostatic attraction between the dipole X^-—H^+ and the unshared pair(s) of electrons on the Y atom. Some evidence on this point comes from comparisons of hydrogen and deuterium compounds. Theoretical considerations indicate that whereas for normal binding between molecules the substitution of D for H on the outside of the molecule should lead to shorter intermolecular distances, in cases where intermolecular resonance (i.e. H bond formation) occurs there should be an increase in such distances. Preliminary measurements of the spacings of H and D compounds suggest that this expansion does occur in the case of short H bonds. Since, however, the net effect observed is always the resultant of the expansion of the H bridges and the contraction of other intermolecular separations, the results are not easily interpreted.

The energy of the H bond is small, of the order of 5–10 k.cals./mole, which we may compare with the energy of the bond in the HF molecule, 148 k.cals./mole, or with that of a normal O—H bond, 109 k.cals./mole. The average energy of the bonds F—H—F would therefore be about 77 k.cals./mole. The small value of the energy of the H bond may appear surprising in view of its large effect on the physical properties of compounds and the fact that such bonds evidently persist in water right up to the boiling-point and in the vapour of HF. However, at ordinary temperatures the average kinetic energy of a molecule is only of the order of 0·5 k.cals./mole, so that it would appear that collisions between molecules would rarely break H bonds. This consideration may not be important in associated liquids like water, the properties of which suggest a constant making and breaking of the bonds as the molecules move over one another.

The Hydrogen Bond and Physical Properties

Since the H bond is largely responsible for the interaction between the molecules of associated liquids, we shall expect to find considerable differences between the physical properties of such liquids and the corre-

sponding properties of non-associated liquids consisting of similar kinds of molecules. We should distinguish between properties of the discrete molecules, which are modified because certain atoms of the molecule interact with atoms of adjacent molecules (e.g. the infra-red absorption,

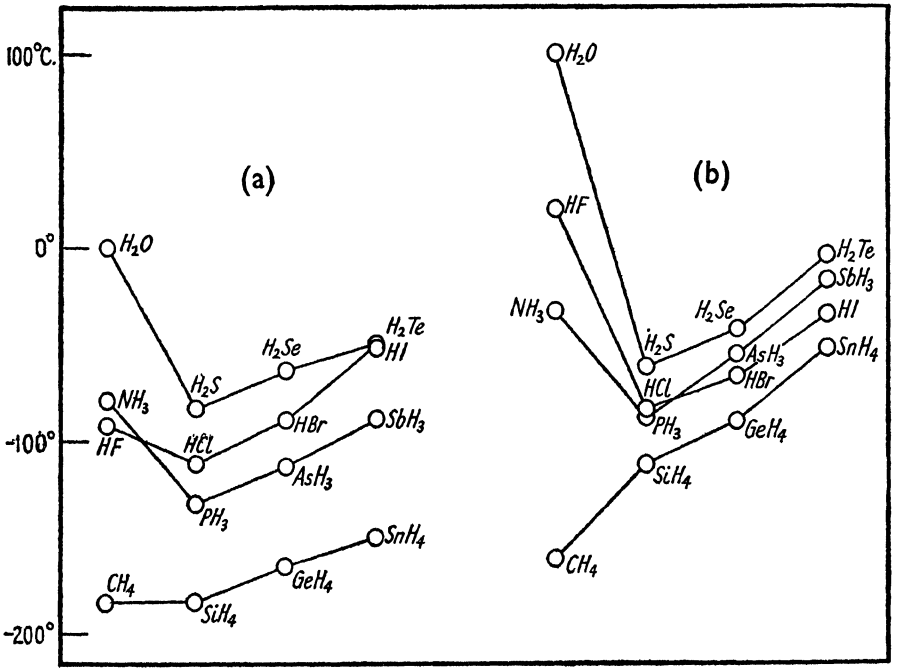


FIG. 57. Melting-points (*a*) and boiling-points (*b*) of series of isoelectronic hydrides.

which is approximately the arithmetic sum of the absorptions of the separate molecules), and properties such as melting- and boiling-points which are properties of the liquid in bulk and have no meaning when applied to single molecules.

We have already said that H bonds are formed only between the most electronegative elements, chiefly N, O, and F. The hydrides NH_3, OH_2, and HF are therefore the simplest compounds in which these bonds are formed. If we compare such properties as melting-point, boiling-point, and heat of evaporation of a series of hydrides such as H_2Te, H_2Se, H_2S, and H_2O, we find that these properties form a fairly regular sequence until we reach the last member of the series, H_2O. The hydrides of Groups V B and VII B show similar behaviours, NH_3 and HF being 'abnormal' and HCl slightly so. The hydrides of Group IV B, including CH_4, form, on the other hand, a regular sequence; see Fig. 57. Instead of a melting-point in the region of −100° C., as might be expected from extrapolation of the melting-points of H_2Te, H_2Se, and H_2S, we find a melting-point of 0° C. It is not possible to account for the relative magnitudes of these effects in the case of NH_3, H_2O, and HF until a satisfactory theoretical

treatment of the H bond is evolved, and we must content ourselves with saying that they are associated with the formation of intermolecular H bonds. From the fact that the boiling-points and heats of vaporization show the same type of abnormality as the melting-points we deduce that many H bonds must exist in liquid NH_3, H_2O, and HF up to their boiling-points. In the case of HF they persist in the vapour state.

The abnormally high dielectric constants of NH_3 and H_2O are also attributable to the polymerization due to H bond formation, but there is no direct connexion between the value of the dielectric constant and the *degree* of association. For example, the dielectric constant of liquid HCN is greater than that of H_2O, but this does not necessarily mean a higher degree of polymerization in the former liquid. The dielectric constant depends on the dipole moments of the polymers, and these in turn are dependent on the mutual orientation of the H bonds in the polymers. The polymerization of HF leads to non-linear or ring polymers with small or zero dipole moments, whereas the polymers of HCN are linear chains with high dipole moments.

The Hydrogen Bond in Crystals

We may expect H bonds to play an important part in determining the crystal structures of compounds containing F, O, and N in addition to H. These include acid fluorides, oxy-acids and their acid salts, hydroxides, hydrates (of oxy-salts and fluorides), ammonium compounds, and the hydrides of F, O, and N. It will be seen that a survey of the structures of these groups of compounds would cover a considerable part of inorganic chemistry. Such a survey is unfortunately not possible at present as in most of these groups only isolated examples have been studied. We shall give examples from all the groups except the simple inorganic oxy-acids, which have so far not been studied in the crystalline state, and hydroxides and hydrates, which will be described in Chapters X and XI. Before dealing with some of these compounds grouped according to this chemical classification it is worth while to examine briefly the geometry of structures in which H bonds operate.

The atoms between which the H bonds are formed may be single isolated atoms or they may be part of finite, infinite linear, or infinite layer complexes, as shown in the chart on p. 142. There is little choice in the way in which very long straight chains or layers of atoms can pack in crystals. The former will have their axes parallel and the latter their planes parallel. H bond formation between atoms of adjacent chains or layers merely affects the details of the packing (as is shown by the structures of certain hydroxides, p. 354) and properties which depend on the cohesion of the chains or layers. The geometrical possibilities for finite complexes are, on the other hand, far more complicated and a brief discussion may help the chemist, who is so used to dealing with finite groups of atoms, to a better understanding of the solid state. The structures of quite simple compounds sometimes appear at first sight unnecessarily

complicated and it is essential to discover at least some of the reasons for this complexity. When finite complexes are joined by H bonds the larger aggregates so formed may be (1) finite, (2) infinite chains, (3) infinite layers, or (4) infinite 3-dimensional networks. In each class the simplest

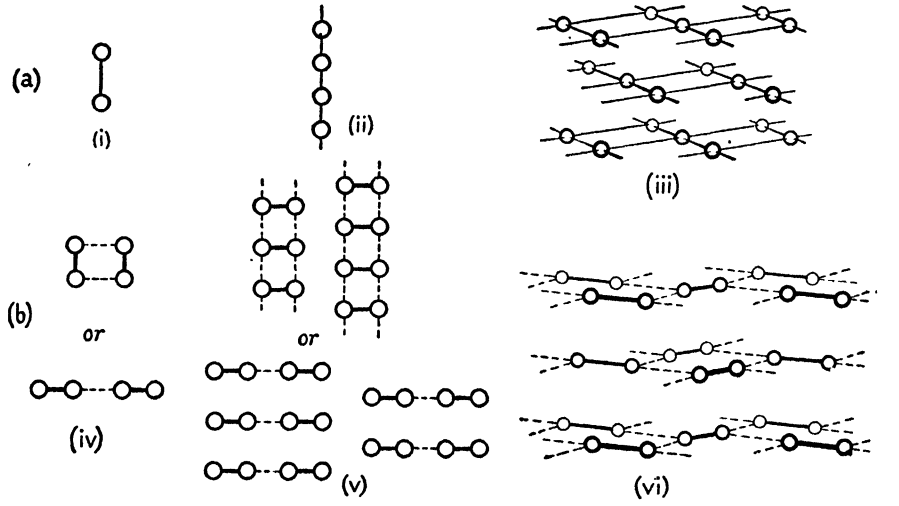


FIG. 58. In (*a*) are shown examples of (i) finite, (ii) infinite 1-dimensional, and (iii) infinite 2-dimensional complexes (portions of three layers in perspective). Hydrogen bonds (broken lines) then link the finite complexes (i) into (iv) finite, (v) infinite 1-dimensional, or (vi) infinite 2-dimensional aggregates.

cases arise when the finite complexes are all identical as in the finite $[F—H—F]^-$ ion or the structure of ice, which is a 3-dimensional network of O atoms linked by H bonds. The original unit may, however, be a group of atoms so that we have already increased the number of possible structure types in the way shown in Fig. 58. More complex cases may arise according to the shape of the molecule and the positions in the molecule of the atoms forming the H bonds. Thus long-chain carboxylic acids associate in pairs and the pairs then stack in layers with their axes parallel. Residual forces hold together the pairs of molecules in the layers and are also responsible for the cohesion of the layers. Still further elaboration of this scheme is introduced when we remove the restriction that all the original finite complexes are identical. Class (4) would now present the following possibilities:

Three-dimensional networks of finite complexes joined by H bonds

Nature of finite complex	*Number of kinds of complex*		
	1	2	3
Atom	Ice	NH_4F	
Molecule	Resorcinol		
Complex ion	H_6TeO_6	$[M(H_2O)_6]SO_4$	$[M(H_2O)_6]SO_4.H_2O$
	$H_2PO_4^-$, H_3IO_6		e.g. $NiSO_4.7H_2O$

Since a geometrical classification of this kind obviously does not group together chemically related compounds, we shall not adhere to it in the following pages, but we shall summarize here examples of the four classes for purposes of reference. The aggregates of finite complexes are:

(1) Finite groups: HF_2^- ion, carboxylic acids—associated together in pairs in the solid, liquid, and, at least in the case of formic acid, in the vapour state.

(2) Infinite chains: HCO_3^- ion (in $NaHCO_3$), β-oxalic acid, diketopiperazine.

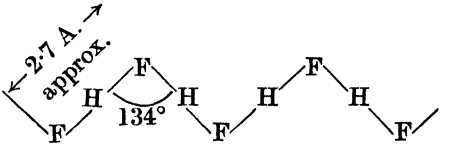
(3) Infinite layers: α-oxalic acid, boric acid, pentaerythritol, hydrazinium difluoride.

(4) Infinite 3-dimensional network: see table on p. 256.

We shall now give examples of the structures of the following groups of compounds: hydrides, fluorides, acid salts, and organic molecules containing OH or NH groups. The latter do not strictly come within the scope of this book, but any account of the H bond would be very incomplete if we confined ourselves to purely inorganic examples.

Hydrides

As already mentioned, the hydrides of N, O, and F alone show evidence of strong H bonds. The simplest structures would arise if every atom were joined to all its nearest neighbours by H bonds and if every H atom were utilized in forming such bonds. Then in the solid hydride AH_n every A atom would be surrounded by $2n$ neighbours, i.e. the coordination number of A by A atoms would be 6 for NH_3, 4 for H_2O, and 2 for HF. An early study of solid NH_3 assigns to it a structure which may be regarded as a distorted form of cubic close-packing. Instead of twelve equidistant nearest neighbours each N atom has six neighbours at 3·38 A. and six more at a much greater distance, 3·95 A. This 6+6 coordination may indicate that a N atom forms six weak H bonds. In ice the structure is of the simple type expected, every O atom being tetrahedrally coordinated by four others. The structure of solid HF cannot be a 3-dimensional network since although F can, and does, form four tetrahedral H bonds (see the structure of NH_4F, p. 259), the fact that there is only one H atom for each F atom limits the coordination number of both H and F to two and the only possibilities are infinite chains or closed rings. Accordingly it is found that solid HF (studied at 91° K.) consists of infinite zigzag chains



An electron diffraction study of the vapour indicates the existence of polymers (probably up to $(HF)_5$) with F—H—F = 2·55 A. and the F bond angle 140°±5°. This difference between H_2O and HF is quite analogous

from the geometrical point of view to the difference between the structures of diamond (in which C forms four tetrahedral bonds) and those of S, Se, and Te (see p. 539).

Fluorides

The presence of chain polymers $(HF)_n$ in the vapour of hydrogen fluoride has been shown by electron diffraction studies, which do not confirm the earlier suggestion of $(HF)_6$ ring molecules. The HF_2^- ion has

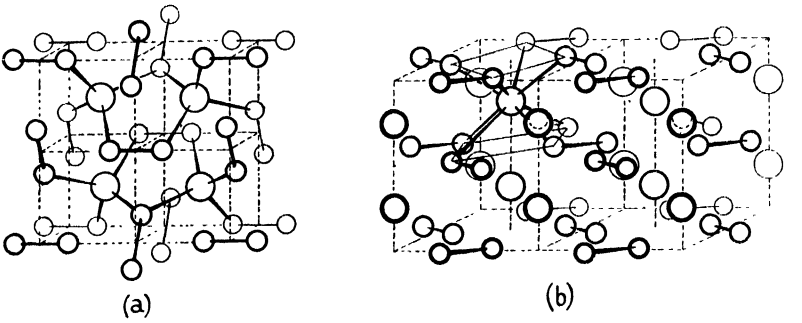


FIG. 59. The crystal structures of (*a*) NH_4HF_2 and (*b*) KHF_2. Hydrogen atoms are not shown. The small circles represent fluorine atoms, joined in pairs by F—H—F bonds.

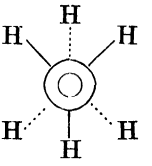
already been mentioned as the simplest complex containing a H bond. The F—H—F distances 2·26 A. and 2·36 A. in KHF_2 and NH_4HF_2 respectively may be compared with the distance H—F, 0·92 A., in the single molecule HF. Assuming the extreme ionic picture $F^-H^+F^-$ the separation of the F atoms has been calculated as 2·32 A., in good agreement with the experimental value.

For the so-called acid fluorides of the alkali metals we should expect less symmetrical structures than for the simple fluorides owing to the non-spherical shape of the $[HF_2]^-$ ion. Whereas KF has the simple rock-salt structure, that of KHF_2 is more complex—it is illustrated in Fig. 59 (*b*). Potassium and ammonium salts are often isomorphous, the K and NH_4 ions being very similar in size, but a comparison of the structures of KHF_2 and $NH_4[HF_2]$ shows an interesting difference. In KHF_2 each K ion is surrounded by eight equidistant F neighbours. The general structure of $NH_4[HF_2]$ is similar to that of KHF_2 except that the NH_4 ion has only four nearest neighbours, at $2{\cdot}76 \pm 0{\cdot}06$ A., and four more at 3·07 A.; see Fig. 59 (*a*) and (*b*). The separation of the coordination group of eight into two sets of four is due to the formation of four N—H—F bonds—compare the structure of solid NH_3, above.

Just as $NH_4[HF_2]$ differs in this way from the corresponding Na and K salts, so NH_4F crystallizes with a structure different from those of the other alkali and ammonium halides. Ammonium chloride, bromide, and iodide have the CsCl structure at temperatures below 184·3°, 137·8°, and −17·6° C. respectively, and the NaCl structure at temperatures above

these transition points, but NH_4F crystallizes with the wurtzite structure in which each N atom forms N—H—F bonds of length 2·66 A. with its four neighbours which are arranged tetrahedrally around it. There is also evidence of the formation of N—H—F bonds in crystals of complex ammonium fluorides.

Hydrazinium difluoride, $N_2H_6F_2$, provides a very interesting example of a crystal in which the structural units are linked by hydrogen bonds (in this case N—H—F bonds) into layers. In NH_4F, with the wurtzite structure, every NH_4^+ ion forms four tetrahedral N—H—F bonds to surrounding F^- ions (which also form four tetrahedral N—H—F bonds), resulting in an infinite 3-dimensional complex. In $N_2H_6F_2$ the structural units are $N_2H_6^{2+}$ and F^- ions. In the $N_2H_6^{2+}$ ion the N—N distance is 1·42 A. and the N—N—H bond angles 110°. Viewed along its axis the ion has the configuration



The hydrazinium ions form six octahedral N—H—F bonds and every F^- ion forms three such bonds (to different $N_2H_6^{2+}$ ions) arranged pyramidally.

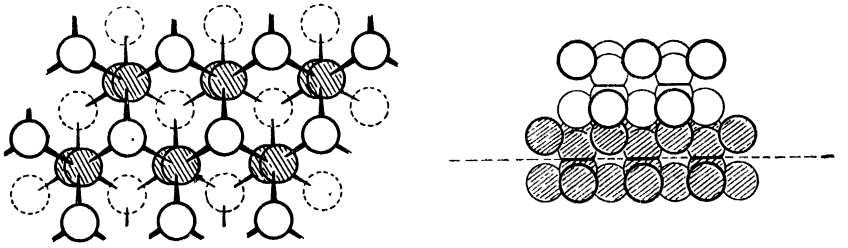
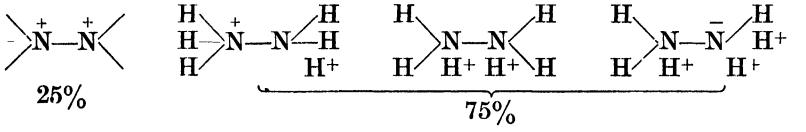


FIG. 60. The structure of hydrazinium fluoride, $N_2H_6F_2$ (after Kronberg and Harker): (*a*) Plan of one layer. The lower N atoms of each $N_2H_6^{2+}$ ion (shaded) are slightly displaced. The open circles, full and dotted lines, represent F^- ions respectively above and below the plane of the paper. All lines are N—H—F bonds. (*b*) Elevation, showing the packing of the layers. The broken line is the trace of the plane of the paper in (*a*).

This is exactly the same bond arrangement as in the $CdCl_2$ or CdI_2 structures. In $N_2H_6F_2$ the halogen atoms are not close-packed as in $CdCl_2$ or CdI_2. The layers have a very open structure (F—F = 4·43 A.) owing to the long N—H—F bonds (2·62 A., compare 2·68 A. in NH_4F and 2·76 A. in NH_4HF_2). The mode of packing of the layers on one another is geometrically similar to that in the dihalides with layer structures. In these a halogen atom of one layer rests on three of the layer below, so that throughout the structure the halogen atoms are close-packed. In

$N_2H_6F_2$ the layers are superposed in a similar way, but owing to the large separation of F atoms in a layer, a F atom of one layer (shown as a large open circle in Fig. 60) drops between the three F atoms of the next layer and comes in contact with a N atom (and/or its three associated H atoms). This inter-layer F—N distance is 2·80 A., and the F—F, 3·38 A. It is estimated that the charge on the $N_2H_6^{2+}$ ion is about equally distributed over all the atoms, giving a charge of $+\frac{1}{4}$ on each. The inter-layer bonds are therefore weak ionic bonds between F^- ions and N (and/or H) atoms of adjacent layers. The weakness of these bonds accounts for the very good cleavage parallel to the layers.

A point of interest concerning the $N_2H_6^{2+}$ ion is that the ordinary formulation with single covalent bonds gives both the N atoms formal charges of +1. There is probably resonance with ionic structures to the extents indicated below:



Just as NH_4F and NH_4Cl have different structures owing to the fact that F but not Cl can form hydrogen bonds, so the corresponding chloride, $N_2H_6Cl_2$, has a different type of structure from $N_2H_6F_2$. It forms a somewhat deformed fluorite structure—compare the relation between CaC_2 and FeS_2 and the rock-salt structure.

Acid Salts

The term acid salt is applied to compounds in which part of the hydrogen in the empirical formula of the acid is replaced by metal atoms or other positive ions. Typical examples are the bicarbonates $MHCO_3$ and bisulphates $MHSO_4$ of the alkali metals. Until the crystal structures of these compounds had been studied little was known of their constitution, and even now the detailed structure is known in only a few cases. We shall confine our attention to three examples: $NaHCO_3$, KH_2PO_4, and $(NH_4)_2H_3IO_6$. The outstanding feature of these three structures is that they contain infinite complex ions, HCO_3^-, $H_2PO_4^-$, and $H_3IO_6^{2-}$, consisting of the simple ions CO_3^{2-}, PO_4^{3-}, and IO_6^{5-} joined together by H bonds. In the bicarbonate ion the planar CO_3 groups are linked to form infinite chains of composition HCO_3^-, and these chains are held together laterally by the Na^+ ions between them. A geometrical analogy may be drawn between this structure and that of diopside, (Ca, Mg)SiO_3, as shown in Fig. 61, in which tetrahedral SiO_4 units join by sharing O atoms to form infinite chain ions SiO_3^{2-}. No example of an infinite 2-dimensional ion in an acid salt is known.

The other two examples we have chosen illustrate the linking of tetrahedral PO_4 and octahedral IO_6 groups respectively into 3-dimensional networks by means of H bonds. A plan (Fig. 62) of part of the structure

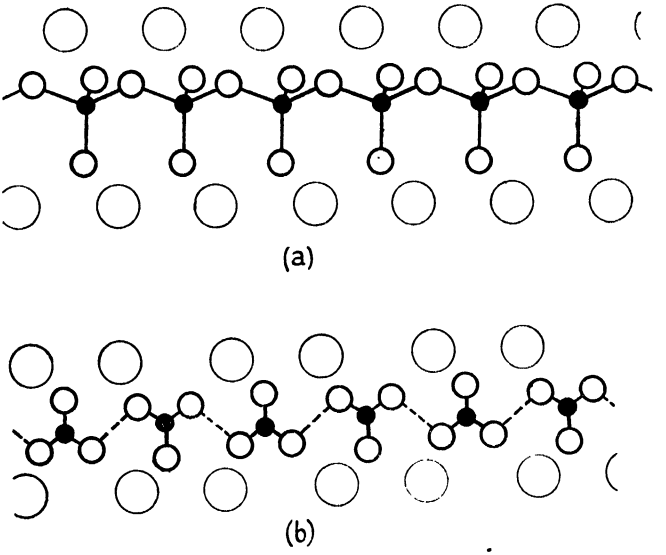


FIG. 61. Projections of portions of the structures of (*a*) diopside, (Ca, Mg)SiO_3, and (*b*) $NaHCO_3$. Large circles represent metal atoms and small open circles oxygen atoms. Broken lines indicate hydrogen bonds.

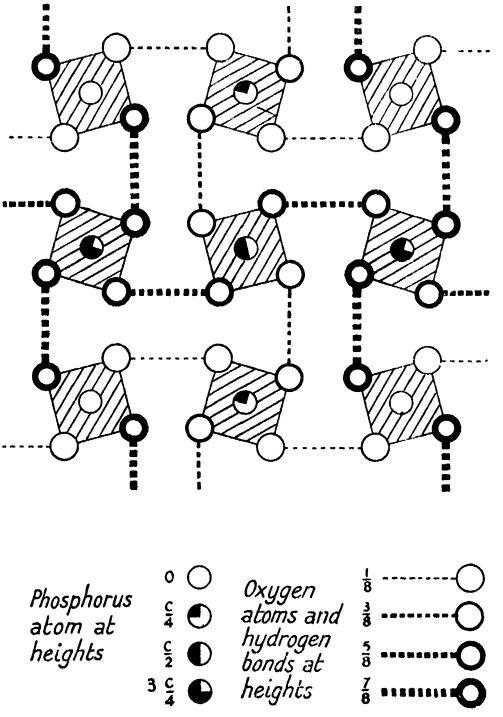


FIG. 62. Part of the structure of KH_2PO_4 projected on to the basal plane. The broken lines represent hydrogen bonds which link the PO_4 tetrahedra into an infinite 3-dimensional network.

of KH_2PO_4 will suffice to indicate the general structural scheme. It will be noticed that in KH_2PO_4 and also in $(NH_4)_2H_3IO_6$ the ratio of O:H in the anion is 2:1. There are therefore sufficient H atoms to provide a H bond between every O atom and one other in a neighbouring PO_4^{3-} or IO_6^{5-} ion. In this way are built up 3-dimensional frameworks in the interstices of which the positive ions are accommodated. In our discussion of the probable structures of the simple oxy-acids it was suggested that the structure of H_2SO_4 must consist of SO_4 ions linked by H bonds, and reference was made to the structures of these acid salts. This structural analogy between acids and acid salts is clearly seen if we set them out as below, aligning them horizontally according to the H:O ratio which we assume will be the determining factor.

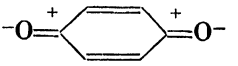
H:O *ratio*				
2:3	H_2CO_3			
1:3	$M(HCO_3)$	HNO_3		
3:4	H_3PO_4			
2:4	$M(H_2PO_4)$	H_2SO_4		
1:4	$M_2(HPO_4)$	$M(HSO_4)$	$HClO_4$	

It is tempting to speculate on the structures of these acids and of the other types of acid salts, but a systematic X-ray study of the crystalline compounds would be more valuable and is long overdue.

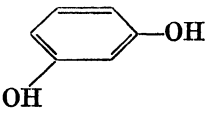
Organic Compounds

We have seen that the molecules of certain organic compounds, more particularly those containing hydroxyl groups, show, in solution or in the vapour state, the property of associating together in pairs or in larger groups. Also, the crystals of such compounds have properties not usually associated with molecular crystals, hardness or brittleness. These abnormalities were attributed to the formation of intermolecular H bonds. We shall now describe briefly some of the features of the structures of these crystals. In the solid aromatic hydrocarbons such as naphthalene and the methyl benzenes the packing of the molecules is determined by their shape, i.e. the only condition determining the structure is that the molecules pack in such a way that the distances between the nearest carbon atoms of different molecules are never less than certain minimum values. These depend on the numbers of hydrogen atoms attached to the carbon atoms and generally lie between 3·5 and 4·2 A., smaller values, 3·5–3·8 A., being found between C atoms of unsubstituted aromatic nuclei, i.e. CH—CH, and larger values, 3·9–4·2 A., between CH_3 groups in, e.g., tetra- and hexa-methyl benzene. An important feature of such structures is that the intermolecular forces are not directed bonds and compared with the bonds within the molecules they are very weak, so that the crystals are soft and have low densities. If now we look at the structure of benzoquinone, the molecule of which contains strong dipole groups,

we find that the smallest intermolecular distance is that between the C+ and the O⁻ of neighbouring molecules, but that this distance (3·4 A.) is nearly as large as the minimum separation of aromatic nuclei. When, however, we come to a compound like resorcinol we find a quite different type of structure. The hydroxyl groups of neighbouring molecules are all adjacent and the O—O distance has fallen to 2·7 A. while all the other

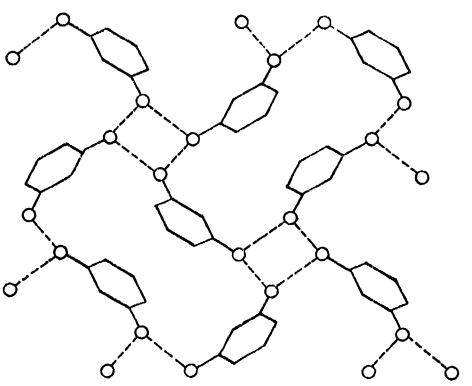


Benzoquinone

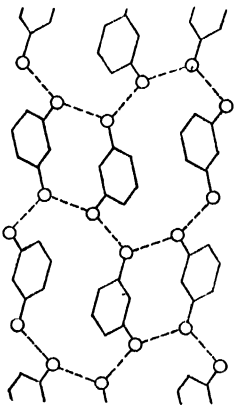


Resorcinol

intermolecular distances are greater than 3·5 A. There is also another striking fact. In spite of the close contact of the hydroxyl groups, the density of resorcinol is less than that of benzoquinone, showing that the



α resorcinol



β resorcinol

FIG. 63. Arrangement of hydrogen bonds in the two crystalline forms of resorcinol (projections along the *c* axes).

interaction between the OH groups leads to an open structure suggesting directed bonds between these groups. The atoms between which H bonds operate act, so far as packing is concerned, like localized charges, leading to specific structure types rather than the most economical packing characteristic of non-polar molecules like hydrocarbons. The analogy in 3-dimensional complexes is found in the open structure of diamond, resulting from the tetrahedrally directed C bonds, compared with the close-packed structures of inert gases and many metals. In ice, H bonds also lead to a structure of low coordination (4) compared with that in solid H_2S (12), and on melting, the structure to some extent collapses, forming a liquid of higher density. Resorcinol is of particular interest since on heating to about 74° C. it is transformed into another modification (β) in which the molecules are packed more closely, the transformation

involving a rearrangement of the H bonds. Plans of portions of the structures of the two forms of resorcinol are shown in Fig. 63. It must be remembered that the actual structures are 3-dimensional networks of molecules and not in any sense layer structures, as might be supposed from such projections.

We now come to two examples of crystals in which the molecules are held together in layers by H bonds (Class 3). Pentaerythritol, $C(CH_2OH)_4$, crystallizes with a tetragonal structure in which the molecules are arranged in layers parallel to the basal plane (001). A portion of one layer is shown in Fig. 64. The disposition of the H bonds should be compared with that

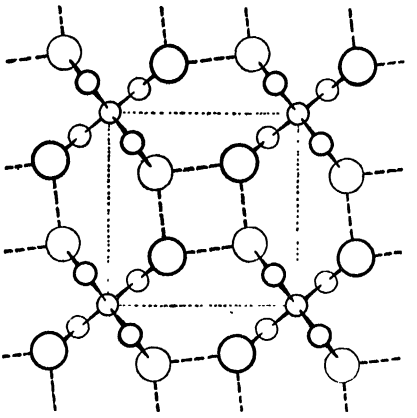
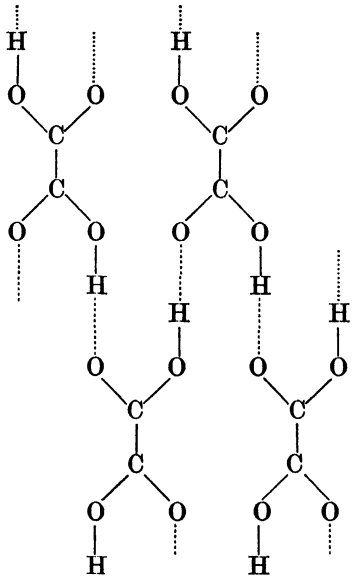


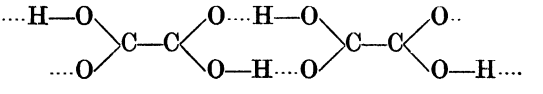
FIG. 64. Portion of a layer of the structure of pentaerythritol, $C(CH_2OH)_4$. Small circles represent C and large circles O atoms. The molecules are held together in layers by hydrogen bonds (broken lines).

in α-resorcinol. Each hydroxyl group is attached to two others by bonds of length 2·69 A. which hold the molecules together in the layers. The forces between adjacent layers are only the weak van der Waals bonds. The difference in the relative strengths of these two types of intermolecular binding is reflected in the physical properties of the crystals. Gentle treatment separates the layers, the crystals cleaving very readily parallel to the basal plane, without breaking the H bonds. These are broken when the crystal dissolves (or vaporizes), but the far stronger bonds within the molecule are still unaffected. The two forms of oxalic acid also illustrate this point. In crystals of the α form the molecules are arranged in layers and in the β form in chains. The former accordingly cleave into flakes and the latter into laths, the process of cleaving again leaving intact the layers and chains within which the molecules are linked by H bonds—compare the cleavage of silicate minerals such as micas with that of amphiboles and pyroxenes.

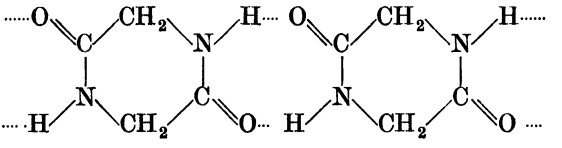
Diketopiperazine is a second example of a crystal in which the molecules form infinite chains, in this case by the formation of N—H—O bonds.



α-oxalic acid

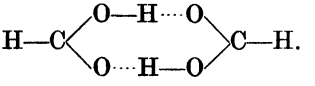


β-oxalic acid

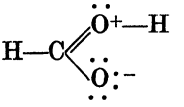


diketopiperazine

We have now given examples of structures in which molecules are linked by H bonds into infinite 3-, 2-, and 1-dimensional complexes. The remaining possibility is the formation of finite groups of molecules in this way (Class 1). Many carboxylic acids are remarkable for the stability of their dimeric forms. Those of formic, acetic, and trifluoroacetic acid have been studied in the vapour phase by the electron diffraction method and shown to consist of pairs of molecules held together by O—H—O bonds, e.g.



These compounds are discussed in more detail on p. 434. The great strength of the H bonds in such dimers has been attributed to resonance involving the structure



in which two effects act in the same sense, viz. the increased positive charge on the hydroxylic O increasing the tendency to share the proton

with another O atom and the negative charge on the ketonic O attracting the proton of the OH group of the second molecule.

This brief account of the H bond should serve to indicate the importance of this type of binding in both inorganic and organic chemistry. In the latter it seems likely that it plays a very large part in determining the constitution and properties of many of the biologically important compounds such as proteins, sugars, starches, chlorophyll, haemoglobin, and many others.

CHAPTER VIII

THE HALOGENS

THE halogens, fluorine, chlorine, bromine, and iodine, have the following electronic structures:

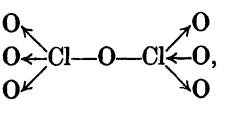
	K	*L*		*M*			*N*				*O*		
		2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*
F	2	2	5										
Cl	2	2	6	2	5								
Br	2	2	6	2	6	10	2	5					
I	2	2	6	2	6	10	2	6	10	—	2	5	

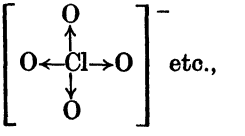
All can therefore acquire the structure of an inert gas (Ne, A, Kr, Xe respectively) by (*a*) forming an ion X^-—the letter X will be used to denote a halogen—(*b*) forming one covalent bond. The third simplest possibility is to form a positive ion of the type $[R—X—R]^+$, but only iodine behaves in this way. These elements can therefore form only diatomic molecules, X—X, in the vapour, liquid, or solid state, in which each atom forms one covalent bond. In the crystals of chlorine, bromine, and iodine these diatomic molecules are held together by van der Waals bonds. The distance between halogen atoms of different molecules is much greater than the intramolecular X—X distance:

	X—X	
	intra-molecular	*inter-molecular*
Cl . .	1·99 A.	2·79 A.
Br . .	2·27	3·30
I . .	2·70	3·54

and the weakness of the inter- as opposed to the intra-molecular binding is also seen by comparing the heat of evaporation of, e.g., solid chlorine (4·5 k.cals./mole) with the heat of dissociation of the molecule (58·5 k.cals./mole).

An ion X_3^- is formed by iodine and also by bromine, and the halogens combine with one another to form compounds XX'_n, where n is 1, 3, 5, or 7, which are described later. In other compounds the halogens form various numbers of bonds, and on the assumption that such bonds are covalent and that, at least in the case of the lighter atoms, the completion of their octets confers stability, Sidgwick assigned to these compounds a set of self-consistent formulae using the coordinate link:





etc.,

but we shall find that this type of formulation is an over-simplification. All the halogens have seven electrons in the outermost shell, but, as we have already seen, this electronic structure alone does not determine the properties of the elements and does not account for the very considerable differences in behaviour between the elements of such a Periodic Group. The atoms of the first row in the Periodic Table have their valency electrons in the *L* shell, in which there are only four orbitals available for bond formation. The 'octet rule', which limits these elements to four covalencies, is therefore rigidly obeyed. In the atoms of the second row the 3*s* and 3*p* orbitals are much more stable than the 3*d*, so that while the 3*d* electrons may in some cases be used (e.g. in PCl_5) in general bond formation ceases when a stable octet is reached. With the heavier elements a larger valency group becomes commoner, though the four tetrahedral sp^3 bonds may still be formed.

When we examine the maximum covalencies of the halogens we find a more complex state of affairs. Fluorine apparently never forms more than one covalent bond; compounds in which there is an apparent covalency of two are mentioned below. Chlorine, on the other hand, forms up to four bonds, but bromine exceeds three only in BrF_5, and iodine is 6-covalent in some oxy-compounds and forms a heptafluoride IF_7. We shall shortly indicate in more detail the differences between the halogens by considering some of their more important compounds, but we may say here that fluorine is sharply differentiated from the other halogens and that iodine is different in many ways from chlorine and bromine. We give below the ionic and covalent radii and the electronegativities of the halogens:

	Ionic radius	*Tetrahedral covalent radius*	*Electro-negativity*
F . .	1·36 A.	0·64 A.	4·0
Cl . .	1·81	0·99	3·0
Br . .	1·95	1·11	2·8
I . .	2·16	1·28	2·5

The characteristics of the extreme elements, fluorine and iodine, may be summarized as follows. Fluorine has a great tendency to ionization—its electronegativity indicates that the bonds it forms with most other elements will have considerable ionic character. The structures of most crystalline metallic fluorides are different from those of the other halides of the same metal. A number of difluorides and dioxides have the same structure, whereas the corresponding dichlorides, dibromides, and diiodides have in many cases structures similar to those of disulphides, diselenides, and ditellurides. The extreme electronegativity of fluorine enables it to form hydrogen bonds, unlike the other halogens, resulting in the abnormal properties of HF as compared with the other acids HX (compare the difference between H_2O and H_2S, etc.), the formation of the ion $[F—H—F]^-$, and the hydration of the fluorides of certain metals the other halides of which are anhydrous. Other characteristics of fluorine

include its inability to form more than one covalent bond, its very small affinity for oxygen, and the fact that many non-metals exhibit in their fluorides a valency higher than in their other halides (compare the fluorides AsF_5, SF_6, SeF_6, IF_7, and OsF_8 with the highest chlorides $AsCl_3$, SCl_4, $SeCl_4$, ICl_3, and $OsCl_4$).

We have mentioned certain properties peculiar to iodine—its 6-covalency in oxy-salts and the formation of IF_7 and of the ions I_3^- and $[R—I—R]^+$. In the latter the groups R are usually aromatic organic radicals (for short Ar). The halides [Ar—I—Ar]X are not very stable, but the hydroxides are strong bases, proving the dissociation to $[Ar—I—Ar]^+$ ions. These iodonium compounds are analogous to the ammonium and sulphonium compounds:

$$[NR_4]X, \quad [SR_3]X, \quad \text{and} \quad [IR_2]X.$$

Other compounds peculiar to iodine include the iodoso- and iodoxy-compounds of general formulae Ar—I=O and $Ar—IO_2$ and the so-called salts of iodine, IPO_4, $I(CH_2Cl.COO)_3$, and others of unknown constitution.

We will follow these general remarks on the halogens with brief accounts of the interhalogen compounds, poly-halides, the hydrogen halides, and the oxy-compounds of the halogens.

THE INTERHALOGEN COMPOUNDS

All these compounds are of the general form XX'_n, where $n = 1, 3, 5$, or 7, and none containing more than two different halogens is known. All except IF_7, which is prepared from IF_5, are made by direct combination of the appropriate elements. Of the six possible compounds, XX′ all have been prepared except IF. Of the higher compounds ClF_3, BrF_3 and ICl_3, BrF_5 and IF_5, and finally IF_7 are known. It will be noticed that fluorine forms no compounds (as far as is known) of the kind FX_3, FX_5, or FX_7, that iodine alone shows a covalency of seven, and that of the penta- and hepta-compounds only fluorides have so far been prepared. In these latter the bonds have appreciable ionic character, since bromine and iodine are considerably less electronegative than fluorine. Little is known so far of the stereochemistry of these compounds and we shall return to this in connexion with the polyhalide ions.

THE POLYHALIDES

These are salts containing singly charged ions of the types X_n^-, XX'_n^-, or $XX'X''^-$. They are prepared by crystallizing solutions containing a simple halide and excess halogen or halogen halide. Thus KI and I_2 yield KI_3 while $CsICl_4$ may be prepared either by the action of chlorine on the iodide or from ICl_3 and the chloride. No trifluorides or trichlorides are known, but tribromides of NH_4, Rb, and Cs and triiodides of K, Rb, Cs, and NH_4 have been prepared. The stability of these salts is connected with the size of the positive ion, and apart from the alkali metals few, if any, other metals form triiodides. Substituted ammonium ions and

complexes such as $Co(NH_3)_6^{2+}$ and $Ni(NH_3)_6^{2+}$ also form triiodides. More complex ions X_n^- may exist in crystals such as CsI_5, but the structures of such salts are not yet known. The simplest mixed polyhalides include $CsICl_2$, $CsIBr_2$, $CsBrCl_2$, CsIBrCl, and a comparatively large group of salts $M[ICl_4]$. On heating, these salts lose halogen or halogen halide, forming the simple halide containing the more electronegative halogen, e.g.

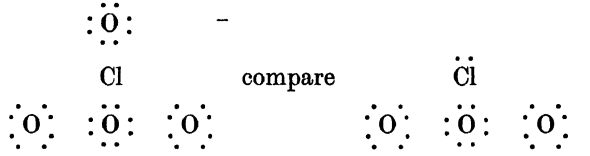
$$MICl_4 \rightarrow MCl + ICl_3, \textit{ not } MI + 2Cl_2.$$

The stability of the dichloriodides depends, as in the case of the triiodides, on the size of the positive ion, and of the alkali metal salts only $CsICl_2$ is stable at ordinary temperatures. The ions I_3^-, ICl_2^-, and $IBrCl^-$ are all linear, with the iodine atom in the centre of the latter two, as shown by X-ray studies of the salts NH_4I_3, $CsICl_2$ and $N(CH_3)_4ICl_2$, and NH_4IBrCl respectively.

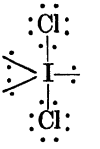
The stereochemistry of these ions and of the closely related halogen halides is of some interest. It will be noticed that the ions all contain even numbers of electrons—molecules or ions containing odd numbers of electrons, and therefore some unpaired electrons, being rare apart from those containing atoms of transition metals—so that the formulae of the two sets of compounds are, in the case of iodine:

ICl	and	$[ICl_2]^-$
ICl_3		$[ICl_4]^-$
IF_5		
IF_7		

In these molecules and ions there are various numbers of pairs of unshared electrons. In the case of light elements such as chlorine such pairs of unshared electrons affect the arrangement of the other bonds formed by the atom in a simple way. For example, the pyramidal configuration of the ClO_3^- ion is simply related to the tetrahedral arrangement of bonds in ClO_4^-, for we may regard the unshared pair of electrons in ClO_3^- as occupying one of the tetrahedral bond positions:

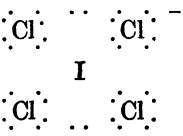


The linear configuration of [Cl—I—Cl]$^-$ and similar ions is to be expected if we assume that five bonds from iodine (having no pairs of



unshared electrons) would be disposed towards the apices of a trigonal bipyramid, which is the configuration of various AX_5 molecules. The

three pairs of unshared electrons in $[ICl_2]^-$ would then be disposed in the equatorial plane as shown. The ion ICl_4^- has been shown to be planar by X-ray analysis of the structure of $KICl_4$. In this ion the iodine atom has two pairs of unshared electrons which may be regarded as completing the octahedron. The planar bonds in such an ion are therefore quite



different in type from those of transition elements like Pt and Pd which form four coplanar dsp^2 bonds (see p. 86).

Less is known of the stereochemistry of the interhalogen compounds. Applying to ICl_3 and IF_5 the same arguments as we have used above, we should expect the former to be planar, since the I atom has two pairs of unshared electrons, and IF_5 to have the form of a square pyramid, one pair of unshared electrons occupying the sixth octahedral position. Iodine trichloride forms a yellow solid but the vapour is almost entirely dissociated into ICl and Cl_2, and the structure of the molecule is as yet unknown. The trigonal bipyramidal configuration assigned to IF_5 as the result of electron diffraction studies may not be correct, as the interatomic distances are not very satisfactory. The stereochemistry of iodine in oxy-compounds is dealt with later.

THE HYDROGEN HALIDES

We have already referred to the abnormal properties of HF. The physical properties of the acids HF, HCl, HBr, and HI do not form regular sequences, HF differing from the others in much the same way as H_2O from H_2S, H_2Te, and H_2Se. We may quote the heats of formation of the gaseous compounds, the melting-points and boiling-points, and the properties of the constant-boiling mixtures they form with water:

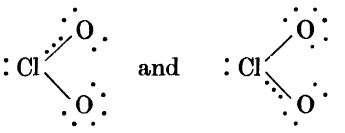
	HF	HCl	HBr	HI
Heat of formation . .	+38·5	22·0	8·6	−6·4 k.cals.
Melting-point . . .	−83	−111	−87	−52° C.
Boiling-point . . .	+19·4	−83	−68	−36° C.
Constant boiling mixtures:				
Boiling-point . .	120	110	126	127° C. (760 mm.)
Density . . .	1·14	1·10	1·49	1·70 g./c.c.
Approx. ratio of molecules H_2O : HX . .	2	8	5	2·5

The polymerization of HF and the formation of 'acid fluorides' containing the HF_2^- ion are not paralleled by the other halogens. These abnormal properties of HF have been related in the last chapter to the extreme electronegativity of F, leading to the formation of hydrogen bonds. Whereas the bond H—F is probably about 50–60 per cent. ionic, the

bonds in HCl, HBr, and HI are respectively 17, 11, and 5 per cent. ionic, as deduced from the dipole moments of the molecules HX.

OXY-COMPOUNDS

In the formation of oxides, oxy-acids, and their salts the halogens behave very differently. Certain oxides of chlorine and iodine have been known for many years—the unstable Cl_2O, ClO_2, and Cl_2O_7, I_2O_5 which possesses considerable stability, and a rather doubtful solid with empirical formula IO_2. Oxides of fluorine and bromine were unknown until recent years, when various oxides of these elements have been described (F_2O_2, FO, F_2O, Br_2O, and BrO_2) and also further oxides of chlorine, ClO_3 and ClO_4. Apart from Cl_2O (see p. 78) and ClO_2 little is known of the structures of these compounds. Chlorine dioxide is of interest as an example of a molecule containing an odd number of electrons. It has been studied in the vapour states by electron diffraction. The Cl—O distance of 1·53 A. as compared with 1·68 A., the sum of the single-bond radii, is interpreted as indicating the existence of 2- and 3-electron bonds, resonance occurring between the two possible configurations:



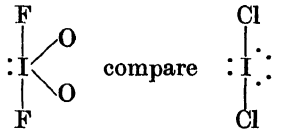
the interbond angle is given as $137 \pm 15°$. The structure of the chlorite ion, ClO_2^-, has been studied in NH_4ClO_2 and the ion is stated to be non-linear with Cl—O approximately 1·6 A. A more detailed study of this and other chlorites is desirable.

In the stability of their oxy-acids there are again great differences between the halogens. The definite existence of oxy-acids of fluorine has not yet been satisfactorily proved. Chlorine, bromine, and iodine all form acids HXO, the stability (in all cases small) decreasing from the chlorine to the iodine compound. The ions XO^- are oxidizing agents, reverting to X^- ions, but they also decompose at higher temperatures to XO_3^- and X^- ions. These halogens also form acids HXO_2, but except for one chlorite little is known of the structures of the salts of these unstable HXO and HXO_2 acids. The acids $HClO_3$, $HBrO_3$, and HIO_3 do not form a regular sequence, as is seen from the heats of formation: 24, 12·5, and 56 k.cals. respectively. Here the iodine acid is more stable than the chlorine and bromine compounds, for aqueous solutions of $HClO_3$ and $HBrO_3$ can be concentrated (*in vacuo*) only up to about 50 per cent. molar, whereas an aqueous solution of HIO_3 may be concentrated until it crystallizes. The ions ClO_3^- and BrO_3^- have been studied in a number of crystalline salts. They form low pyramids with Cl or Br at the apex, the unshared pair of electrons occupying the fourth tetrahedral bond position. Iodates are structurally quite different from chlorates and bromates, owing to the

preference of iodine for 6-coordination by oxygen. In all the alkali metal iodates the iodine is apparently 6-coordinated, though the structures are different for the various salts owing to the increasing size of the alkali ions. Thus in $LiIO_3$ the metal ions are surrounded by six oxygens, in $NaIO_3$ (with a deformed perovskite structure) by ten, and in the K, Rb, and Cs iodates, which have the normal perovskite structure, by twelve oxygen atoms. With this structure for KIO_3 should be contrasted the CsCl type of packing of K^+ and BrO_3^- ions in $KBrO_3$. In α-HIO_3 there are discrete IO_3 groups bound together by hydrogen bonds. The three nearest neighbours of an I atom are oxygen atoms at a distance of 1·80 A., the O—I—O bond angles being $98° \pm 3°$. Three more oxygen atoms (at 2·45, 2·70, and 2·95 A.) complete a very distorted octahedron around the I atom.

In the formation of per-acids the halogens show still less resemblance to one another. Perchloric acid and the perchlorates contain the tetrahedral ClO_4^- ion (for further remarks on this and similar ions see p. 318). Bromine forms no per-acid, and periodic acid is H_5IO_6. Whereas perchlorates are all of the type $M_x(ClO_4)_y$, periodates appear to be derived from both the simple acid HIO_4 and from H_5IO_6. Thus the salt $NaIO_4$ consists of Na^+ and tetrahedral IO_4^- ions, whereas salts such as $(NH_4)_2H_3IO_6$ contain octahedral IO_6^{5-} groups. The structure of this salt and other 'acid salts' is described elsewhere (p. 260).

Intermediate between the iodine halides and oxy-compounds are the oxy-fluorides IO_3F and IO_2F, of which the structures have not yet been determined, and the interesting 'oxy-fluoriodides' such as KIO_2F_2. These oxyhalide ions and similar ions, derived from the simple oxy-ions by replacing one or more of the oxygen atoms by halogen or other elements, are described later. The $IO_2F_2^-$ ion has an unusual configuration which is, however, consistent with the stereochemistry of the other iodine compounds already discussed. In this ion the I atom has one pair of unshared electrons, and the four bonds are therefore disposed approximately towards the apices of a trigonal bipyramid, one equatorial bond position being occupied by the unshared pair. The O—I—O bond angle is contracted to 100°:



THE HALIDES OF THE ELEMENTS

In this section we shall attempt to give a general picture of the structures of solid halides as far as they are at present known. Concerning metallic halides we may make two generalizations. First, the fluorides often differ in structure from the other halides, except in the case of the alkali metals all the halides of which are essentially ionic. The extreme electronegativity

of fluorine results in many differences between the compounds of F and those of the other halogens, and the metallic halides are no exception to this rule. We shall find that in many cases the fluoride of a metal has a '3-dimensional complex' structure, whereas the chloride, bromide, and iodide form crystals consisting of layer or chain complexes. Secondly, many fluorides and oxides of similar formula type crystallize with the same structure, whereas chlorides, bromides, and iodides often have the same types of structure as sulphides, selenides, and tellurides. The following examples will illustrate these two points:

FeF_3: 3 dimensional complex; $FeCl_3$: layer structure
BiF_3: 3-dimensional complex; BiI_3: layer structure

CaF_2	:	$CaCl_2$	:	$CaBr_2$	:	CaI_2
Fluorite		Rutile		?		CdI_2 layer structure

PdF_2: rutile structure; SnO_2: rutile structure
$PdCl_2$: chain structure; SnS_2: layer structure.

It is unfortunate that there are comparatively few cases in which the structures of all the halides of a given metal have been determined. We shall find it convenient to consider the halides in the following groups:

I. Crystalline halides
  (1) Consisting of 3-dimensional complexes.
  These comprise (*a*) the halides of the alkali metals and of NH_4, Tl^I, and Ag (except AgI); (*b*) cuprous halides and AgI; (*c*) fluorides MX_2 and MX_3.
  (2) With layer and chain structures—mostly chlorides, bromides, and iodides.
  (3) Molecular halides, or more generally structures containing finite groups which are molecules except in the case of certain phosphorus halides. This group includes all non-metallic halides and some of the halides of Group IV metals.

II. Metallic halides in the vapour state.

I. Crystalline Halides

(1) *Halides consisting of 3-dimensional Complexes*

(*a*) At ordinary temperature and pressure AgF, AgCl, and AgBr and all the alkali halides except CsCl, CsBr, and CsI crystallize with the rock-salt structure. The chloride, bromide, and iodide of caesium and Tl^I crystallize with the caesium chloride structure. Ammonium chloride, bromide, and iodide crystallize with the NaCl structure at temperatures above 184·3°, 137·8°, and −17·6° C. respectively, at which temperatures the structures change to the CsCl structure. Ammonium bromide and iodide have also less symmetrical (tetragonal) forms at low temperatures and are therefore trimorphous. Just as CsF, in contrast to the other caesium halides, has at ordinary temperatures the NaCl structure, so TlF has a deformed NaCl structure with, instead of six equidistant neighbours,

two F at 2·59 A., two at 2·75, and two much farther away at 3·04 A. The exceptional structure of NH_4F (wurtzite structure) has already been mentioned in the section on the hydrogen bond. The rock-salt and caesium chloride structures have been described and illustrated on p. 98, where the interionic distances also were discussed.

(*b*) The cuprous halides crystallize with the zinc-blende structure (p. 83) in which the metal atoms are surrounded by four halogen atoms. The only silver halide with this structure is the iodide, to which we have already referred in connexion with 'defect lattices'. The structures of aurous and auric halides in the solid state are unknown.

(*c*) For ionic compounds of the type AX_2 there are two simple structures, the fluorite and rutile structures. The metal ions are surrounded in the former by eight and in the latter by six negative ions. Many dioxides and difluorides have these structures, and the following 'crystal radii' show that the larger ions form the 8-coordinated fluorite structure and the smaller ions the 6-coordinated rutile structure.

		Radius			*Radius*
Difluorides with fluorite structure	Cu^{2+}	0·96 A.	Difluorides with rutile structure	Mg^{2+}	0·65 A.
	Ca	0·99		Ni	0·70
	Sr	1·13		Co	0·72
	Ba	1·35		Zn	0·74
	Cd	0·97		Fe	0·75
	Hg	1·10		Mn	0·80

Few halides other than fluorides crystallize with these structures, but $SrCl_2$ with the fluorite structure and $CaCl_2$ with a slightly deformed rutile structure may be mentioned as exceptions.

A number of metallic trifluorides crystallize with closely related structures—AlF_3, ScF_3, FeF_3, CoF_3, RhF_3, and PdF_3. In all of these crystals the fluorine ions are approximately close-packed and the metal ions occupy certain of the octahedral holes between them. The arrangement of the metal ions is such that the structures are not layer or chain structures. The idealized ScF_3 structure is shown in Fig. 65. (The actual structure is slightly less symmetrical than that shown.) This is the same structure as that of ReO_3, and WO_3 has a very similar atomic arrangement. A quite different structure has been assigned to BiF_3 (Fig. 66) derived from the fluorite structure by adding extra F ions as indicated.

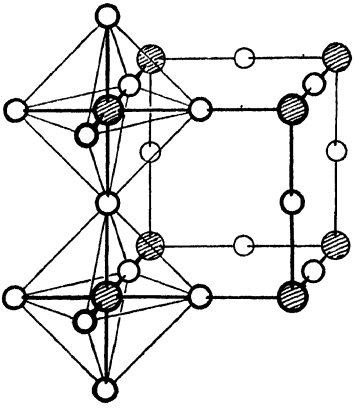


FIG. 65. The crystal structure of ScF_3 (idealized). Shaded circles represent scandium atoms.

The halide structures we have so far described, with the exception of the zinc-blende structure, are adopted by essentially ionic crystals. There

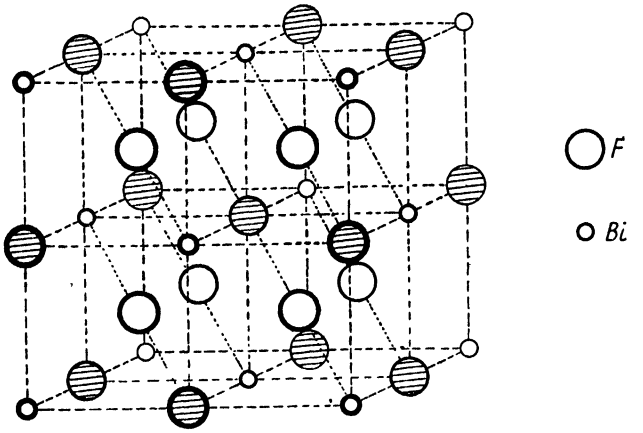


FIG. 66. The crystal structure of BiF_3. The metal ions and two-thirds of the fluorine ions are in the same positions as in the CaF_2 structure, but there are additional F^- ions (shown here as shaded circles) at the body-centre and at the mid-points of the edges of the cube.

are high coordination numbers of the positive ions, and generally the arrangement of one kind of ion around the other is the most symmetrical arrangement possible, as may be seen from the appended list.

	Structure	*Environment of A*	*Environment of X*
AX	NaCl	Octahedral AX_6	Octahedral XA_6
	CsCl	Cubic AX_8	Cubic XA_8
AX_2	MgF_2 (rutile)	Octahedral AX_6	Triangular XA_3
	CaF_2	Cubic AX_8	Tetrahedral XA_4
AX_3	ScF_3	Octahedral AX_6	Linear XA_2

(2) *Halides with Layer and Chain Structures*

The structures of many di- and tri-chlorides, bromides, and iodides are quite different from those of the tri-fluorides. We have said that in AlF_3, ScF_3, etc., the halogen atoms are arranged approximately in close-packing. This is generally true also in the other halides and equally of the O and S atoms in many oxides and sulphides. In these crystals the halogen, O, or S atoms are appreciably larger than the metal atoms (ions) and these large atoms pack together in the most compact way possible. It is the arrangement of the metal atoms in the interstices of this close-packed array of atoms which determines whether the complex (in the sense used in Chapter IV) is infinite (in 3, 2, or 1 dimension(s)) or is finite. This is easily seen by considering a 2-dimensional analogy. In Fig. 67 the arrangement of the open circles is the same in (*a*), (*b*), and (*c*), but the black circles, representing metal atoms in the interstices of the halogen lattice, are arranged differently in the three cases leading to the formation of (*a*) chains, (*b*) finite molecules, and (*c*) an infinite planar net. Now a close-packed array of atoms may be built up by the superposition of close-packed layers, of identical composition, as already described on

p. 109. According to whether we place metal atoms between each pair of adjacent layers or between alternate pairs we have possibilities of the kinds shown in Fig. 67 (*d*), (*e*), (*f*), and (*g*). These represent diagrammatically the elevations of the close-packed structures, i.e. viewing the

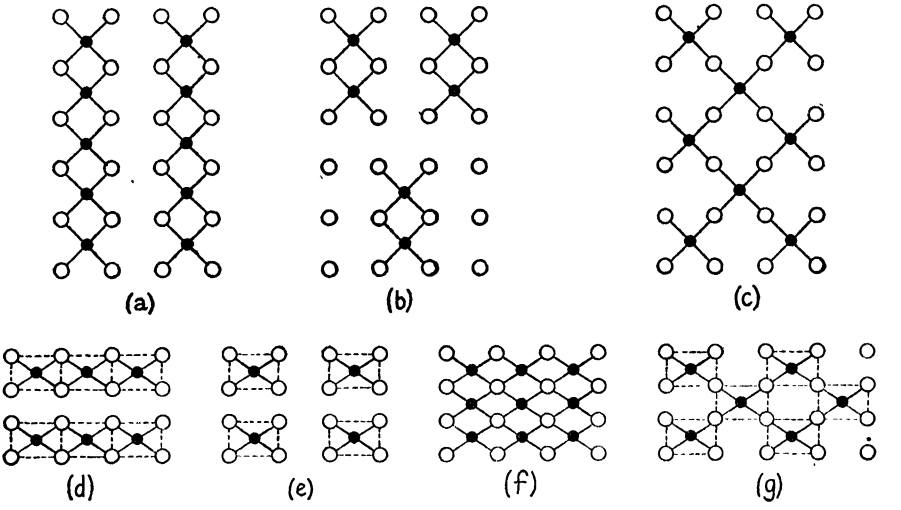


FIG. 67. Plans, (*a*)–(*c*), and elevations, (*d*)–(*g*), of structures containing complexes of various types (diagrammatic).

structures in a direction parallel to the layers. There are various possible combinations of the plans (*a*), (*b*), and (*c*) with the elevations (*d*), (*e*), (*f*), and (*g*). Thus the combination (*a*)(*e*) gives a structure built up of infinite chains, (*c*)(*d*) leads to a layer structure, (*c*)(*f*) gives an infinite 3-dimensional complex, and (*a*)(*g*) also a 3-dimensional complex of a rather interesting type.

Cubic and hexagonal close-packing differ in the way in which the close-packed layers are superposed, but in any form of close-packing two adjacent layers are fitted together in the same way, the atoms of one layer falling above the hollows of the lower layer. In Fig. 68 the small circles (representing atoms in a plane midway between those of the close-packed atoms) mark the centres of octahedra. Some or all of these octahedral holes may be occupied by metal atoms, forming a composite layer X—M—X consisting of two adjacent layers of halogen atoms with a layer of metal atoms between them. This is the sort of layer shown (diagrammatically) in elevation in Fig. 67 (*d*). Since the primary valencies of the M and X atoms are satisfied within such a layer, there being only van der Waals forces between adjacent layers, it may be regarded as an infinite 2-dimensional molecule and from a chemical point of view we are more interested in the internal structure of a layer than in the way in which successive layers pack together. We need only remember that these composite layers may pack together in different ways to result in cubic or hexagonal (or other form of) close-packing of the halogen atoms in the

structure as a whole. We may therefore expect to find pairs of structures related in this way and containing identical X—M—X layers. The composition of the layer (i.e. the ratio of M:X atoms) is determined by the proportions of octahedral holes occupied by metal atoms. In a close-packed array of atoms the number of octahedral holes is equal to the

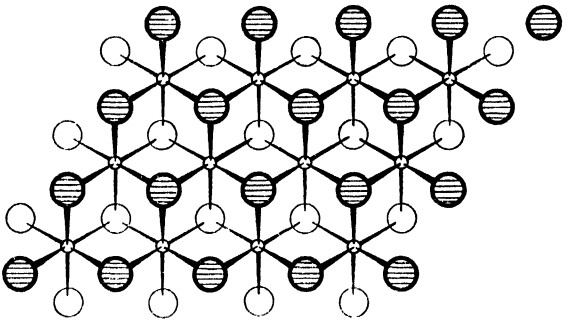


FIG. 68. Composite layer, of composition MX_2, consisting of two layers of close-packed X atoms with a layer of metal atoms (small circles) in the octahedral holes between them.

number of close-packed atoms, so that if they are all occupied the compound has the formula MX. In the rock-salt structure the Cl^- ions are in the positions of cubic close-packing with Na^+ ions in the octahedral positions between six Cl^- ions. However, in most of the alkali halides the alkali metal ions are too large for the octahedral holes between close-packed halogen ions with the result that the latter are no longer in contact with one another but only with the surrounding six alkali metal ions. Only for LiCl, LiBr, and LiI is this picture of a close-packed halogen lattice valid.

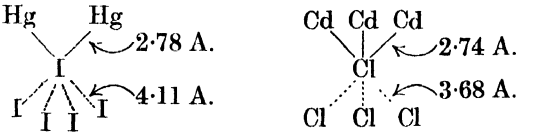
In the layer structures we are now considering the maximum number of octahedral holes to be occupied is one-half of the total, as may be seen by comparing Fig. 67 (*d*) with (*f*). Thus, if all the positions indicated by the small circles in Fig. 68 are occupied, the compound has the formula MX_2. If only two-thirds of these positions are filled (i.e. one-third of the total number of octahedral holes in the close-packed structure) we have a layer structure of formula MX_3. The structures arising in this way are summarized below:

Proportion of octahedral holes occupied by M atoms	*Type of close-packing of halogens*	
	Cubic	*Hexagonal*
All	$LiCl$	
$\frac{1}{2}$	$CdCl_2$	CdI_2
$\frac{1}{3}$	$CrCl_3$	BiI_3

The structures of the $CdCl_2$ (or CdI_2) and $CrCl_3$ (or BiI_3) layers have been illustrated (in plan) in Fig. 34 (i) and (iii), p. 145. The following are among the compounds crystallizing with these structures:

$CdCl_2$ structure:	$CdCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, NiI_2, $MgCl_2$, $ZnCl_2$, $MnCl_2$.
CdI_2 structure:	CdI_2, CaI_2, MgI_2, PbI_2, MnI_2, FeI_2, CoI_2, $MgBr_2$, $FeBr_2$, $CoBr_2$, $CdBr_2$, $NiBr_2$. Also many dihydroxides and disulphides (see pp. 353 and 386).
$CrCl_3$ structure:	$CrCl_3$.
BiI_3 structure:	BiI_3, SbI_3, AsI_3, $FeCl_3$, $CrBr_3$.

In Fig. 34 are also shown the layers of $HgBr_2$ and HgI_2. The $HgBr_2$ layer is closely related to (i) and is shown in a similar orientation. The structure of this compound may be regarded as intermediate between a layer and a molecular lattice, two of the six Br neighbours of a Hg atom being much closer (2·48 A.) than the remaining four, at 3·23 A. The HgI_2 layer is built up of HgI_4 tetrahedra sharing corners with other tetrahedra. We have already noted HgF_2 as crystallizing with the fluorite structure; $HgCl_2$ crystallizes as a molecular crystal (see p. 513). An important feature of these layer structures is the unsymmetrical environment of the halogen atoms, in contrast to the symmetrical arrangement of the neighbours in the essentially ionic 3-dimensional complexes. Thus in the HgI_2 or $CrCl_3$ layers each Cl is linked to two metal atoms within the layer (*a*) and in the $CdCl_2$ layer to three Cd (*b*). The only other contacts with atoms in adjacent layers are with halogen atoms, and to these there are only van der Waals bonds—indicated by dotted lines.



(*a*) (*b*)

The only type of chain structure so far found in simple halides is that of $PdCl_2$, illustrated in Fig. 69. The infinite chains are built up of planar

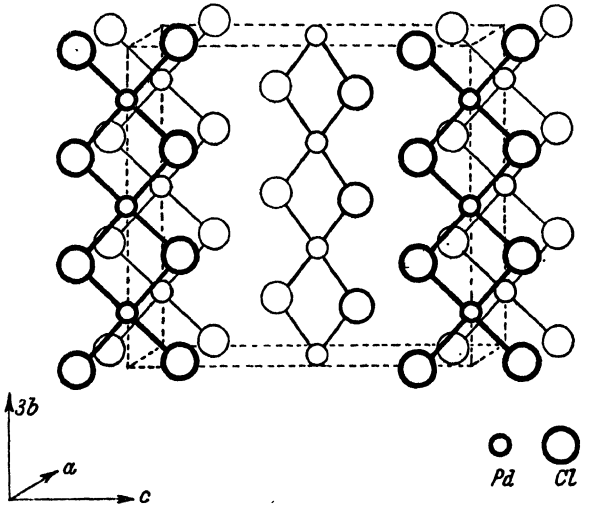
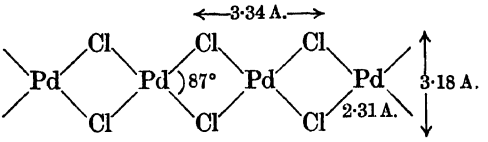


FIG. 69. The crystal structure of $PdCl_2$.

$PdCl_4$ groups sharing opposite edges. There is slight distortion of the Cl—Pd—Cl bond angles as shown below:



This chain is the analogue, for an atom forming four coplanar bonds, of the SiS_2 chain (p. 144) in which the Si atoms form four tetrahedral bonds.

Review of the Metallic Dihalides

It is worth while reviewing very briefly the structures of the dihalides if only to indicate the gaps in our knowledge. These compounds fall naturally into three groups: those of the Group II elements, the transition metals, and the Group IV B metals. Of the transition metals we give only the first row—the cupric halides are conveniently included here. Ionic radii are given where known, without, of course, implying that all the dihalides of these elements form ionic crystals. The values are those of Pauling except where otherwise indicated.

(*a*)	Be 0·31		Ca 0·99		Zn 0·74 A.			
	Mg 0·65		Sr 1·13		Cd 0·97			
			Ba 1·35		Hg 1·10			
(*b*)	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	(Cu^{2+})
				0·80	0·75	0·72	0·70	(1·01*)
(*c*)	Ge^{2+}	Sn^{2+}	Pb^{2+}					
	0·98†		1·21					

Goldschmidt. † Estimated from the Ge—I distance in GeI_2 (CdI_2 structure).

In the first group the fluorides have the fluorite or rutile structures characteristic of essentially ionic salts, except in the case of BeF_2 which crystallizes with the β-cristobalite structure. The remaining halides have, in general, layer structures, as already described. Little appears to be known of the structures of the halides other than the fluorides of the extreme elements Be and Ba, and the mercuric compounds are exceptional, as is the case with other compounds of this element (see Chapter XVI). Of the dihalides of the transition elements (*b*) only those of Mn, Fe, Co, and Ni have been studied and they are similar to the Group II compounds. Of the structures of the other Group VIII dihalides only that of $PdCl_2$ is known, and those of the anhydrous cupric halides other than the fluoride (fluorite structure) are unknown.

Of the dihalides (*c*) of the elements of Group IV a number have been studied. Germanous iodide crystallizes with the CdI_2 structure (Ge—I = 2·94 A.). (For the structures of the tin and lead dihalides in the vapour state see p. 518.) Lead iodide has the CdI_2 structure, but we might expect the more ionic dihalides of lead to have exceptional structures on account of the large size of the Pb^{2+} ion. The chloride and bromide have, in fact,

a structure in which the metal ions have nine halogen neighbours, a structure peculiar to these compounds.

(3) *Molecular Halides*

In this section we shall confine our attention to halides which exist as molecules in the solid state. When metallic halides vaporize they do so in the form of molecules, as we saw when considering the relation between the structures of substances in the different states of aggregation. The infinite 1-, 2-, or 3-dimensional complexes of the crystal break up into finite molecules of quite different structure. These are the subject of the next section. We are concerned here chiefly with the halides of the non-metals, i.e. those of H, the first Period elements from B to O, the second Period elements Si, P, and S, and those of the B sub-groups of the fourth and later Periodic families. In addition certain Group IV A halides form molecular crystals.

The crystal structures of molecular halides have received comparatively little study. This is due partly to the fact that many non-metallic halides would have to be studied at low temperatures owing to their low melting-points and also to the fact that the development of the electron diffraction method has made possible the study of the molecules in the vapour state. To the chemist the interest of these molecules lies in their internal structure (bond lengths and interbond angles) rather than in the way in which they are packed together in the crystal. This latter is determined largely by their shape and is therefore only of secondary interest. The structures of SnI_4 and GeI_4 illustrate the packing of tetrahedral molecules, and it is interesting to compare their structure with that of, say, NiI_2 or CdI_2. We have seen that in many halide structures the halogen atoms are close-packed and that, according to the number and disposition of the metal atoms in the interstices of the close-packed lattice, complexes of various kinds arise. If in a cubic close-packing of iodine atoms we place Ni atoms in one-half of the octahedral holes so that these lie in certain planes only, then we obtain the structure of NiI_2 ($CdCl_2$ structure). Let us now consider the arrangement of tetrahedral holes in the same arrangement of iodine atoms. There are twice as many of these holes as there are close-packed atoms. In CuI one-half of these are occupied in such a way as to form an infinite 3-dimensional complex (zinc-blende structure). In SnI_4 only 1/8 are occupied and in such a way as to lead to discrete molecules SnI_4. It is worth while comparing the structure of SnI_4 with that of CuI. The unit cell of SnI_4 is twice as long in each direction as that of CuI and is illustrated in Fig. 70. In the structures of CuI, SnI_4, NiI_2, and of CdI_2 (in which the halogen atoms are arranged in hexagonal close-packing) every iodine atom has twelve equidistant neighbours, and the observed I—I distances are listed below:

Structure:	CuI	SnI_4	GeI_4	NiI_2	CdI_2
I—I distance:	4·28	4·32	4·20	4·18	4·22 A.

Other halides with the SnI_4 structure include SiI_4, GeI_4, $TiBr_4$, and TiI_4.

For compounds forming such molecular crystals the same molecules exist in the crystals as in the vapour of the compound, and this is in general true of the non-metallic halides. Those of phosphorus are exceptional in this respect; the crystal structures of the pentahalides of the other Group V elements are not known. The pentahalides of P exist in the vapour state

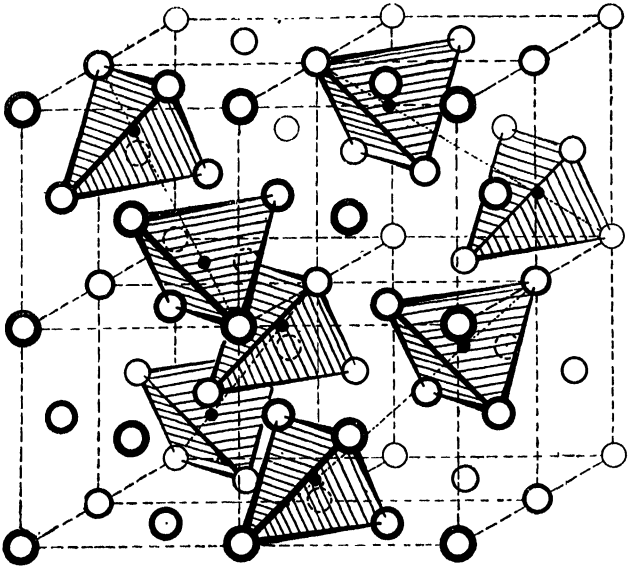


FIG. 70. Unit cell of the structure of SnI_4 (large circles represent I atoms). The arrangement of the iodine atoms is the same as in CuI, with the zinc-blende structure (Fig. 11 (*a*), p. 83).

as trigonal bipyramidal molecules, but crystalline PCl_5 is an assembly of tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$ ions, and should therefore be written as $[PCl_4][PCl_6]$. The pentabromide adopts the other simple way of avoiding 5-coordination in the crystal, for in the solid state it consists of $[PBr_4]^+$ and Br^- ions. In their oxygen compounds also the fifth group elements avoid the coordination number 5; these compounds are described in Chapters IX and XII.

Of the numerous molecular halides which have been studied by electron diffraction in the vapour state we may give the following examples:

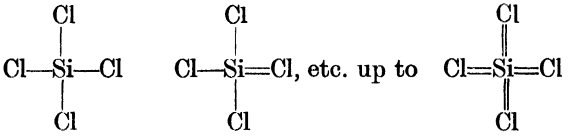
AX_2	linear: $HgCl_2$, $HgBr_2$, HgI_2, ZnI_2, CdI_2
	angular: OF_2, OCl_2, $SnCl_2$, $SnBr_2$, SnI_2, $PbCl_2$, $PbBr_2$, PbI_2
AX_3	planar: BF_3, BCl_3, BBr_3
	pyramidal: PF_3, PCl_3, PBr_3, PI_3, AsF_3, $AsCl_3$, $AsBr_3$, AsI_3, $SbCl_3$, $SbBr_3$, SbI_3
AX_4	tetrahedral: CF_4, CCl_4, SiF_4, $SiCl_4$, $GeCl_4$, $SnCl_4$, $TiCl_4$
AX_5	trigonal bipyramidal: PF_5, PF_3Cl_2, PCl_5, $MoCl_5$, IF_5(?)
AX_6	octahedral: SF_6, SeF_6, TeF_6

The interatomic distances in certain of these halides have been discussed by Pauling. In the halides of the elements of the second and later Periodic

rows the distances M—Cl are in some cases less than the sums of the single-bond tetrahedral radii (Table 7, p. 83) which give the observed distances in the methyl derivatives $M(CH_3)_n$ of similar formula type.

	MX_4	MX_3	MX_2	X_2
	Si—Cl	P—Cl	S—Cl	Cl—Cl
Observed	2·00	2·00		
'Tetrahedral radius' sum	2·16	2·09		
Covalent radius sum corrected for electronegativity difference	2·05	2·01	These values are normal to within the experimental error (*c.* ±0·03 A.)	
	Ge—Cl	As—Cl		
Observed	2·08	2·16		
'Tetrahedral radius' sum	2·21	2·20		
Covalent radius sum corrected for electronegativity difference	2·09	2·11		
	Sn—Cl	Sb—Cl	Te—Cl	I—Cl
Observed	2·30	2·37		
'Tetrahedral radius' sum	2·39	2·40		
Covalent radius sum corrected for electronegativity difference	2·27	2·29		

The short distances were attributed to partial double-bond character of the M—Cl bonds, assuming that these elements are not restricted by the octet rule but can utilize the *d* orbitals of the outermost or of the penultimate shell. (It was then thought that the shortening could not be due simply to the partial ionic character of the bonds since the C—F distance in CH_3F has normal length, yet there is a large electronegativity difference (1·5) between C and F. This actually proves that the 'tetrahedral' radii were not *covalent* radii; see p. 81.) On this view there was assumed to be resonance between the normal single-bonded molecule and various forms involving one or more double bonds:



If, however, we use the *covalent* radii given in Table 6 (p. 81) and correct the bond lengths for the differences in electronegativity between the atoms concerned, we find good agreement with observed values (see above), and the assumption of partial double-bond character is unnecessary.

II. Metallic Halides in the Vapour State

The vaporization of a simple molecular crystal involves only the separation, against van der Waals forces, of the molecules already existing in the crystal. In other cases there is rearrangement of the atoms to form finite groups of atoms which cannot be distinguished in the crystal. According to the extent of this rearrangement we could divide metallic halides into a number of groups. It has long been known that some metallic halides do not exist in the vapour as simple molecules AX_n, for

this may be demonstrated by measurements of vapour-density. In other cases the molecule in the vapour corresponds to the simple empirical formula, and we shall consider these first.

When the alkali halides are vaporized they form simple molecules AX which have been studied by electron diffraction. For a halide AX with the rock-salt structure there are other more complex molecules possible, as outlined in Fig. 71—(i) AX, (ii) A_2X_2, and (iii) A_4X_4—but for the alkali

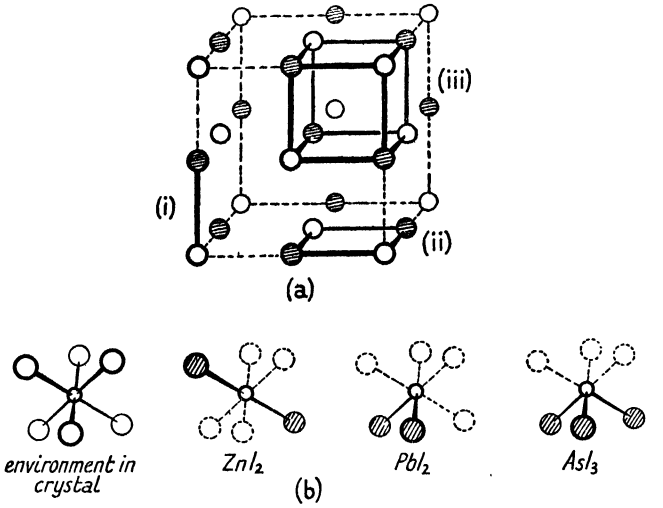
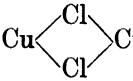


FIG. 71. Relation between crystal structure and configuration of molecule in the vapour state: (*a*) molecules AX, A_2X_2, and A_4X_4 derivable from the rock-salt structure, (*b*) molecules AX_2 and AX_3 derived from halides with layer structures.

halides the last two are presumably less stable than AX. Cuprous chloride does, however, form double molecules Cu_2Cl_2. Their configuration is unknown—they may be of the type (ii). This compound crystallizes with the zinc-blende structure and reference to Fig. 11 shows that the system



does not exist in the crystal. Other halides which have been shown to vaporize as simple molecules AX_n include ZnI_2 and CdI_2, which form linear molecules X—M—X, $SnCl_2$, $SnBr_2$, SnI_2, $PbCl_2$, $PbBr_2$, and PbI_2 (non-linear molecules), and the tribromides and triiodides of As and Sb. The latter form pyramidal molecules with interbond angles of about 100°. In the crystals of all these iodides the metal atoms are surrounded octahedrally by six halogen atoms, so that the structures of the vapour molecules are simply related to the environment of the metal atoms in the crystals, as shown in Fig. 71 (*b*).

Certain other trihalides show more complex behaviour. Instead of vaporizing directly to the simple AX_3 molecule a dimeric molecule A_2X_6 is formed which only breaks down to AX_3 at higher temperatures. Among halides which behave in this way are $AlCl_3$, $AlBr_3$, AlI_3, $AuCl_3$, $AuBr_3$,

and $FeCl_3$. The aluminium halides have been studied by electron diffraction and shown to form (below about 400° C.) molecules Al_2X_6 of the type shown in Fig. 72, in which each Al is surrounded tetrahedrally by four halogen atoms. The structures of the crystalline halides are still in doubt, but it is reasonably certain that in these the Al atoms are octahedrally coordinated by six halogen atoms as in most other trihalides (see above), including $FeCl_3$. The Fe_2Cl_6 molecule presumably has the same configuration. In the case of the gold trihalides, however, the molecule Au_2X_6 will be planar, trivalent gold forming four coplanar bonds as in the compounds $Au_2Et_2Br_4$ and $Au_2Et_4Br_2$ (see p. 508).

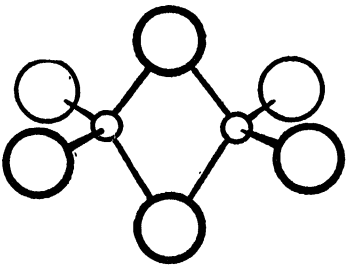


FIG. 72. The structure of the molecules Al_2Cl_6, Al_2Br_6, and Al_2I_6 according to Palmer and Elliott.

Complex Halides

Any solid phase containing more than one kind of metal atom (or other electropositive group) and/or more than one kind of halogen atom may be termed a complex halide. There are obviously three types, containing:

(1) various kinds of metal atoms and one halogen;
(2) one kind of metal atom and two or more halogens;
(3) more than one kind of metal and of halogen.

Mixed crystals of halides (e.g. (Na, K)Cl), which are included in our definition, will not be dealt with here as we have already mentioned these under defect structures. We shall confine our attention to compounds of the first class, except for mentioning that the second class includes such salts as PbFCl, on the one hand, and on the other, the various mixed polyhalides such as $CsICl_2$. Lead fluorochloride, PbFCl, has the same (layer) structure as BiOCl, BiOBr, and BiOI, and this is described in a later section. Reference has already been made to the mixed polyhalides. Salts containing only two kinds of positive ion and a common anion are called 'double halides'. Some are anhydrous, others are hydrated to various degrees, and except in one or two special cases we shall exclude hydrated salts from the present discussion. (See the section on Hydrates in Chapter XI.) The formulae of many of these hydrates, e.g. $2KCl.FeCl_3.H_2O$, $K_2CuCl_4.2H_2O$, become intelligible in the light of structure determinations.

The empirical formulae of complex halides are of all degrees of complexity, as may be seen from the following selection: $CsAgI_2$, $CsHgCl_3$, $TlAlF_4$, Cs_3CoCl_5, Na_3AlF_6, $(NH_4)_3ZrF_7$, Na_3TaF_8, $Cs_3Tl_2Cl_9$, and $Na_5Al_3F_{14}$. We may make here a few general observations before proceeding to describe the structures of some of these salts. Firstly, similarity in formula-type does not mean that compounds have similar structures, and this is generally true throughout the chemistry of solids. Thus the salts $KMgF_3$, NH_4CdCl_3, and $CsAuCl_3$ have quite different structures.

The third of these compounds illustrates a second point. It is not always sound to adopt the simplest empirical formula. The 'double' chloride $CsAuCl_3$ should be written $Cs_2Au^{I}Au^{III}Cl_6$, for it contains both univalent and trivalent gold and there is a triple salt $Cs_2AgAuCl_6$ of similar structure. Thirdly, a compound A_mBX_n does not necessarily contain a complex BX_n. As in the case of many other classes of complex compounds such as 'basic salts', p. 381, mixed oxides, p. 328, and heteropoly acids, p. 339, attempts have been made to formulate many of these complex halides as Werner coordination compounds, but except for one class such structural formulae are quite false and must be abandoned. These Werner coordination formulae have been assigned to compounds of the general formula A_mBX_n and associate the halogen atoms with one of the metal atoms by writing the formula $A_m(BX_n)$. They are correct only when the atoms B and X form a finite complex ion BX_n. The study of the structures of complex halides has shown that this is only one of many possible types of structure, and although only a comparatively small number of the more complex compounds have been studied up to the present, many of the general principles of their structures are becoming apparent. The treatment adopted below will follow the lines of the general classification of crystal structures outlined in Chapter IV.

For a compound of formula A_mBX_n, assuming that all the atoms of each kind have similar environments in the crystal, there are four main possibilities:

(*a*) A, B, and X form an infinite 3-dimensional array of ions in which no finite or infinite 1- or 2-dimensional complex can be distinguished. The coordination numbers of A and B will be determined by the sizes of these ions relative to that of X, and the coordination polyhedra AX_p and BX_q will share X ions in such a way as to form an electrically stable arrangement (see the structure of complex ionic crystals and Pauling's rules, Chapter III).

(*b*) B and X form infinite 2-dimensional complexes.

(*c*) B and X form infinite 1-dimensional complexes.

(*d*) B and X form finite complexes BX_n.

In (*b*), (*c*), and (*d*) it is convenient to write the formula $A_m(BX_n)$ but only in (*d*) is BX_n a coordination group in the sense used by Werner, i.e. that each B atom is surrounded by n X atoms forming a finite complex ion BX_n. In (*b*) and (*c*), as in (*a*), the value of n is *not* the coordination number of a B atom, for the halogen atoms are joined to more than one B atom, thus linking these atoms into an infinite complex. In addition to these four simple structure types, (*a*) to (*d*), more complicated arrangements are possible. For example, a compound A_mBX_n may contain, not ions BX_n, but ions BX_{n-p} and p separate X ions, as is the case in Cs_3CoCl_5 which should accordingly be written $Cs_3(CoCl_4)Cl$. The examples described below may not be the most obvious or well-known compounds with a given type of formula; they are chosen merely because their structures happen to have been determined.

(a) Complex Halides consisting of Infinite 3-dimensional Complexes

A number of double fluorides crystallize with the perovskite structure which has already been illustrated in Fig. 27. They include $KMgF_3$, $KZnF_3$, and $KNiF_3$, and the same structure has been assigned to $CsCdCl_3$ and $CsHgCl_3$. It will be seen that the K^+ and F^- ions in $KMgF_3$ together occupy the positions of cubic close-packing. For two atoms to form a close-packed array they must be approximately equal in size, and the values of the crystal radii of the ions, F, 1·36, K, 1·33, and Cl, 1·81, Cs, 1·69 A., show why the salts with the perovskite structure are trifluorides of K and a second metal or trichlorides of Cs and a second metal. The second metal must, of course, form a divalent ion, to preserve electrical neutrality; otherwise its chemical nature is immaterial. It merely has to be small enough to fit into the octahedral holes between six F^- or Cl^- ions in the close-packed KF_3 or $CsCl_3$ lattice respectively. Many mixed oxides also crystallize with the perovskite structure, which is further discussed on p. 330.

(b) and (c) Complex Halides containing Layer and Chain Complexes

We have seen that metallic fluorides in general differ from other halides in forming 3-dimensional complexes, whereas many chlorides, bromides, and iodides form layer lattices and $PdCl_2$ a chain lattice. This difference is to be associated with the fact that all bonds from metals to fluorine are essentially ionic, whereas bonds to the other halogens have progressively more covalent character as we go from Cl to I. We may expect to find similar structural differences in complex halides. As yet no layer structures have been found for complex chlorides, bromides, or iodides, but two examples of chain structures will be described below. In complex fluorides all the bonds A—X and B—X will be rather similar as regards percentage ionic character and there will therefore be no complexes BX_n containing bonds essentially different in nature from the bonds between the X and A atoms. However, the structures of some aluminofluorides are of interest in this connexion. The coordination group AlF_6^{3-} is similar in one respect to the SiO_4^{4-} tetrahedron (and to the WO_6^{6-} group, see p. 327), since if we represent these as ionic complexes we see that the electrostatic strength of the Al—F bond has, like that of the Si—O bond, the value one-half. These AlF_6 groups can therefore join together to form extended complexes, just as the infinite chain and layer ions in silicates are formed by the linking of SiO_4 tetrahedra. In describing aluminofluorides in this way we should remember that the bonds within Al_mF_n complexes are not appreciably different in nature from the other M—F bonds in the structure, whereas in silicates the Si—O bond is about 50 per cent. covalent and therefore far less ionic than most metal-oxygen bonds. A systematic study has been made of a number of aluminofluorides, and we shall therefore devote a short section to these compounds later.

The structures of NH_4CdCl_3 and $K_2HgCl_4.H_2O$ are good examples of

complex chlorides containing infinite chain ions. Infinite chains of composition AX_4 result if octahedral AX_6 groups share opposite edges, Fig. 73 (*a*), and more complex chains, or bands, result if two sets of octahedra are joined laterally as shown at (*b*). Comparison of these chains with the layer shown in Fig. 34 (i) will show that they are simply portions

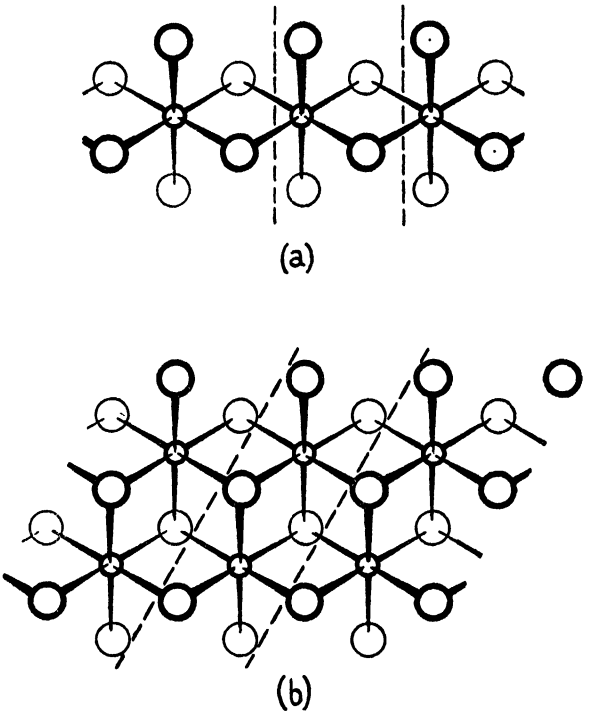


FIG. 73. Infinite chains and bands formed by the linking of octahedral AX_6 groups. The broken lines mark off the repeat units, of compositions AX_4 and AX_3 respectively.

of $CdCl_2$ layers. The composition of the chain (*b*) is AX_3, as may be verified by counting the numbers of metal and halogen atoms between the dotted lines, which mark off one repeat unit of the chain. In NH_4CdCl_3 (and the isomorphous $RbCdCl_3$) chains of this sort are held together by the positive ions. In $K_2HgCl_4.H_2O$ and $K_2SnCl_4.H_2O$ chains of type (*a*) are held together by K^+ ions and the water molecules are also found in the tunnels between these chains (see also Fig. 39).

(*d*) *Complex Halides containing Finite Complex Ions*

This group includes a very large number of complex halides. Certain of the salts ABX_4 and A_2BX_4 containing tetrahedral BX_4 ions are isomorphous with oxy-salts. Thus NH_4BF_4 and $RbBF_4$ are isomorphous with $BaSO_4$, and $(NH_4)_2BeF_4$ with K_2SO_4, but K_2PtCl_4 (and the isomorphous K_2PdCl_4 and $(NH_4)_2PdCl_4$) has quite a different structure since

it contains planar $[PtCl_4]^{2-}$ ions. The structure is shown in Fig. 74. (That of $Pd(NH_3)_4Cl_2.H_2O$ is similar, planar $[Pd(NH_3)_4]^{2+}$ groups replacing $PtCl_4^{2-}$ and Cl^- replacing K^+, with H_2O molecules at the points indicated by small black circles; see also Fig. 37 (*a*).)

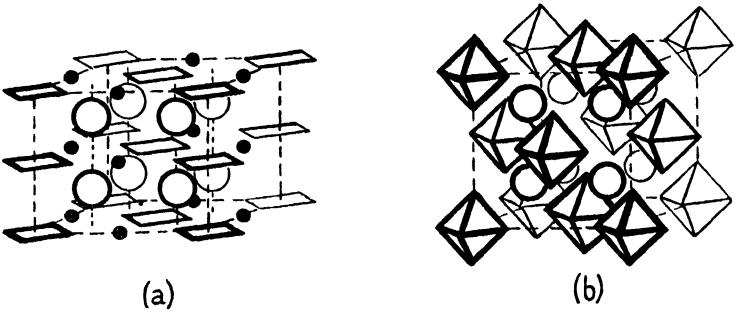


FIG. 74. The crystal structures of (*a*) K_2PtCl_4 and (*b*) K_2PtCl_6.

Halides of the type A_2BX_6 are extremely numerous and many crystallize with the same structure, that of K_2PtCl_6. In this structure (Fig. 74 (*b*)) K^+ ions and octahedral $PtCl_6^{2-}$ ions occupy respectively the F^- and Ca^{2+} positions of the fluorite structure (see Fig. 18 (*a*)). The metal ion in these compounds must be one of the larger alkali metals (K, Rb, Cs) or NH_4 or Tl^I, since for stability the radius of A must lie between certain limits. The Li and Na chloroplatinates crystallize as hexahydrates like the acid $H_2PtCl_6.6H_2O$ itself and are obviously of the type $[M(H_2O)_6][PtCl_6]$. Among the compounds crystallizing with this structure are the silicofluorides of K, Rb, Cs, NH_4, and Tl^I, K_2ReF_6, Cs_2GeF_6, K_2SeBr_6, K_2OsBr_6, and all the following hexachlorides:

	$TiCl_6$	$ZrCl_6$	$SnCl_6$	$PbCl_6$	$SeCl_6$	$TeCl_6$	$PtCl_6$
K			+			+	+
Rb	+	+	+	+	+	+	+
Cs	+	+	+	+	+	+	+
NH_4			+	+	+	+	+
Tl			+			+	+

There is a considerable number of salts which were originally written $2AX.BX_3.H_2O$. Where A is one of the large positive ions already mentioned these salts also crystallize with the K_2PtCl_6 structure, the water molecule occupying one of the six positions in the octahedral complex ion. They should therefore be written $A_2(BX_5.H_2O)$. Examples are: $(NH_4)_2[VF_5.H_2O]$ and the isomorphous Rb and Tl^I salts, $Tl_2[CrF_5.H_2O]$ and $Rb_2[CrF_5.H_2O]$.

The structure of certain salts A_3BX_6 is very simply related to that of K_2PtCl_6. In $(NH_4)_3AlF_6$, NH_4^+ and AlF_6^{3-} ions occupy the positions of the K^+ and $PtCl_6^{2-}$ ions in Fig. 74 (*b*), and in addition there are NH_4^+ ions

at the mid-points of the edges and at the centre of the cubic unit cell. The compounds $(NH_4)_3FeF_6$ and $(NH_4)_3[MoO_3F_3]$ have the same structure. As in the case of the K_2PtCl_6 structure such an arrangement is stable only for positive ions of a certain size, and accordingly we find that Na_3AlF_6 has a different structure with only 6-coordination of the Na^+ ions instead of 12-coordination by halogen in the K_2PtCl_6 structure.

A third type of complex halide we may mention here has the general formula $A^I_3B^{III}_2X_9$. The salt $Cs_3Tl_2Cl_9$ is built up of a close-packing of the large Cs^+ and Cl^- ions (compare $CsCdCl_3$ above) with Tl^{3+} in certain pairs of adjacent octahedral holes. In this way complex ions $Tl_2Cl_9^{3-}$ arise, with the structure shown in Fig. 75. Similar ions $W_2Cl_9^{3-}$ exist in $K_3W_2Cl_9$. Although $Cs_3As_2Cl_9$ has a similar formula its structure is different and no ions $As_2Cl_9^{3-}$ can be distinguished. In $K_3W_2Cl_9$ each W atom has six equidistant Cl neighbours, at 2·45 A. (and also incidentally the other W atom of the complex ion at about the same distance), surrounding it octahedrally, but in $Cs_3As_2Cl_9$ the neighbours of an As atom are three Cl at 2·25 A. and three more at 2·75 A., so that this structure would appear to contain pyramidal $AsCl_3$ molecules embedded among Cs^+ and Cl^- ions.

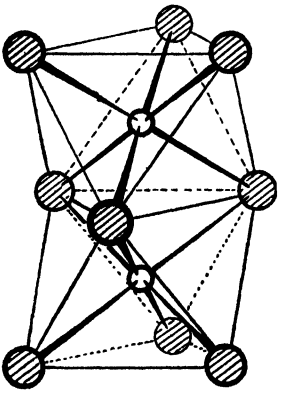


FIG. 75. The $Tl_2Cl_9^{3-}$ ion.

We may conclude this section by mentioning two more complex structures. All those we have described so far contain one type of complex ion BX_n and a number of A ions. In Cs_3CoCl_5, on the other hand, there are tetrahedral $CoCl_4^{2-}$ ions together with odd Cl^- ions and, of course, Cs^+ ions. The salt with the empirical composition $CsAuCl_3$ is interesting for a number of reasons. It is jet black in colour, whereas CsCl is colourless and the gold chlorides $AuCl_3$ and AuCl are orange and yellow respectively. As written above the salt appears to contain divalent gold, but in compounds of this sort the deep colour has been attributed to the presence of an element in two valency states. We shall see shortly that this compound is in fact $Cs_2Au^IAu^{III}Cl_6$. Its structure is closely related to the perovskite structure adopted by a number of fluorides such as $KMgF_3$, but the structure is distorted so that instead of all the gold atoms being surrounded by six Cl atoms half of them are surrounded by four and the other half by two Cl atoms. The linear $[Cl—Au^I—Cl]^-$ and the square $Au^{III}Cl_4^-$ ions can be clearly seen in Fig. 76 (*b*). The Cs^+ and Cl^- atoms are close-packed as in $Cs_3Tl_2Cl_9$, which has the same ratio of Cs : 3Cl. In Fig. 76 (*a*) we show a corresponding portion of the true perovskite structure. This has already been illustrated in Fig. 27 (p. 112) as the structure of $KMgF_3$. It is redrawn here with the origin at a Mg atom and with axes at 45° to those in the earlier figure. The inscribed cube is the unit cell of Fig. 27. There is also a compound $Cs_2AgAuCl_6$ with the

same structure as $Cs_2Au^{I}Au^{III}Cl_6$ which also has a metastable cubic form apparently with a random perovskite structure.

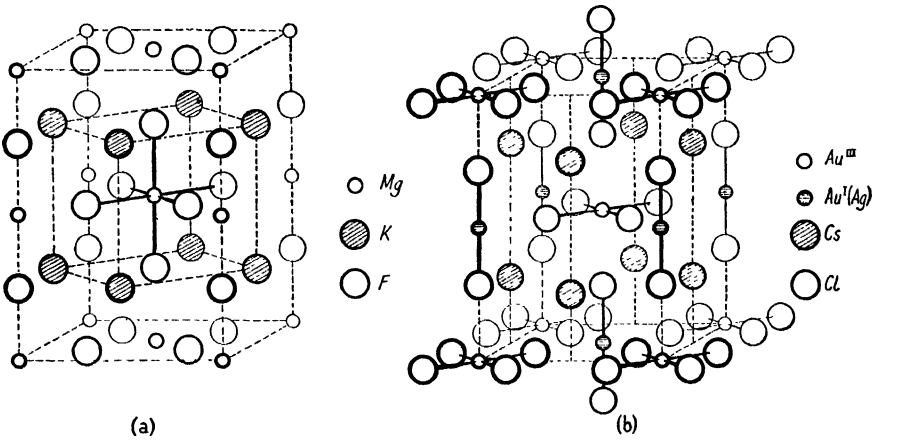


FIG. 76. The structures of (*a*) $KMgF_3$, perovskite structure, and (*b*) $Cs_2Au^{I}Au^{III}Cl_6$ in similar orientations.

Complex Aluminofluorides

We remarked above that the structures of complex aluminofluorides, of the general formula $M_xAl_yF_z$, may be conveniently described in terms of the geometrical arrangement of the AlF_6 octahedra. As examples we shall describe the structures of the following compounds:

Na_3AlF_6 (cryolite) and $Na_3Li_3Al_2F_{12}$ (cryolithionite)
Tl_2AlF_5, $TlAlF_4$, and $Na_5Al_3F_{14}$.

These formulae become intelligible when we consider the possible ways in which AlF_6 octahedra may be linked together. In the first two, Na_3AlF_6 and $Na_3Li_3Al_2F_{12}$, the F:Al ratio of 6:1 shows the presence of finite AlF_6^{3-} ions as in the $(NH_4)_3AlF_6$ structure previously mentioned. In Na_3AlF_6 the Na^+ and AlF_6^{3-} ions are packed together in such a way as to give each Na^+ ion six F^- neighbours. The second compound has the same structure as the silicate mineral $Al_2Ca_3(SiO_4)_3$, so that its formula may alternatively be written $Al_2Na_3(LiF_4)_3$. This illustrates the point already mentioned that the description of these aluminofluorides in terms of AlF_6 octahedra is arbitrary in the sense that the Al—F bonds are not appreciably different in nature from the other M—F bonds in the structure. Different F:Al ratios will arise when AlF_6 octahedra share corners with one another; the sharing of edges is unlikely in these essentially ionic compounds on account of the high charge on the Al^{3+} ions. The simplest possibility is the formation of infinite chains in which two opposite corners of each octahedron are shared, as in Fig. 77. This chain has the composition $(AlF_5)_n^{2n-}$ and it is found in Tl_2AlF_5. If all four equatorial F atoms of each octahedron are shared, layers of composition AlF_4 result, and these occur in $TlAlF_4$

(and the isomorphous K, NH_4, and Rb salts). More complex arrangements can, of course, be built up, and in $Na_5Al_3F_{14}$ there are layers, of composition Al_3F_{14}, in which one-third of the AlF_6 octahedra share four corners and two-thirds share only two corners. Perspective drawings of the AlF_4^- and $Al_3F_{14}^{5-}$ layers are shown in Fig. 78.

We shall conclude this chapter with a brief account of three other types of compounds containing halogens, the oxy-, hydroxy-, and amino-halides.

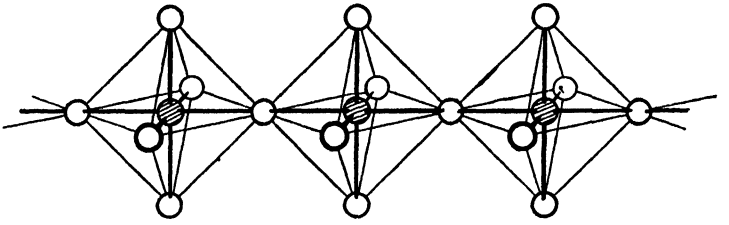


FIG. 77. Chain, of empirical composition AX_5, formed by AX_6 octahedra sharing opposite corners.

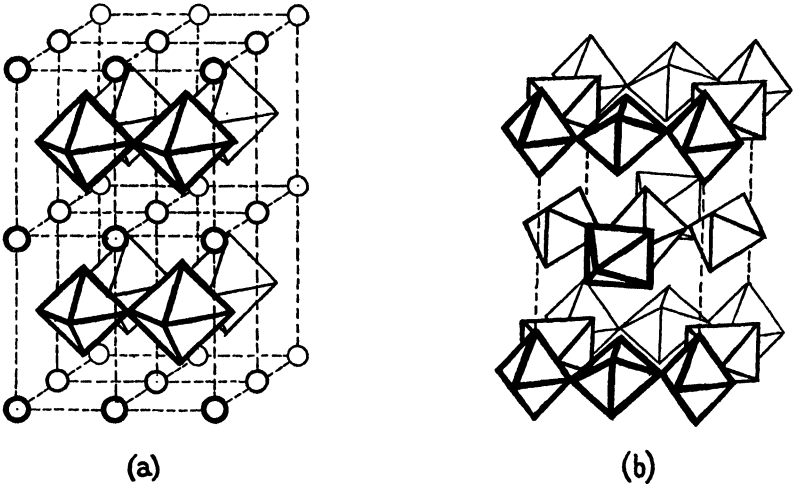


FIG. 78. Portions of (*a*) the AlF_4 layers in $TlAlF_4$ and (*b*) the Al_3F_{14} layers in $Na_5Al_3F_{14}$ (after Brosset).

Oxyhalides, Hydroxyhalides, and Related Compounds

Compounds containing one or more elements combined with oxygen and halogen atoms include a number of quite different types:

(1) The salts of the halogen oxy-acids, which will not be further considered here.

(2) The oxyhalides, which we shall consider in three groups.

(3) The hydroxyhalides.

(4) Salts containing oxy-halogen ions, $(MO_xX_y)^{n-}$.

(2) (*a*) *Oxyhalides of the non-metals.* The compounds in this class include the following:

$COCl_2$	NOF		
	NOCl		
	NOBr		
	NO_2F		
	POF_3	SOF_2	
	$POCl_3$	$SOCl_2$	
		SO_2F_2	IOF_3
		SO_2Cl_2	IO_2F
		$S_2O_5Cl_2$	

Apart from these simple compounds containing, other than the iodine oxyfluorides, only one kind of halogen, there are mixed oxyhalides such as $POCl_2Br$, $POBr_2Cl$, etc. Where they are of particular interest the structures of these molecules are given under the stereochemistry of the central elements, C, N, P, S, or I.

(*b*) *Oxyhalides of the elements of the 4th, 5th, and 6th A sub-groups*, of which the following are examples:

	VOF_3	CrO_2Cl_2*
	$VOCl_3$*	
$ZrOCl_2$	$NbOF_3$	$MoOF_4$
$ZrOBr_2$	$NbOCl_3$	
$ZrOI_2$	$NbOBr_3$	MoO_2F_2
		MoO_2Cl_2
		MoO_2Br_2
		WOF_4
		$WOCl_4$
		$WOBr_4$
		WO_2Cl_2
		WO_2Br_2
		UO_2F_2
		UO_2Cl_2
		UO_2Br_2

* These two compounds have been studied in the vapour state by electron diffraction. The molecules have slightly distorted tetrahedral configurations.

There is no systematic nomenclature for the compounds of these two groups. The use of the suffix -yl to indicate the attachment of oxygen to an atom M forming a radical MO_x was adopted long before we had any knowledge of the constitution of these compounds and was usually suggested by the existence of a number of compounds in which the halogen was replaced in the empirical formula by other electronegative atoms or groups—for example, nitrosyl, NO, thionyl, SO, antimonyl, SbO, uranyl, UO_2. In some of these compounds such ions do exist, e.g. $[NO]ClO_4$ and uranyl salts, $[UO_2]X_2$, but in SbOCl there is no 'antimonyl' group—see below. As we shall find in many other cases, empirical formulae give no indication of structure, as may be seen from the formulae of the following compounds:

$$CaO_2Cl_2, \quad UO_2Cl_2, \quad SO_2Cl_2.$$

The first, calcium hypochlorite, is a simple salt containing $[ClO]^-$ ions, so that the formula is preferably written $Ca(ClO)_2$. Uranyl chloride consists of uranyl ions and chlorine ions and should therefore be formulated $[UO_2]Cl_2$, while sulphuryl chloride is a molecular oxychloride.

The non-metallic and metallic oxyhalides may be prepared in a number of ways (not all of which are applicable to any one compound) such as by direct union of halogen and appropriate oxide:

$$SO_2+Cl_2 \rightarrow SO_2Cl_2 \quad \text{or} \quad UO_2+Cl_2 \rightarrow UO_2Cl_2,$$

action of HX on an oxide (UO_2Cl_2 from UO_3, $ZrOCl_2$ from ZrO_2 and HCl), passage of the vapour of a higher halide over a heated oxide (VOX_3 and

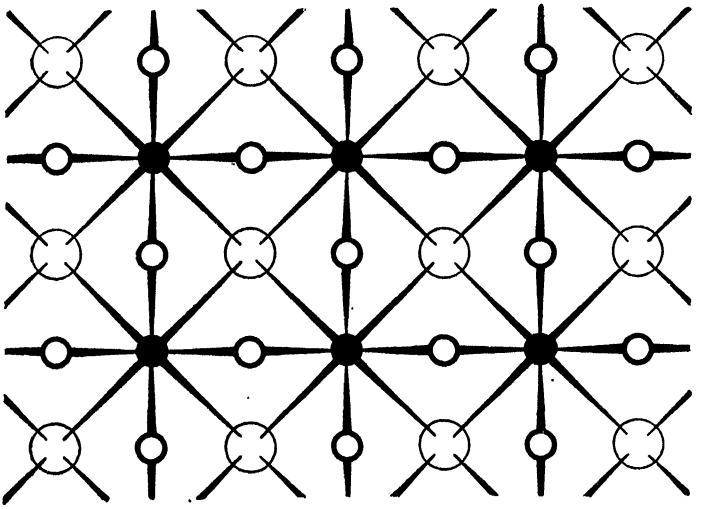


FIG. 79. Atomic arrangement in a layer of the structure of BiOCl or PbFCl.

$NbOX_3$ from the pentahalides), or by the partial hydrolysis of the higher halide ($POCl_3$ from PCl_5). Many of these compounds may be distilled without decomposition. Many are hydrolysed by water, including those of V, Nb, and Cr, but the zirconyl compounds crystallize from acid aqueous solution, as the octahydrates ($ZrOCl_2.8H_2O$, etc.). The uranyl compounds are essentially different from the V, Nb, Mo, and W compounds. There are numerous uranyl salts (nitrate, sulphate, acetate, etc.) in which the UO_2^{2+} ion behaves like a metal, and this ion is of interest on account of its catalytic properties and its brilliant yellow-green fluorescence.

(*c*) *Oxyhalides of Sb, Bi, and Fe.* These compounds, of general formula MOX, are structurally quite different from those of (2) (*a*) and (*b*), and are more closely related to certain other groups of compounds. The bismuth oxyhalides, BiOCl, BiOBr, and BiOI, all have the same structure as the compounds PbFCl and PbFBr, Bi taking the place of Pb and Cl of F. Their structures are built of layers, one of which is shown in plan

in Fig. 79. If the metal atoms (small black circles) lie in the plane of the paper, then the small open circles represent oxygen atoms (or F in PbFCl) lying above the paper and the large circles halogen atoms lying in a plane below that of the paper.

FeOCl also has a layer structure and the constitution of the layers is of the same type as in FeO.OH, the structure of which is described on p. 357.

(3) *Hydroxyhalides*

A few of the B sub-group metals form hydroxyhalides, e.g. Cd(OH)Cl, $SnCl_3(OH)$. The former is usually included among basic salts since it was formerly written $Cd(OH)_2.CdCl_2$. It is, however, in no sense a compound of hydroxide and chloride, for it forms a layer structure in which every Cd atom is surrounded by three Cl and three OH—compare BiOCl, in which a Bi atom is surrounded by four Cl and four O. These compounds exist, of course, only in the solid state. (For Cd(OH)Cl see also p. 383.)

(4) *Salts containing Oxy-halogen Ions*

Intermediate between halogen- and oxy-ions there are oxy-halogen ions, MO_xX_y, containing both oxygen and halogen atoms. We have already discussed the configuration of the ion $IO_2F_2^-$. Corresponding to the tetrahedral MO_4 and octahedral MO_6 ions there are possible ions MO_2X_2, MO_3X, MO_2X_4, MO_3X_3, and so on with the same configurations. Salts have been prepared containing the following ions:

$PO_2F_2^-$	SO_3F^-	$IO_2F_2^-$	$OsO_2Cl_4^{2-}$
PO_3F^{2-}			
	CrO_3F^-		
	CrO_3Cl^-		
$NbOCl_5^{2-}$	$MoO_2Cl_4^{2-}$		
	$MoO_3F_3^{3-}$		

Such salts may be prepared in various ways. For example, $(NH_4)PO_2F_2$ and $(NH_4)_2PO_3F$ can be obtained by heating together ammonium fluoride and phosphorus pentoxide, KSO_3F from $K_2S_2O_7$ and KF, and $KCrO_3Cl$ from CrO_2Cl_2 and a saturated aqueous solution of KCl. The structures of several of these salts have been determined by X-ray methods. The ion CrO_3F^- forms an almost regular tetrahedron in $KCrO_3F$, the sizes of O and F being very similar. Thus $(NH_4)_3MoO_3F_3$ has the same structure as $(NH_4)_3AlF_6$ with octahedral MoO_3F_3 ions. There is rather more difference between the sizes of O and Cl, so that whereas K_2OsCl_6 has the K_2PtCl_6 structure, the salt $K_2OsO_2Cl_4$ has a rather deformed version of that structure.

Aminohalides

The absorption of ammonia by many solid salts has been known for a very long time. The products vary widely in composition and stability. Thus $CaCl_2.8NH_3$ and $CuCl_2.6NH_3$, prepared from the anhydrous salts and ammonia gas, readily lose ammonia, but many other aminohalides

may be prepared from ammoniacal salt solutions and some possess considerable stability. The simplest compounds of this type have the general formula $MX_n.mNH_3$ (with sometimes water of crystallization), where m is the normal coordination number of M. They contain complex ions $[M(NH_3)_m]^{n+}$ and X^- ions. Typical ions of this sort are $[Ag(NH_3)_2]^+$, $[Cu(NH_3)_4]^{2+}$, and $[Co(NH_3)_6]^{3+}$. Many salts $[M(NH_3)_6]X_2$ and $[M(NH_3)_6]X_3$ have simple structures, e.g. $[M(NH_3)_6]Cl_2$, Br_2, I_2, and $(ClO_4)_2$ (where M = Mn, Fe, Co, Ni, Mg) with the anti-fluorite structure of K_2PtCl_6, and $[Co(NH_3)_6]I_3$, $(ClO_4)_3$, $(BF_4)_3$, and $(PF_6)_3$ with the $(NH_4)_3AlF_6$ structure (p. 289).

The coordination group around M may, however, be made up of NH_3 and X as in $[Co(NH_3)_5Cl]Cl_2$ or $[Pt(NH_3)_3Cl_3]Cl$. The constitution of these compounds was at first difficult to understand since they could be represented as the normal halide plus a number of NH_3 molecules, and in some cases there was a series of compounds with different numbers of ammonia molecules, as in

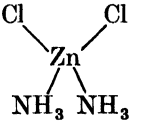
$$CoCl_3.6NH_3, \quad CoCl_3.5NH_3, \quad CoCl_3.4NH_3.$$

Their formulation as 6-coordinated complexes was due to Werner, who wrote them in the form

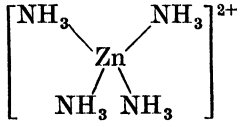
$$[Co(NH_3)_6]Cl_3, \quad [Co(NH_3)_5Cl]Cl_2, \quad \text{and} \quad [Co(NH_3)_4Cl_2]Cl.$$

The different functions of the two types of X atoms were confirmed in a number of ways. Conductivity measurements, for example, showed that $CoCl_3.5NH_3$ yields only two, and $CoCl_3.4NH_3$ only one chlorine ion per 'molecule'. Moreover, the latter compound exists in two isomeric forms, with cis- and trans- configurations. An interpretation of the formulae of such compounds in terms of the electronic theory of valency was not possible until much later. These coordination compounds are discussed in more detail in Chapter XVI.

The compounds of type $MCl_x(NH_3)_x$, where $2x$ is the coordination number of M, are interesting since they are non-electrolytes. Zinc, for example, forms $Zn(NH_3)_2Cl_2$ consisting of tetrahedral molecules (*a*), which may be compared with the ions $[Zn(NH_3)_4]^{2+}$, (*b*), in a salt such as $Zn(NH_3)_4Cl_2.H_2O$.



(*a*)



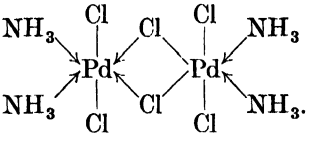
(*b*)

The compound $Pd(NH_3)_2I_2$ is similarly constituted to (*a*) but planar instead of tetrahedral. It does not, however, follow that all compounds with similar empirical formulae are of this type, for one form of $Pt(NH_3)_2Cl_2$ consists of planar ions $[Pt(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$, and $Cd(NH_3)_2Cl_2$ has an entirely different structure since the coordination number of cadmium by Cl and NH_3 is six.

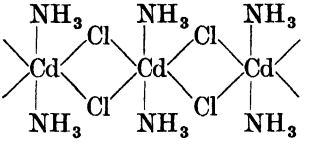
In the compounds we have mentioned so far the total number of NH_3+X is equal to or greater than the coordination number of M. A halogen atom may, however, form bonds to two or more metal atoms as in the structures of the metallic halides, and hence more complicated molecules are possible. Since in these some or all of the halogen atoms are shared between M atoms, the total number of $X+NH_3$ in the empirical formula will be less than the coordination number of M. This is exactly analogous to the sharing of, for example, X atoms of MX_6 octahedra in simple halides. We may have discrete MX_6 ions or compounds containing other X:M ratios built up of MX_6 octahedra sharing corners, edges, or faces in various ways. The following chlorides illustrate this point:

Compound	*Ratio* X:M	*Nature of* MX_n *grouping*
K_2PtCl_6	6:1	Finite $PtCl_6$ ions
$K_3W_2Cl_9$	$4\frac{1}{2}$:1	,, W_2Cl_9 ,,
$K_2SnCl_4.H_2O$	4:1	Infinite chains
NH_4CdCl_3	3:1	,, complex chains
$CdCl_2$	2:1	,, layers

Few complex aminohalides have been studied. The compound with the empirical formula $(NH_3)_2PdCl_3$ almost certainly contains polynuclear finite complexes of the type



It has already been mentioned on p. 233 in connexion with the colour of compounds containing elements in two valency states. As an example of an aminohalide consisting of infinite chains we may give $Cd(NH_3)_2Cl_2$, in which there are chains:

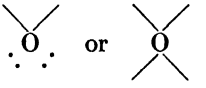


which should be compared with the MX_4^{2-} chains in $K_2SnCl_4.H_2O$ and $K_2HgCl_4.H_2O$ illustrated on p. 150.

CHAPTER IX

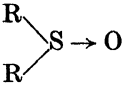
OXYGEN AND SULPHUR

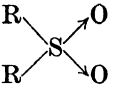
In this chapter we shall deal with some aspects of the chemistry of oxygen and sulphur. Selenium and tellurium will be mentioned only when the properties of their compounds illustrate some general point. Each of these elements has a group of six electrons in the outermost shell, the electronic structures of O and S being 2, 6 and 2, 8, 6, In each case an inert gas configuration can be attained by acquiring, or acquiring a share in, two more electrons. The simplest ways in which this can be done are (*a*) the formation of the ions O^{2-} and S^{2-}, (*b*) the formation of two electron-pair bonds, and (*c*) the formation of one such bond and the addition of one electron (OH^-, SH^-). When one or two bonds have been formed the remaining unshared electron pairs can form further bonds to a total of four, utilizing in this way the one *s* and the three *p* orbitals. When less than four bonds are formed it is reasonable to suppose that the *p* orbitals are used, but this point will be considered in more detail when we come to the 2-covalent compounds of these elements. In most of their compounds we find these elements in one of the forms

O^{2-} $:\ddot{O}:$ OH^- $:\ddot{O}—H^-$  or

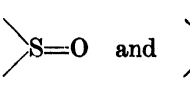
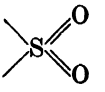
Covalencies of 2 and 4 are far more usual than 3, which is found in such compounds as $(Et_3S)I$—the compounds SEt_2 and $(SEt_3)I$ may be compared with NEt_3 and $(NEt_4)I$—and in many crystalline sulphides (see below). The utilizing of the pairs of unshared electrons after the formation of two covalent bonds is shown in the formation of sulphoxides and sulphones:


Sulphide

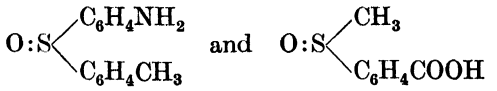

Sulphoxide


Sulphone

These compounds illustrate another point. We have mentioned three ways in which the octet of valency electrons in O and S may be completed. There are other simple ways, e.g. the formation of one double bond (O=) or the formation of an electron-pair bond both electrons of which come from another atom—the coordinate link (→O or $^{+-}$O). More complex possibilities include the formation of one single and two 3-electron bonds as suggested for the O_2 molecule (see below). The sulphoxides and sulphones were originally assumed to contain double bonds, viz.

 and 

but it was found that the S—O bonds behave as single and not as double bonds. According to the ideas of classical stereochemistry the three bonds in a sulphoxide should be coplanar on the above formulation, but it is found that they are not, for the compounds



are optically active. This was considered an important justification for representing the S—O bonds in such compounds by the symbol S→O. We have already discussed the use of this symbol in Chapter II.

As might be expected from the similarity in outer electronic structure of O and S, these elements form many series of compounds with analogous formulae, but in their chemistry they show many differences. In the sixth Periodic Group there is a steady change in properties with increase in atomic weight as we go from the typical elements through the B sub-group. The light elements are typical non-metals and the heavier elements become progressively more metallic in their properties. As we proceed from O to Te the atoms increase in size and we may associate the change in behaviour of the outer valency electrons with the increased screening of the nuclear charge by the intervening completed shells of electrons. This shows itself in a number of ways:

(1) The decreasing stability of negative ions. The alkali oxides, sulphides, selenides, and tellurides all crystallize with typical ionic structures showing that all the ions O^{2-}, S^{2-}, Se^{2-}, and Te^{2-} exist in solids. These compounds are all soluble in water, but the anhydrous compounds cannot be recovered from the solutions. If Na_2O is dissolved in water the solution on evaporation yields solid NaOH. A concentrated solution of Na_2S on evaporation yields the hydrate $Na_2S.9H_2O$, but in dilute solution the sulphur is almost entirely in the form of SH^- ions. This hydrosulphide ion is much less stable than the hydroxyl ion and, on warming, solutions of hydrosulphides evolve H_2S. Solutions of selenides and tellurides hydrolyse still more readily, liberating the hydrides, which are easily oxidized to the elements. In the case of oxygen, therefore, we have the combination of O^{2-} with H^+ giving the very stable OH^- ion. Sulphur behaves similarly, giving the less stable SH^- ion, but with Se^{2-} and Te^{2-} the process easily goes a stage farther to H_2Se and H_2Te. The increasing tendency for the divalent ion to form the hydride ($X^{2-} \rightarrow XH^- \rightarrow XH_2$) is not due to the increasing stability of the hydrides, for this decreases rapidly from H_2O to H_2Te, the latter being strongly endothermic, but to the decreasing stability of the negative ions.

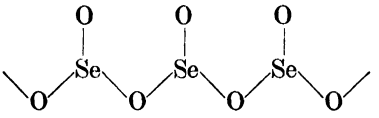
These elements do not, with the possible exception of Te, form stable positive ions. In compounds such as $Te(NO_3)_4$ and $Te(SO_4)_2$ the Te^{4+} ion may exist, but their structures are not known. The formation of the ion Te^{4+} rather than Te^{6+} would be due to the inertness of the two *s* electrons —compare the inert pair of Tl, etc., Chapter XVI.

(2) The bonds formed by S with a particular element have less ionic character than those between O and the same element. Pauling assigns the following electronegativity values:

O	3·5	compare	F	4·0
S	2·5		Cl	3·0

Whereas many dioxides have simple ionic structures, the corresponding disulphides have often layer structures, and in general the same structure types are found for crystalline oxides as for fluorides of the same formula type, and similarly for sulphides and chlorides.

The dioxides of S, Se, and Te form an interesting series. Sulphur dioxide is a simple molecular oxide. SeO_2, of course, exists in the vapour as simple molecules but in the solid state consists of infinite chains



while TeO_2, which is dimorphous, forms ionic crystals. We should mention here that the structures of the molecules SO_2 and SeO_2 suggest that the S—O and Se—O bonds are not simple electron-pair bonds. The observed S—O distance in SO_2 is 1·43 A. and Se—O in SeO_2 1·61 A. These values are approximately the same as in the SO_4^{2-} and SeO_4^{2-} ions respectively and are considerably less than the sums of the single-bond radii. Moreover, the O—S—O bond angle calculated from the entropy is $121\pm5°$, which is close to the value (125° 16′) expected for one single and one double bond. The approximate bond angle determined by an electron diffraction study is $120\pm5°$. It is therefore suggested that these dioxides resonate between the forms $S\langle^{O}_{O}$ and $S\langle\!\!\langle^{O}_{O}$ and similarly for SeO_2 (see also p. 307).

The structures of many oxides and sulphides are discussed in more detail in a later section.

(3) The halogen compounds of O, S, Se, and Te show remarkable differences. The highest known fluoride of O is OF_2, but the other elements all form hexafluorides. Oxygen and fluorine show little tendency to combine (the first of the three known fluorides OF_2, O_2F_2, and OF was not prepared until 1927), but the more electropositive elements readily form fluorides in which the elements exhibit high coordination numbers. In such compounds the bonds have appreciable ionic character, though their formulae are often taken to indicate the maximum covalency of the element concerned. Thus S forms SF_6, which is remarkable for its stability, but there are no other elements with which S forms more than four bonds.

(4) A further difference between O and S, also associated with the greater tendency of S to form covalent bonds, is the easy formation of S—S compared with O—O bonds. The elements themselves, and also Se and Te, all form diatomic molecules. The O_2 molecule does not contain

a double bond ($\left(\cdot\dot{O}=\dot{O}\cdot\right)$ since the solid is paramagnetic—practically all other molecular crystals are diamagnetic—and the magnetic moment shows that the molecule contains two unpaired electrons. In the O_2 molecule in its normal state the atoms are probably linked by one electron-pair and two 3-electron bonds, leaving the remaining orbital of each atom occupied by a pair of unshared electrons, $:O\dot{\cdot}\dot{\cdot}O:$. The molecules S_2, Se_2, and Te_2 are probably similarly constituted and also the molecule SO, which is said to be formed by passing an electric discharge through a mixture of SO_2 and S vapour.

Studies of the magnetic susceptibility of solutions of liquid oxygen in liquid nitrogen suggest the presence of O_4 molecules, in which O_2 molecules may be held together by weak interaction between their unshared pairs of electrons. Other examples of compounds containing O atoms directly linked to one another are few in number. There are the peroxides and superoxides, containing the ions O_2^{2-} and O_2^-, ozone O_3, hydrogen peroxide H_2O_2, and the per-acids and their salts.

(5) The last important difference between O and S which we shall mention here is the formation by the former of H bonds, a property of only the most electronegative elements. As a result of the formation of H bonds many compounds of O have properties very different from those to be expected by analogy with the corresponding compounds of S. These 'abnormalities' will be dealt with in later sections devoted to the structure of water and the structures of hydrates and hydroxides. For example, the existence of many heavy metal hydroxides is associated with this formation of H bonds by O; the corresponding hydrosulphides do not exist, only ionic hydrosulphides being known.

MOLECULES AND IONS CONTAINING O—O BONDS

Peroxides and Superoxides

On heating in excess of oxygen the alkali metals yield the following products: Li_2O, Na_2O_2, KO_2, RbO_2, and CsO_2. The analogues of Na_2O_2 can be prepared in other ways. Anhydrous compounds CaO_2, SrO_2, and BaO_2 are also known. The latter two are prepared by heating the normal oxide in oxygen and the former by dehydrating the octahydrate formed from $Ca(OH)_2$ and H_2O_2 or Na_2O_2 in aqueous solution. These peroxides are obviously related to H_2O_2 since decomposition of BaO_2, for example, by dilute H_2SO_4 yields a solution of that compound. Examination of the crystal structures of SrO_2 and BaO_2 shows the presence of O_2^{2-} ions with presumably the simple structure, $^-:\dot{\underset{\cdot\cdot}{O}}—\dot{\underset{\cdot\cdot}{O}}:^-$. Such compounds as lead 'peroxide', PbO_2, and manganese dioxide, MnO_2, are of an entirely different type and contain the ordinary O^{2-} ion.

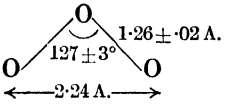
The final oxidation products of the heavier alkali metals, KO_2, RbO_2, and CsO_2, were formerly called tetroxides and written with the doubled

formulae, K_2O_4, etc. They are now known to contain the 'superoxide' ion O_2^-, the evidence being the crystal structure of KO_2 and the magnetic susceptibility of the compound. The compounds KO_2, RbO_2, and CsO_2 all crystallize with the CaC_2 type of structure, and there are discrete O_2^- ions analogous to C_2^{2-}. Crystalline KO_2 is paramagnetic with a magnetic moment of about 2 Bohr magnetons, corresponding to one unpaired electron (theoretical value 1·85 Bohr magnetons), indicating the presence of the O_2^- ion with a total of thirteen electrons. The double ion O_4^{2-} would contain an even number of electrons. The ion may be represented with one single and one 3-electron bond, $\left[\cdot\dot{O}\cdot\cdot\!-\!\dot{O}\cdot\right]^-$.

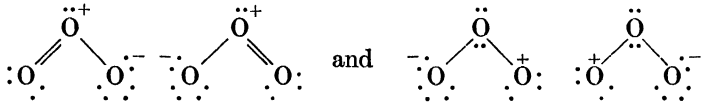
Intermediate between the superoxides and the peroxides are the oxides of formula M_2O_3 which are supposed to be formed by all the alkali metals except Li, either by heating the superoxide or by the action of oxygen on a solution of the alkali metal in liquid NH_3. It has been suggested that they contain both the peroxide ion, O_2^{2-}, and the superoxide ion, O_2^-, i.e. that K_2O_3 should be represented by $K_4O_2^{2-}(O_2^-)_2$. It has also been suggested, however, as a result of studies of the rate of decomposition of $2KO_2 \rightarrow K_2O_2 + O_2$ that there is no intermediate product K_2O_3 in the decomposition of KO_2, so that the evidence for the existence of these compounds is not very satisfactory. It appears safe to say that there is no discrete ion O_3^{2-}.

Ozone

An electron diffraction study indicates the following configuration for the O_3 molecule:



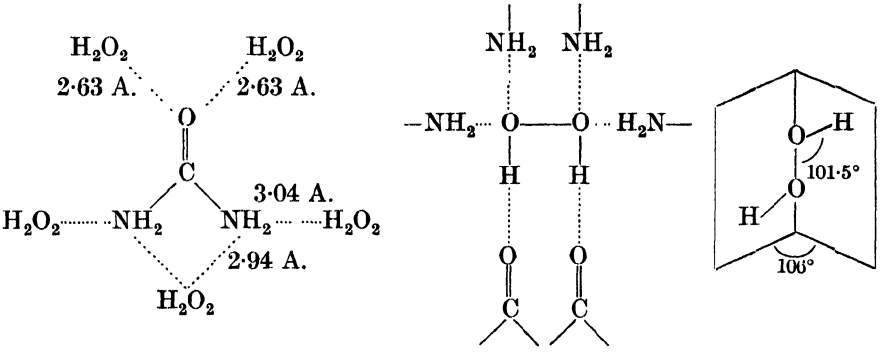
The O—O distance is much smaller than that in H_2O_2, 1·46 A., which is taken as the standard length of a single O—O bond. It may be compared with O=O, 1·27 A., and the approximate value 1·28±0·07 A. found in the O_2^- ion. Resonance between the following structures has been suggested:



Hydrogen Peroxide

A complete study of solid H_2O_2 has not yet been made. An electron diffraction study of the vapour gives only the O—O distance (which agrees with that given below), for the H atoms cannot be located in this way. An X-ray study of the liquid indicated cubic close-packing of the O atoms. The model calculated by wave-mechanical methods (the Penney-Sutherland model), with angles of about 100°, is in agreement with the dipole

moment ($2{\cdot}13\times10^{-18}$ e.s.u.) and is confirmed by the X-ray crystallographic study of the addition compound with urea, $CO(NH_2)_2.H_2O_2$. The structure of this compound is of particular interest because certain interatomic distances indicate hydrogen bonds, and from the orientation of these bonds relative to the O—O bond in the H_2O_2 molecule the interbond angles in that molecule can be determined. In $CO(NH_2)_2.H_2O_2$ the urea and hydrogen peroxide molecules are linked together by hydrogen bonds. These are of two kinds: strong O—H—O bonds between carbonyl O atoms of urea and O atoms of H_2O_2, and weaker N—H—O bonds between NH_2 groups of urea and O atoms of H_2O_2 molecules. The arrangement of these bonds is shown diagrammatically below, and the configuration of the molecule is shown. The O—H distances cannot be determined by X-ray methods. The O—O distance in H_2O_2 is $1{\cdot}46\pm0{\cdot}03$ A.



Per-acids

The per-acids have already been mentioned in Chapter VII. Little is known of the structures of these compounds or of their salts except in the case of the perdisulphates. By the electrolysis of sulphuric acid with separate anode and cathode compartments two acids, H_2SO_5 and $H_2S_2O_8$, are formed in proportions depending on the conditions. Well-crystallized salts (of the alkalis, Ba and Pb) of $H_2S_2O_8$ are known, but no crystalline salts of H_2SO_5 have been prepared. There are interesting relations between these acids. For example, $H_2S_2O_8$ may be converted into H_2SO_5 in solution in concentrated H_2SO_4:

$$H_2S_2O_8+H_2O \rightarrow H_2SO_4+H_2SO_5$$

or by the action of H_2O_2:

$$H_2S_2O_8+H_2O_2 \rightarrow 2H_2SO_5.$$

The structure of the $S_2O_8^{2-}$ ion is known from the structure of the salt $(NH_4)_2S_2O_8$ and is shown in Fig. 80 (*d*).

Unstable percarbonates (e.g. $K_2C_2O_6$) may also be prepared electrolytically, and compounds such as Na_2CO_4 are said to be obtained by the action of H_2O_2 on Na_2CO_3 solution. It is not, however, certain that the latter compounds contain mononuclear ions CO_4^{2-}, for until the anhydrous crystalline compounds can be obtained and examined we cannot rule out

the possibility that they contain H_2O_2. For example, a 'hydrate' $Na_2CO_4.H_2O$ might actually be $Na_2CO_3.H_2O_2$. Many compounds apparently containing, or derived from, H_2O_2 are loosely described as

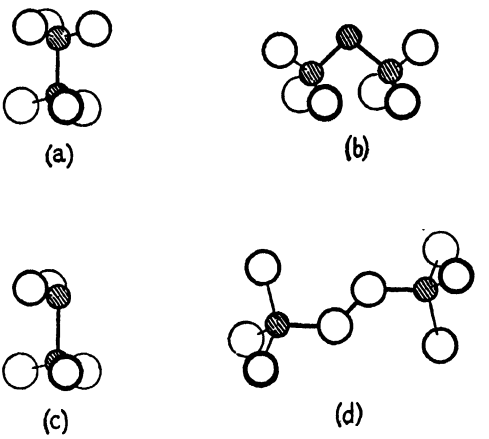


FIG. 80. The structures of some complex sulphur oxy-ions: (*a*) the dithionate ion, $S_2O_6^{2-}$, (*b*) the trithionate ion, $S_3O_6^{2-}$, (*c*) the metabisulphite ion, $S_2O_5^{2-}$, (*d*) the perdisulphate ion, $S_2O_8^{2-}$.

derivatives of per-acids, but much more experimental study of such substances is required.

MOLECULES AND IONS CONTAINING S—S BONDS

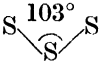
We have now reviewed the various classes of compounds containing directly linked O atoms, and we have seen that except in the case of ozone the linking of O to O never proceeds beyond the stage O—O. Sulphur, however, presents a very different picture, a feature of its chemistry being the easy formation and breaking of chains of S atoms. Let us first consider the structures of the elements O, S, Se, and Te. The diatomic forms of the elements have already been mentioned. The most complex covalent molecule formed by O is the diatomic O_2 molecule, other than ozone and the O_4 'molecule' noted previously, in which form it exists in the solid state. In orthorhombic sulphur the unit of structure is the S_8 molecule, forming a puckered 8-membered ring. The properties of liquid sulphur are complex, and to account for them the existence of various other molecular forms has been postulated, e.g. S_6 and S_4. It is more probable that in the liquid some, if not all, of the S_8 rings open out and that there is a constant breaking and joining up of S chains of different lengths. A recent thermodynamical treatment of the properties of liquid sulphur is based on the view that the mobile liquid at temperatures below about 160° C. (S_λ) consists essentially of S_8 ring molecules and that the viscous liquid (S_μ) at high temperatures consists of chains of various lengths. Plastic S, obtained by quenching the liquid, contains

such chains. The X-ray diffraction effects from liquid S have been interpreted as showing that every S atom has two nearest neighbours at a distance of 2·05 A., very nearly the same distance as in rhombic S (2·12 A.). The vapour of sulphur contains S_8 molecules at temperatures just above the boiling-point, but as the temperature is raised dissociation to S_2 molecules takes place and is complete at 900° C. In solid Se and Te the atoms form infinite zigzag chains (see p. 538).

The complex ions formed by S provide many examples of S—S bonds. If a solution of potassium sulphite is saturated with sulphur dioxide and allowed to crystallize, the stable salt potassium metabisulphite, $K_2S_2O_5$, is obtained. X-ray examination of this salt shows that the ion has the structure shown in Fig. 80 (*c*). A warm solution of an alkali sulphite dissolves S, forming a thiosulphate. An X-ray study of the potassium salt, $K_2S_2O_3$, shows that the $S_2O_3^{2-}$ ion has, like the SO_4^{2-} ion, a tetrahedral configuration.

Polysulphides

These are formed, with the normal sulphide, when an alkali or alkaline-earth carbonate is fused with S or better when S is digested with a solution of the sulphide or hydrosulphide. From the resulting deeply coloured solutions various salts can be obtained, e.g. from K_2S_2 to K_2S_5. The ions S_n^{2-} are chain ions, and from an X-ray study of BaS_3 the S_3^{2-} ion is assigned the structure



In solution the longer ions are not very stable and apparently form an equilibrium mixture of the lower ions, some S being deposited. They are immediately decomposed by acids, but if a polysulphide is poured into aqueous HCl a yellow oil separates from which pure H_2S_2 and H_2S_3 may be separated by fractional distillation as yellow liquids. H_2S_5 and H_2S_6 have been prepared, but H_2S_4 does not seem to have been isolated.

The highly interesting association of two S atoms in the covalent S_2 group in FeS_2 and other disulphides is not paralleled by oxygen.

Thionates

The known thionate ions have the general formula S_nO_6, where n is 2, 3, 4, 5, or 6. The dithionate ion, $S_2O_6^{2-}$, is formed by the direct union of two SO_3^{2-} ions. Its structure is shown in Fig. 80 (*a*), and that of the trithionate in Fig. 80 (*b*), derived from X-ray studies of $K_2S_2O_6$ and $K_2S_3O_6$ respectively. As might be expected, $S_2O_6^{2-}$ is not formed by the methods which give rise to the higher thionates. These require S as well as SO_3 groups, as may be seen from their formulae, $O_3S—S_n—SO_3$, and they are formed whenever S and SO_3^{2-} ions are present together in aqueous solution. A mixture of all the ions from S_3O_6 to S_6O_6 is usually produced in such circumstances (compare the polysulphides), and, moreover, when any one of the higher thionic acids is dissolved in water it is converted,

though very slowly, into a mixture of them all. The alkali and alkaline-earth salts, however, are very stable in solution and interconversion of the ions takes place only in the presence of hydrogen ions. Certain reactions tend to produce more of one particular $S_nO_6^{2-}$ ion, a fact which is utilized in their preparation. The controlled decomposition of a thiosulphate by acid gives largely $S_5O_6^{2-}$, while the oxidation of $S_2O_3^{2-}$ by H_2O_2 gives $S_3O_6^{2-}$ and by iodine (or electrolytically) yields the tetrathionate ion, $S_4O_6^{2-}$, e.g.

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-.$$

As mentioned above, the dithionates are made by special methods such as the electrolysis of neutral alkali sulphite solution or by passing sulphur dioxide into a suspension of MnO_2 in water. The final oxidation product of all the thionate ions is the SO_4^{2-} ion. Further examples of the numerous reactions between oxy-ions of S are the action of a sulphite on tetra- and penta- thionates:

$$S_4O_6^{2-} + SO_3^{2-} \rightarrow S_3O_6^{2-} + S_2O_3^{2-}$$
$$S_5O_6^{2-} + 2SO_3^{2-} \rightarrow S_3O_6^{2-} + 2S_2O_3^{2-}$$

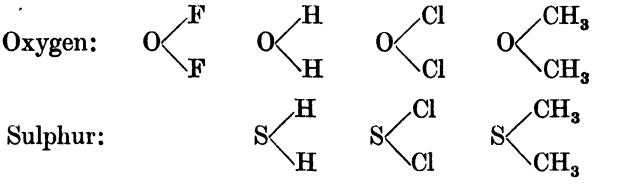
and the action of KOH on the higher thionates:

$$2S_5O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 3H_2O$$
$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O$$
$$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O.$$

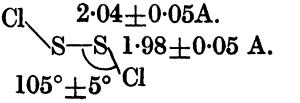
Apart from the compounds just mentioned, our main concern now is to give, to the extent our present knowledge allows, a comprehensive survey of the structures of oxides and sulphides. Before proceeding to this, however, we shall refer briefly to a few simple molecules and ions formed by O and S.

MOLECULES CONTAINING 2-COVALENT O OR S

Structural studies of a few halides, of the hydrides, and of certain organic derivatives have been made. These show that molecules OR_2 or SR_2 (where R is a group or atom forming a single bond to O or S) are non-linear. Examples are:



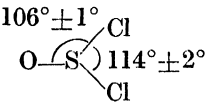
The values of the interbond angles in such molecules have been given and discussed in Chapter III. The more complex molecule of S_2Cl_2 has the configuration shown below.



MOLECULES CONTAINING 3-COVALENT S

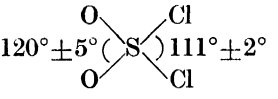
Sulphur trioxide, SO_3, has been shown by electron diffraction to form a symmetrical planar molecule in the vapour state with bond angles of $120° \pm 2°$ and S—O = $1{\cdot}43 \pm 0{\cdot}02$ A. (see below). This molecule may be compared with the planar NO_3^- and CO_3^{2-} ions. The planar configuration is consistent with the zero dipole moment.

Thionyl chloride, $SOCl_2$, on the other hand, is found to be pyramidal with bond angles as indicated, S—Cl = $2{\cdot}07 \pm 0{\cdot}03$ A. and S—O = $1{\cdot}45 \pm 0{\cdot}02$ A.



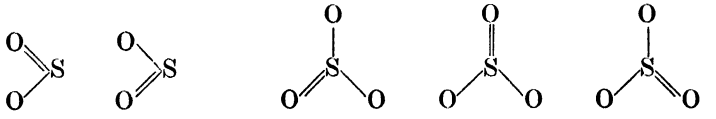
MOLECULES AND IONS CONTAINING 4-COVALENT O OR S

There are many complex ions and molecules containing 4-covalent S, e.g. SO_4^{2-}, SO_3F^- (in the very stable alkali fluorsulphonates), SO_2F_2, and SO_2Cl_2, $S_2O_3^{2-}$ (see above), $[SO_3NH_2]^-$, $SO_2(NH_2)_2$, and the more complex $[O_3S—SO_3]^{2-}$ and $[O_3S—O—SO_3]^{2-}$ ions already mentioned. The SO_4^{2-} ion has been found to be tetrahedral in many crystalline sulphates, and $[SO_3NH_2]^-$ has the same configuration in KSO_3NH_2. An electron diffraction study of sulphuryl chloride, SO_2Cl_2, shows that the molecule forms a distorted tetrahedron



with S—Cl = $1{\cdot}99 \pm 0{\cdot}02$ A. and S—O = $1{\cdot}43 \pm 0{\cdot}02$ A.

The observed S—O distances in SO_2, SO_3, $SOCl_2$, and SO_2Cl_2 are all approximately the same and as short as, or shorter than, the length expected for S=O. This is 1·54 A. for the double-single bond-length factor 0·91 and 1·47 A. for the factor 0·87. The similarity in these distances does not appear to be consistent with the types of resonance postulated in these molecules. In SO_2 (*a*) we should expect bonds with 50 per cent. double-bond character, and in SO_3 (*b*) 33 per cent. double-bond character.



(*b*)

Molecules containing 4-covalent oxygen are very few in number. The molecule of basic beryllium acetate, $OBe_4(CH_3COO)_6$ is an interesting example of 4-coordinated oxygen—Fig. 81.

The simplest crystal structures containing 4-covalent oxygen and

sulphur are those of certain oxides and sulphides with the zinc-blende structure (see, however, p. 66).

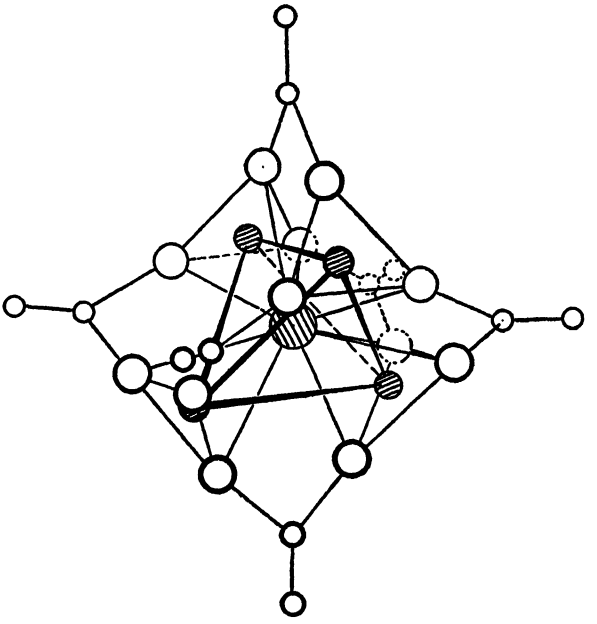


FIG. 81. The molecule of basic beryllium acetate, $OBe_4(CH_3COO)_6$, drawn (not strictly to scale) to show the central oxygen atom (large shaded circle) surrounded tetrahedrally by four Be atoms (small shaded circles). An acetate group lies beyond each edge of the tetrahedron. Each Be atom has four O atoms arranged tetrahedrally as nearest neighbours, the central one and three of different acetate groups. (Small unshaded circles represent C atoms; H atoms are omitted.)

OXIDES AND SULPHIDES

There are a few general points which are worth noting before we proceed to the actual structures of these compounds. Oxygen is more electronegative than sulphur. By this we mean that oxygen shows a greater tendency to complete its octet by acquiring two electrons than is the case with sulphur, which prefers to complete its octet by sharing electrons, i.e. by forming covalent bonds. Alternatively we may say that when the ion O^{2-} or S^{2-} is formed, the latter is more easily 'polarized', the term polarization meaning a distortion of the electronic system of the ion which in the extreme case leads to sharing of some of the electrons with other atoms. The result is that a bond M—O with a given element has more ionic character than the corresponding bond M—S. We therefore find the following differences:

(1) The only ionic sulphides are those of the most electropositive metals, the alkalis and the alkaline-earths, in which the positive ions have low charges, and the sulphides of certain transition elements which can also form ions of low charge. Such sulphides have structures similar to those

of the corresponding oxides—compare the structures of the alkali and alkaline-earth sulphides and oxides, MnO and MnS, containing ions M^+ or M^{2+}.

Many oxides M_2O_3 are ionic, but there are apparently few ionic sulphides containing M^{3+} ions, though little is known of the structures of sulphides M_2S_3. Aluminium sulphide is probably ionic since it is immediately decomposed by water, but others, such as V_2S_3 and Cr_2S_3, which have the appearance of graphite, are probably layer lattices.

When we come to compounds MO_2 and MS_2 we find that many dioxides are ionic but there are no essentially ionic disulphides, i.e. the ion S^{2-} is not capable of existence in the neighbourhood of M^{4+} ions. Instead of ionic structures the disulphides crystallize with layer structures or the very interesting pyrites type of structure which is illustrated on p. 390. The only point which we need note here is that this structure contains discrete S_2 groups. A survey of the empirical formulae of the various oxides and sulphides of the transition metals shows that in some cases an oxide AO_n exists but the analogous sulphide AS_n does not. In other cases a particular sulphide is known but the corresponding oxide does not exist. We may relate such facts to the properties of oxygen and sulphur in the following way. Let us consider the dioxides and disulphides of lead and iron. Lead peroxide has the rutile structure (p. 100) containing Pb^{4+} ions, but the S^{2-} ion is not stable in such an arrangement and PbS_2 does not exist. Strictly this only relates to the non-existence of PbS_2 with an ionic structure—the inability of lead to form PbS_2 with some other structure involving covalent bonds must be accounted for in terms of the properties of the Pb atom. In the case of Fe the disulphide FeS_2 has the pyrites and marcasite structures, both containing S_2 groups. No such covalent group is formed by oxygen and FeO_2 does not exist. A comparison of the structures of pairs of compounds like TiO_2 and TiS_2 or MoO_2 and MoS_2 shows the difference in bond type of bonds M—O and M—S. These two dioxides have the rutile structure,* in which the O^{2-} ion is surrounded by three metal ions in a triangular planar arrangement, a configuration associated with essentially ionic bonds. The disulphides TiS_2 and MoS_2, on the other hand, form layer lattices, in which the S atom forms three pyramidal bonds.

(2) Resemblance between the structures of oxides and sulphides is confined to those of the alkali metals, of the metals of Group II with the exception of Hg, of Mn and certain other elements of the later groups which form simple molecular oxides and sulphides. Some of the differences between oxides MO_2 and M_2O_3 and the corresponding sulphides have already been mentioned. The monoxides and monosulphides of many transition metals show striking differences in structure. The structures of the sulphides show in general more resemblance to alloys than to covalent compounds and in some cases sulphides with simple formulae

* TiO_2 has two other forms, but the immediate environment of the Ti^{4+} and O^{2-} ions is similar in all three polymorphic forms.

have surprisingly complex structures compared with those of the corresponding oxides—compare, e.g., the complex structure of CuS with that of CuO. The monoxides FeO, NiO, and CoO all crystallize with the rock-salt structure in which each type of atom is 6-coordinated, though it should be noted that FeO is always deficient in Fe. FeS and CoS, however, have the NiAs structure, FeS being a non-stoichiometric crystal like FeO, while NiS has a peculiar 5:5 coordinated structure.

(3) The tendency of many transition metal sulphides to resemble alloys is shown by the formulae of the solid phases in such metal-sulphur systems. As we shall see later, when we consider the structures of alloys, the compositions of such phases are not consistent with the ordinary ideas of chemical valencies since the structures are determined by other considerations such as atomic sizes and electron-atom ratios. In the system Co—S the following well-defined phases are found: Co_9S_8, CoS, Co_3S_4, and CoS_2. In Co_9S_8 the S atoms form a cubic close-packed lattice and the Co atoms are situated in certain of the holes between the S atoms. In both Co_3S_4 and Co_9S_8 some of the Co atoms are surrounded tetrahedrally by four S and some octahedrally by six S.

(4) A very important difference between the structures of complex sulphides $A_mB_n \ldots S_x$ and those of complex oxides is that in the latter, complex oxy-ions of all kinds are found—finite ions and infinite chain and layer ions (as, for example, in the silicate structures), but the analogous infinite thio-ions do not exist. Instead, the complex sulphides are essentially covalent—often with semi-metallic properties—and examples of the relation of the structures of some of these compounds to those of simple sulphides will be given later.

(5) Many heavy-metal sulphides have unusual physical properties which can only be mentioned here. As examples of the optical properties we may quote the metallic appearance of PbS and FeS_2, the characteristic lustre of crystalline zinc-blende and the brilliant colours of CdS (yellow), HgS (vermilion), and CuS (blue). Some of these properties are more pronounced in the selenides and tellurides, which approach even closer to alloys in many respects. A number of solids other than metals conduct electricity to a small extent at ordinary temperatures, the conductivity approaching zero as the temperature is lowered—contrast the behaviour of metals. Such solids are termed semi-conductors, and the experimental evidence suggests that in some cases there is ionic and in others electronic conductivity. Apart from its dependence on temperature the conductivity is also affected by impurity content (including in this the presence of excess atoms of one or other of the constituent atoms) and previous mechanical treatment. The majority of semi-conductors are oxides (CuO, ZnO, NiO, Fe_2O_3, Fe_3O_4, Cu_2O), sulphides (PbS, Ag_2S), or iodides (AgI, CuI). In the case of the non-stoichiometric oxide semi-conductors, alteration of the oxygen pressure above the crystal shows that CuO owes its conductivity to the presence of excess of oxygen atoms in the lattice, whereas the conductivity of ZnO is apparently due to the presence of excess of Zn atoms.

After these preliminary remarks we shall now describe the structures of some oxides and sulphides. In view of their similarity we shall describe the simple ionic compounds together and then deal separately with some of the typical structures of oxides and sulphides.

The Ionic Oxides and Related Compounds

The structure commonly found for the alkali metal oxides M_2O and the corresponding sulphides, selenides, and tellurides is the anti-fluorite structure, with 4:8 coordination, so called because the alkali metal ions occupy the F positions and the O (S, Se, Te) ions the Ca positions of the CaF_2 structure. The compounds which have been shown to crystallize with this structure are:

Li_2O	Li_2S	Li_2Se	Li_2Te
Na_2O	Na_2S	Na_2Se	Na_2Te
K_2O	K_2S	K_2Se	K_2Te
	Rb_2S		

Cuprous sulphide and selenide, Cu_2S and Cu_2Se, also crystallize with this structure, but Cu_2O and Ag_2O have a quite different structure of lower coordination (2:4) which is illustrated later.

The oxides and sulphides, MO and MS, of the elements other than Hg of the second Periodic Group crystallize with one or more of three structures, the rock-salt, zinc-blende, or wurtzite structures. In addition to crystallizing with the zinc-blende structure HgS also has a second form, for which see p. 516. The structures of these Group II compounds are shown in the tables below.

	O	S	Se	Te
Be	W	Z	Z	Z
Mg	NaCl structure			W
Ca				
Sr				
Ba				

	O	S	Se	Te
Zn	WZ	WZ	Z	WZ
Cd	NaCl	WZ	WZ	Z
Hg		Z	Z	Z

(W indicates wurtzite, Z the zinc-blende, and NaCl the rock-salt structure.)

It is seen that the alkaline-earth compounds and those of Mg, except MgTe, crystallize with the 6:6 coordinated NaCl structure. The Be compounds have the 4:4 coordinated zinc-blende or wurtzite structures. The latter structures would be expected for the Be compounds if we treat them as ionic, on account of the small size of the Be^{2+} ion. Only four O^{2-} ions would be expected around that ion, whereas six can be accommodated around the larger ions of the other metals. The situation is not, however, quite as simple as this, for the bonds in the Be compounds certainly have appreciable covalent character. The physical properties of MgO show that the bonds in this compound also, with the NaCl structure, are not purely ionic. The highly symmetrical structures involving

tetrahedral and octahedral coordination of both atoms could arise for 100 per cent. ionic or for pure covalent bonds. Thus the fact that the structure of BeO is geometrically similar to that of diamond, a typical covalent crystal, does not mean that the Be—O bonds are covalent. Similarly the crystal is not necessarily 100 per cent. ionic because it has the NaCl structure. The following oxides, sulphides, etc., also crystallize with this structure: FeO, CoO, NiO, PbS, PbSe, PbTe, MnO, MnS, MnSe, and SnTe.

TABLE 17

The Crystal Structures of some Oxides

Type of structure	*Coordination numbers of* M *and* O *and formula type*	*Name of structure*	*Examples*
Infinite 3-dimensional complexes	6:2 MO_3	..	ReO_3
	8:4 } MO_2	Fluorite	ThO_2, CeO_2, PrO_2, UO_2, (ZrO_2)*
	6:3 }	Rutile	GeO_2, SnO_2, PbO_2, TiO_2, VO_2, NbO_2, TeO_2,† MnO_2, MoO_2, WO_2, RuO_2, OsO_2, IrO_2
	6:4 }	Corundum	α-Al_2O_3, α-Fe_2O_3, Cr_2O_3, Ti_2O_3, V_2O_3, α-Ga_2O_3, Rh_2O_3
	x:x‡ } M_2O_3	'A' rare-earth sesquioxide	La_2O_3, Ce_2O_3, Pr_2O_3, Nd_2O_3
	6:4 }	'C' rare-earth sesquioxide	Mn_2O_3, Sc_2O_3, Y_2O_3, In_2O_3, Tl_2O_3, Sm_2O_3, and other rare-earth oxides M_2O_3
	6:6 MO	Rock-salt	MgO, CaO, SrO, BaO, CdO, VO, MnO, FeO,§ CoO, NiO
	4:8 M_2O	Anti-fluorite	Li_2O, Na_2O, K_2O
	Mixed oxides		
	ABO_3	Perovskite	$CaTiO_3$, $SrTiO_3$, $SrSnO_3$, $SrZrO_3$, $SrHfO_3$, etc.
	ABO_3	Ilmenite	$FeTiO_3$, $NiTiO_3$, $CoTiO_3$, etc.
	AB_2O_4	Spinel AB_2O_4 type	$FeAl_2O_4$, $ZnAl_2O_4$, etc.
		$B(AB)O_4$	$FeMgFeO_4$, $MgTiMgO_4$, etc.
	4:4 MO	Zinc-blende	BeO
		Wurtzite	ZnO
	4:2 MO_2	Silica structures	SiO_2
		Cuprite	Cu_2O, Ag_2O
Layer structures	..	..	MoO_3
Chain structures	..	..	Sb_2O_3
			SeO_2
Molecular: structural units: polymers			Sb_4O_6, As_4O_6
,, ,, : single molecules			All simple molecular oxides

* Distorted (monoclinic) fluorite structure.

† Dimorphous—also structure similar to brookite.

‡ See text (p. 314). § Always deficient in Fe.

We have already mentioned that many metallic dioxides crystallize with the anti-fluorite (8:4) structure. Some of these contain highly charged ions which are not stable in water. Thus when PbO_2 or MnO_2 is dissolved in HCl (they are insoluble in water) the liberated Pb^{4+} or Mn^{4+} ions immediately change into the more stable doubly charged ions, the electrons required being obtained by discharging Cl^- ions, viz.

$$Pb^{4+} + 2Cl^- \rightarrow Pb^{2+} + Cl_2.$$

The process

$$Cl^- + \text{electron} \rightarrow Cl$$

is described as an oxidation process, and these dioxides are therefore described as oxidizing agents.

Survey of Oxide Structures

The crystal structures of some of the simpler oxides are set out in Table 17, which gives the structure type and the coordination numbers of the constituent atoms in the order M:O. The structures are arranged according to the type of complex in the crystal. First there are the ionic 3-dimensional complexes represented by fluorite, rutile, and other structures with high coordination numbers of the metal ions. Then follow the zinc-blende, wurtzite, and other structures in which the metal atom has tetrahedral or lower coordination, after which come the layer and chain structures. Finally there are the finite molecular oxides of the more electronegative elements. The changes in structure type may be associated in a general way with the change in bond type from the essentially ionic structures through the layer and chain structures to the essentially covalent molecular oxides. These changes may be illustrated by the structures of the dioxides of the elements of the fourth Periodic Group. After each compound we give the coordination numbers of M and O and the structure type. Starting with the molecular CO_2 we pass through the silica structures with ionic-covalent bonds to the essentially ionic structures of the later metallic dioxides.

CO_2 (2:1) Molecular

SiO_2 (4:2) Various 3-dimensional complexes

TiO_2 (6:3) rutile, etc.

ZrO_2, HfO_2, ThO_2 (8:4) fluorite

GeO_2 (4:2) quartz; (6:3) rutile

SnO_2 (6:3) ,,

PbO_2 (6:3) ,,

The structures of these compounds should be compared with those of the corresponding disulphides, which are set out in a similar way on p. 387.

Of the structures mentioned in Table 17 the fluorite, rock-salt, and rutile structures have already been illustrated (pp. 98, 100). Of the M_2O_3 structures the three most commonly found are the corundum (Al_2O_3) structure and the A and C rare-earth sesquioxide structures. In the corundum structure six oxygen atoms form an octahedral group around

the metal atom and each O atom is surrounded by four metal atoms. It is sometimes stated that discrete molecules Al<O>Al may be distinguished in this structure. This is not so, for each Al atom has six practically equidistant oxygen neighbours and the structure is best regarded

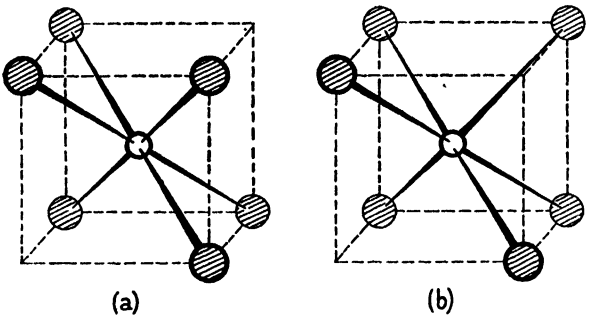


FIG. 82. Environments of the two crystallographically different kinds of metal atoms in the Mn_2O_3 structure (idealized).

as a close-packed lattice of oxygen atoms with Al atoms occupying tetrahedral holes.

The sesquioxides of La, Ce, Pr, and Nd have the A-M_2O_3 structure with the peculiar 7-coordination of the metal atoms to which we refer elsewhere (p. 113). In La_2O_3 a La atom has four O at 2·42 A. and three O at 2·69 A. At high temperatures La_2O_3 and Nd_2O_3 crystallize with the C-M_2O_3 structure. In the C-M_2O_3 structure the M atoms are 6-coordinated but the arrangement of the six neighbours is very unusual (Fig. 82), some of the metal atoms having the coordination group (*a*) and the rest (*b*). The O atoms have four M neighbours. It may be noted that Mn_2O_3 crystallizes with this structure, and the various forms of the element Mn have complex structures (p. 546). The majority of the rare-earth oxides M_2O_3 crystallize with the C-structure and their cell dimensions illustrate the 'lanthanide contraction' (p. 94).

The very simple ReO_3 structure is illustrated later (Fig. 85 (*b*), p. 331). Ferric fluoride, FeF_3, has a somewhat similar structure (based on hexagonal instead of cubic close-packed anions), illustrating the point already mentioned that the structures of many oxides resemble those of fluorides of similar formula type. It is interesting to note that none of the other trioxides of Group VI A metals have such a simple structure as ReO_3. In all of these structures MO_6 octahedra are linked together so that every O is attached to two M atoms (6:2 coordination) to give the required ratio M:O, 1:3. The structures of WO_3 and CrO_3 are only slightly deformed versions of that of ReO_3, each MO_6 octahedron sharing corners with the six surrounding octahedra. In MoO_3, however, the arrangement is quite different and each MoO_6 group shares two edges and two corners

giving rise to a layer structure—a type of structure which is uncommon among oxides (contrast the numerous sulphides with layer structures).

Corresponding to the 6:2 coordinated structures of WO_3 and FeF_3 are the 4:2 coordinated structures of the isomorphous SiO_2 and BeF_2.

In the zinc-blende and wurtzite structures each atom is tetrahedrally coordinated by four of the other kind (see p. 83). The structures of CuO,

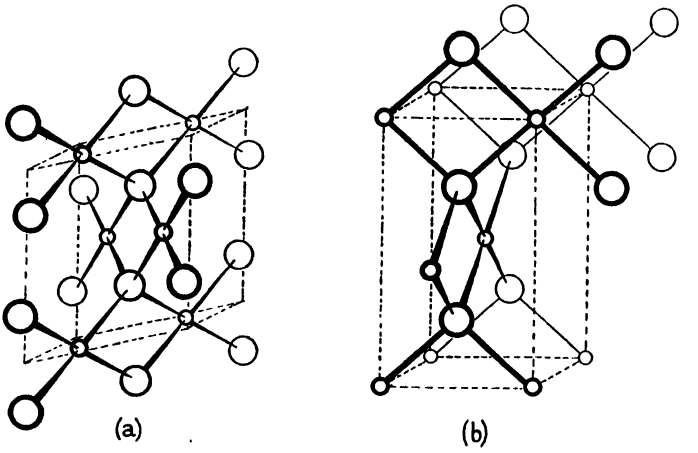
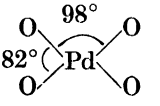


FIG. 83. The crystal structures of (*a*) CuO, tenorite, and (*b*) PdO and PtO.

PdO, and PtO are of quite a different kind, for in these the metal atom forms four planar bonds, and they are good examples of crystals illustrating the stereochemistry of 4-covalent Cu^{2+}, Pd^{2+}, and Pt^{2+}. The structure of CuO should be compared with that of cuprous oxide (p. 316). In PdO and PtO the four O neighbours of a metal atom are arranged in a plane rectangle. The corresponding sulphides, PdS and PtS, are not



isomorphous with one another or with these oxides, but the bonds from the metal atoms in all these structures are approximately of the square planar type. The coordination of O or S is tetrahedral.

The monoxides SnO and PbO have a rather extraordinary layer structure in which the metal atom is bonded to four O atoms which are arranged in a square to one side of it. It is suggested that the inert pair of electrons of the metal atoms occupies the apex of the tetragonal pyramid—for the stereochemistry of Pb see also p. 517.

The structures of the various forms of silica, SiO_2, are described in Chapter XIV. The structure of Cu_2O and the isomorphous Ag_2O is illustrated in Fig. 84.

The existence of linear chains in crystalline SeO_2 has been mentioned in comparing the structures of the oxides of S, Se, and Te. The structure

of the rhombic form of Sb_2O_3 (valentinite) has been compared with that of the cubic form (senarmontite) in Chapter IV. In the former there are infinite chains $(Sb_2O_3)_n$ and in the latter finite molecules Sb_4O_6.

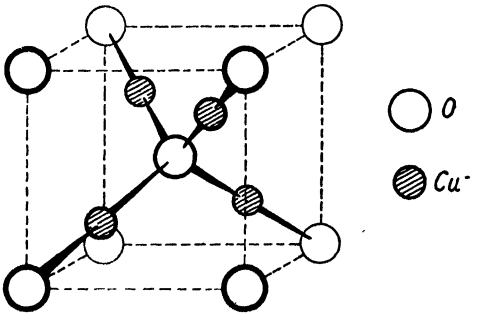


FIG. 84. The crystal structure of cuprite, Cu_2O.

The structures of the molecular oxides of the non-metals are described under the chemistry of the element concerned.

Complex Oxides

The oxides so far described are all simple oxides of general formula A_mO_n. In addition there is a very large class of compounds, which may be written $A_xB_y...O_n$, containing two or more different kinds of atoms in addition to oxygen. Oxygen is the most abundant element in the earth's crust, so that the greater part of the science of mineralogy is concerned with the study of these complex oxides. It is evident that there will be very many geometrical possibilities for the structures of crystals of such compounds and much of this extensive 'oxygen chemistry' remains unstudied. Here we shall be able to give only an outline of this field, which includes some of the most interesting and important groups of inorganic compounds.

First, a few words on the empirical formulae of these compounds. Chemical analysis of the solid gives the ratios of the numbers of atoms of various kinds. It is not always possible to assign a simple formula involving only small integral values of x, y, etc., or to decide which of a number of formulae is the best expression of the analytical results—examples of these difficulties will be given later—but let us assume for simplicity that there is no doubt about the empirical formula of a certain complex oxide. As an example we may take $Be_3Al_2Si_6O_{18}$. In the older text-books such a formula was written in the form $3BeO.Al_2O_3.6SiO_2$ and all such compounds were called 'mixed oxides'. This was followed by attempts to assign 'structural formulae' which grouped the oxygen atoms with the most electronegative element in the compound, and these structural formulae then suggested the postulation of hypothetical acids from which the compounds were supposed to be derived. Thus mixed oxides containing, for example, Zn, Al, or Fe were described as zincates,

aluminates, and ferrates, though the corresponding acids were unknown, and whole series of complex 'acids' of silicon and boron may be found in the literature. The correct formulation of compounds which exist only in the solid state is possible only if we know the exact arrangement of the constituent atoms in the crystal. We then know whether the relation of the oxygen atoms to one kind of atom is different from that to another, and we are justified in grouping the atoms accordingly in the empirical formula. In our survey of the structures of complex oxides we shall find that in many cases some or all of the oxygen atoms are definitely associated with one kind of atom to form oxy-ions. These ions may be finite or infinite. In the latter case they can exist only in the solid state; in the former case they *may* also be stable in solution, but the existence in the crystal of discrete finite ions must not be taken to mean that the ion will necessarily be able to exist in the same form in water, where the conditions are very different from those in the crystal.

Oxy-ions

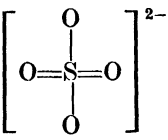
We may define an oxy-ion as a charged group of atoms $A_mB_n...O_p$ in which the forces attaching any (and every) oxygen atom to its nearest A, B, etc., neighbour are greater than the total of all the forces acting between it and atoms external to the group. As we have said, these ions may be of any degree of complexity, from the simplest mononuclear ion AO_n to the infinite ions existing in certain crystals. We may begin by considering what is known of the constitution of the simplest oxy-ions. X-ray crystallographic examination of salts has established the stereochemistry of the following oxy-ions:

TABLE 18

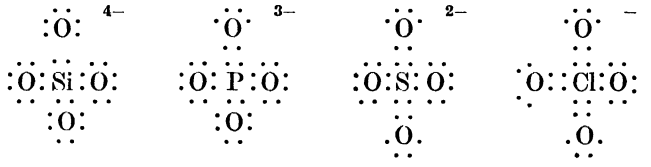
BO_3	CO_3	NO_3			planar
				ClO_2	non-linear
			SO_3	ClO_3	pyramidal
	SiO_4	PO_4	SO_4	ClO_4	tetrahedral
		VO_4	CrO_4	MnO_4	
				BrO_3	pyramidal
		AsO_4	SeO_4		tetrahedral
				IO_6	octahedral

The first problem is to decide what determines, for a given element, the number and arrangement of the O atoms in the ion AO_n. There is no apparent relation between the value of n and the electronic structures of the elements. The only oxy-ion of carbon is the carbonate ion CO_3^{2-}, whereas the only stable oxy-ion of silicon is the orthosilicate ion SiO_4^{4-}. Also, Cl and S form ions AO_3 in addition to AO_4 but P and Si do not—there is no ion $O—Si\langle^{O^{2-}}_{O}$ analogous to CO_3^{2-}. It is clear that in any attempt to answer the above question we must consider the nature of the bonds in these ions. We shall find that this is not easy to state in a simple

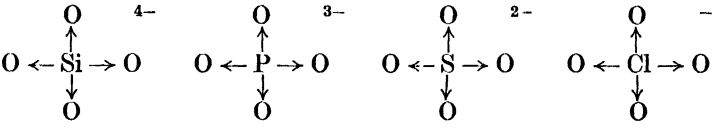
way. The early structural formulae assigned to these ions assumed that the central atom exhibited the group valency, and the sulphate ion, for example, was represented



The SiO_4^{4-}, PO_4^{3-}, and ClO_4^- ions were given similar formulae involving 0, 1, and 3 double bonds respectively. With the application of the electronic theory of valency it was seen that these formulae gave the atoms Si, P, S, and Cl valency groups of 8, 10, 12, and 14 electrons respectively (*a*), but an alternative formulation was possible in which an octet of valency electrons could be maintained in all cases. It was assumed that the two electrons required for a single covalent bond could both be provided by one atom and this coordinate link was distinguished by the symbol →. The atoms Si to Cl could then all form AO_4 ions as shown at (*b*).

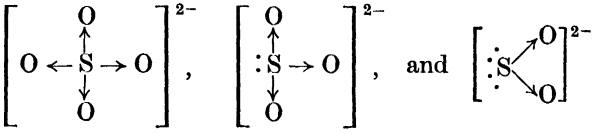


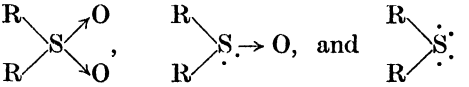
(*a*)



(*b*)

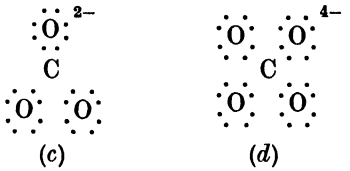
It was possible also to see why the ClO_3^- or SO_3^{2-} ions could be formed, since the relation of ions SO_2^{2-}, SO_3^{2-}, and SO_4^{2-} would be the same as that of organic disulphides to the sulphoxides and sulphones, one or more pairs of unshared electrons not being utilized:

Compare 

with 

However, it must be remembered that the electronic theory of valency provided only a means of representing the structures of such ions and did not account for the existence of some and the non-existence of others. Thus the CO_3^{2-} ion is easily represented as (*c*), but the theory cannot

account for the non-existence of CO_4^{4-} which can equally well be written as at (*d*):



(*c*) (*d*)

The early electronic formulae also accounted for the configurations of the simple ions if it were assumed that a pair of unshared electrons on the central atom affected the spatial disposition of the other bonds in the same way as a pair of electrons forming a single bond. Thus the C atom in CO_3^{2-} has only six valency electrons and therefore forms three bonds arranged in the most symmetrical manner, viz. equally inclined to one another in a plane. The S atom in SO_3^{2-}, on the other hand, has one pair of unshared electrons, so that the three S—O bonds are directed towards three of the corners of a tetrahedron.

So far the bonds in these ions have been regarded as single covalent bonds, and we must now refer to another way of treating these ions. We saw in an earlier chapter that the concept of ionic radius is of considerable value in discussing the structures of ionic crystals. It was pointed out that radii could be assigned, not only to ions of comparatively low charge which there is good reason to believe exist in crystals, but also to the highly-charged positive ions of the atoms of the later Periodic Groups. From studies of many oxides and oxy-compounds we know the oxygen coordination numbers of most atoms (or ions), and it is sometimes suggested that the oxygen coordination numbers of even the more electronegative elements can be accounted for in terms of the radius ratio $r_A:r_O$. While it is quite sound to relate the coordination of Cs^+ by 12 O^{2-} ions to the ratio $r_{Cs}:r_O$, it is quite unjustifiable to extend this treatment to the oxy-ions set out in Table 18 (p. 317) in which the bonds are essentially covalent. We find that in the latter cases the 'univalent' radii have to be used to calculate the radius ratio, but the 'crystal radii' are used to give the interatomic distances in the crystal. Moreover, the interatomic distances derived from the 'crystal radii' are not those actually found within the ions, and considerable polarization of the constituent ions has to be invoked to account for the observed distances. For the further discussion of the structures of these ions the simple ionic model is not of value, but it has been mentioned here because the impression is sometimes given that it accounts for the formulae of these ions. We must conclude that for the present we cannot account for the number and arrangement of O atoms around a given A atom in an ion AO_n and must wait until theory has developed sufficiently to enable us to predict the type of orbitals used in such groups and also the interatomic distances, which could then be checked against the observed values. At present we can only deal with ions which we know do exist, and suggest, from the observed distances, resonance energies, and other properties of the ion, which

electronic configurations of the ions are likely to be involved. Thus the distances within and the resonance energy of the CO_3^{2-} ion appear reasonable if we assume resonance between forms of the type $O{=}C\langle^{O^-}_{O^-}$, etc.

We must now inquire whether the simple electronic formulae given above for the tetrahedral ions account for the observed interatomic distances and bond angles.

If we compare the observed distances A—O in the tetrahedral ions SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, and ClO_4^- with the sums of the appropriate covalent radii we find considerable discrepancies. We may remark here that the dimensions of such groups are essentially independent of their surroundings (except apparently in the case of the PO_4^{3-} ion in Ag_3PO_4*), the Si—O distance, for example, having very similar values in various orthosilicates.

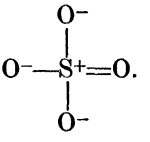
Bond Lengths in Tetrahedral Ions AO_4

	Si—O	P—O	S—O	Cl—O
Observed . . .	1·60	1·55	1·51	1·48
Sum of covalent radii .	1·83	1·76	1·70	1·65
Difference . . .	−0·23	−0·21	−0·19	−0·17

If, instead of the Pauling-Huggins radii (Table 7) we use the covalent radii of Table 6 and correct for differences in electronegativity, we still find large discrepancies, viz.

	Si—O	P—O	S—O	Cl—O
Sum of radii . . .	1·76	1·71	1·69	1·68
Difference . . .	−0·16	−0·16	−0·18	−0·20

One possibility is that the shortening of these bonds is due to the fact that the ion resonates among a number of structures involving double bonds, for example,



Pauling suggested that the tendency to form multiple bonds is greatest in the elements of the first short period and falls off in the later periods, it being assumed that the 3*d* orbitals are used in forming such bonds. Resonance between structures involving one or more double bonds would, however, lead only to partial double-bond character of all the four bonds, whereas the observed S—O distance is very close to that (1·54 A.) expected for pure double bonds, adopting the value for S=O derived in the way

* In this crystal the distance P—O is stated to be $1{\cdot}61 \pm 0{\cdot}03$ A., with which compare the above value, 1·55 A. This has been described as an example of 'contrapolarization', the P—O bonds being weakened by the action of the strongly polarizing Ag^+ ions which surround the group. Alternatively we may say that the O—Ag bonds have some covalent character and that this reduces the amount of double-bond character of the P—O bonds, so leading to an increase in their length.

described in Chapter III. To overcome this difficulty other resonating forms are invoked such as

$$\begin{array}{c} O^{=} \\ O{=}S^{++}{=}O \\ O^{=} \end{array}$$

on the grounds that the double 'formal charge' on the S will reduce the lengths of the $O{=}S^{++}{=}O$ bonds. It will probably be felt that this way of arriving at a picture of an ion apparently so simple as SO_4^{2-} leaves much to be desired, but it seems to be the only method available at present. Similar difficulties are experienced with many molecular halides, oxy- and sulpho-halides, and the more complex oxy-ions of Si, P, S, and the halogens. We should also add that in ions like ClO_2^- and SO_3^{2-}, where the central atom has one or more pairs of unshared electrons and in which considerable double-bond character is assumed according to the above treatment, the bond angles are those to be expected for *single* bonds.

A second possible explanation of the short interatomic distances in these oxy-ions was that the coordinate link is shorter than a normal covalent bond. This was considered untenable since the length of the N—O bond in $(CH_3)_3N{\rightarrow}O$ is exactly equal to the sum of the single bond 'tetrahedral' radii of N and O (1·36 A.), whereas the lengths of the so-called coordinate links in many compounds of S and P are as small as, or even smaller than, the lengths expected for double bonds. However, using the revised radii for N and O given in Table 6, the N–O distance is estimated to be 1·43 A., appreciably larger than the above value. With these facts in view we see that there is no unique way of formulating these oxy-ions which is not open to objection.

Complex Oxy-ions and Molecules

The division of complex oxy-ions into poly-, per-, and pyro-ions has already been made in Chapter VII. The poly-ions contain two or more A atoms directly linked together. They are few in number, comprising—apart from the thionates—only such ions as the hyponitrite ion, $N_2O_2^{2-}$, and the hypophosphate ion, $P_2O_6^{4-}$. The per-ions are also rare and the detailed structure of only one, the persulphate ion $S_2O_8^{2-}$, has been established. The perphosphate and percarbonate ions, $P_2O_8^{4-}$ and $C_2O_6^{2-}$, may be further examples.

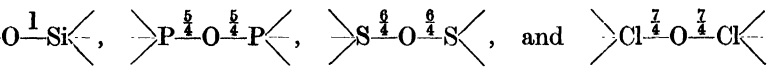
The pyro-ions are far more numerous. They are of the form

$$O_nA{-}O{-}AO_m$$

and may be symmetrical or unsymmetrical.

Those of the form A_2O_7 have been most studied, including $S_2O_7^{2-}$, $P_2O_7^{4-}$, and $Si_2O_7^{6-}$. It is interesting to compare the stabilities of ions A_2O_7 formed by various elements. This is part of the more general question: What determines the extent to which different elements form complex pyro-ions?—a question we shall soon consider. In the series of elements of the second short period, Si, P, S, and Cl, the stability of the pyro-ions A_2O_7

decreases steadily from Si to Cl. The ion Cl_2O_7 is unknown. Pyrosulphates of certain elements may be made by recrystallizing the normal or acid sulphate from warm concentrated H_2SO_4 or by heating the normal sulphate with SO_3 in a closed vessel. Few are known apart from those of the alkalis, alkaline-earths, and silver. They melt without decomposition but are immediately decomposed by water ($S_2O_7^{2-} \rightarrow HSO_4^-$ or SO_4^{2-}). Two types of pyrophosphates are known, the normal salts $M_4P_2O_7$ and acid salts $M_2H_2P_2O_7$, the normal alkali salts being slightly hydrolysed in solution. The alkali and thallous salts are soluble in water; a number of heavy metal salts are also known. The stability of many pyrosilicates is seen from their occurrence as minerals (e.g. $Ca_2MgSi_2O_7$ (melilite), $(OH)_2Zn_4Si_2O_7.H_2O$ (hemimorphite), and $Sc_2Si_2O_7$ (thortveitite)). Pauling relates the stabilities of these ions to the extent to which they represent departures from the electrostatic valence rule. The strengths of the bonds to the central O atom in the four cases are



so that the total strengths of the bonds to the O^{2-} ions are 2, $2\frac{1}{2}$, 3, and $3\frac{1}{2}$ respectively, the increasing departures from neutralization leading to decreasing stability. The validity of such purely electrostatic treatments is discussed below.

Of the elements set out in Table 20 (p. 325) a number show a striking tendency to form complex pyro-ions, notably B, Si, Mo, W, and Te. There are also many complex chromates, phosphates, and vanadates, but little is known of their structures. The characteristic of the groups BO_3, SiO_4, MoO_6, WO_6, and TeO_6 is that the oxygen coordination number of the central metal atom is equal to the number of valency electrons in the free atom (i.e. the number of the periodic Group). We may account for the facility with which these groups condense to form more complex oxy-ions either by adopting an extreme ionic picture or by treating the A—O bonds as simple covalent bonds. In the first case we see that the electrostatic bond strength of the A—O bonds (which is equal to the positive charge on the A ion divided by the coordination number) is equal to unity. The doubly charged O^{2-} ion requires two such bonds, so that the individual AO_n groups may condense by sharing O^{2-} ions. Alternatively we may say that the O atom completes its octet by forming two single bonds $\left(\text{—}\ddot{\underset{\cdot\cdot}{O}}\text{—}\right)$, the central atom A forming N bonds where N is the number of valency electrons. As in the case of simple oxy-ions neither picture is satisfactory since the bonds are not of either extreme type. Also, neither treatment accounts for the bond angles observed in these ions. For example, the O bond angle is usually of the order of 130° as in $S_2O_7^{2-}$ and $S_2O_8^{2-}$ and in the $Si_2O_7^{6-}$ ion in melilite, though in $Sc_2Si_2O_7$ (the mineral thortveitite) and in $Mg_2P_2O_7$ (which has a similar type of structure) the O bond angles are stated to be 180°. A far more important point, however,

is that neither of the above ways of regarding these ions accounts for the fact that several elements of the *fifth* Periodic Group also form complex poly-ions. On the above views we might expect these to be formed by condensation of AO_5 groups, so that we must now consider briefly the actual coordination by oxygen observed for the fifth group elements.

When the radius ratio criterion was first applied to correlate coordination number with ionic size, only the most symmetrical dispositions of the ions were considered, viz. for C.N. 2, linear, 3, triangular, 4, tetrahedral, and so on. Later, examples of 7- and 9-fold coordination were found and the radius ratios for these arrangements were added. Now for ions with charges not exceeding four it is probably reasonable to apply the concept of radius ratio, and in fact the observed coordination numbers agree well with those predicted. For each type of coordination there is a minimum value of the radius ratio, and it is interesting to consider the observed coordination numbers of ions for which the radius ratio is very close to one of these values, which are given in Table 19 (*a*):

TABLE 19 (*a*)

Coordination polyhedron	*C.N.*	*Minimum radius ratio*
Cubo-octahedron	12	1·000
(1)	9	0·732
Cube	8	0·732
Square antiprism	8	0·645
(2)	7	0·592
Octahedron	6	0·414
Tetrahedron	4	0·225
Triangle	3	0·155

(1), (2), see Fig. 28 (*c*) and (*a*), p. 113.

A number of 'borderline' cases are listed below where the observed and predicted oxygen coordination numbers are compared.

TABLE 19 (*b*)

Ion	*Radius ratio*	*Coordination number*	
		Predicted	*Observed*
P^{5+}	0·34	4	4
Al^{3+}	0·41	4 or 6	4, 5, 6
As^{5+}	0·41	4 or 6	4
Ge^{4+}	0·43	4 or 6	4, 6
Zr^{4+}	0·62	6 or 8	6, 8
Ca^{2+}	0·67	8	6, 7, 8, 9
K^{+}	0·75	9	6, 7, 8, 9, 10, 12

Calcium is not strictly a borderline case, but it is included because it shows a range of coordination numbers. The P^{5+} ion is included since it is relevant to the present discussion. In case it should be thought dangerous to draw conclusions from data as limited as those given in the

above table, we may point out that these examples are typical of many others.

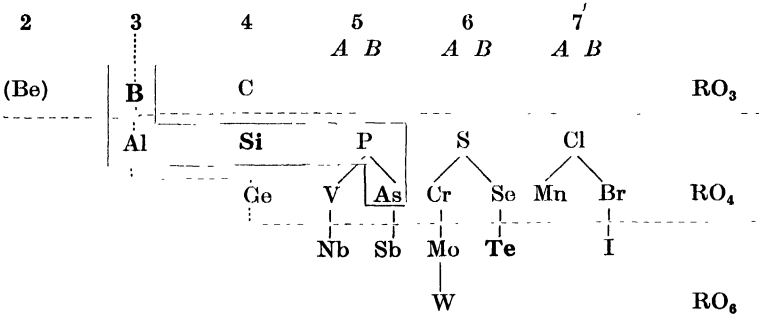
We notice first that the coordination numbers of K^+ and Ca^{2+} are very variable. The bonds from O to these very electropositive atoms are essentially ionic, so that the coordination numbers are not restricted by the number of orbitals available and the ions fit into various structures with coordination numbers in the region of the ideal value. The second point to note is that of the elements Al, Ge, and As, all with radius ratios near to the value for the transition from 4- to 6-coordination, only one (Al) shows the unusual coordination number 5. Arsenic and phosphorus, with the same radius ratio, are found 4-coordinated. This difference between Al and As can be related to the following facts. Aluminium is more electropositive than As, so that in the latter case the bonds to O are appreciably more covalent than the bonds Al—O and the coordination number will be influenced by the stability of four tetrahedral bonds as opposed to five bonds of more than half covalent character.

The rarity of 5-coordination in ionic crystals is presumably associated with the fact that there is no symmetrical arrangement of five ions around another which corresponds to a minimum radius ratio intermediate between the minimum values for 4- and 6-coordination. When five covalent bonds are formed by an element they are directed towards the apices of a trigonal bipyramid—see PCl_5, $Mo(CO)_5$, etc. For an ionic group with this configuration the minimum radius ratio would be that for the equilateral triangle, viz. 0·155; compare the values 0·225 for the tetrahedron and 0·414 for the octahedron. Thus for ions with radius ratio around 0·414 we find in general that the coordination number is either 6 or else it drops to 4. In cases where 5-coordination is observed it would appear that it is incidental in the sense that the structure is determined by the coordination number of another atom. For example, the compound Al_2SiO_5 crystallizes in three forms, sillimanite, andalusite, and cyanite. In each of the three forms there are two crystallographically different kinds of Al ions from the structural point of view. Half of the Al ions in each are 6-coordinated, but the coordination group around the other half is 4 in sillimanite, 5 in andalusite, and 6 in cyanite. The AlO_5 coordination group in andalusite has the form of a rather distorted trigonal bipyramid. If we may put it so, the reluctance of Si to form more than four bonds forces Al into positions of varying coordination dependent on the arrangement of the SiO_4 tetrahedra. The structures of certain 'basic' arsenates and phosphates (e.g. $Cu(CuOH)AsO_4$, $Zn(ZnOH)AsO_4$, and $Cu(CuOH)PO_4$) are similar to that of andalusite. The 5-coordination of Cu and Zn (by 4 O^{2-} and 1 OH^-) is not characteristic of these elements as is the 4-coordination of As and P in the ions AsO_4^{3-} and PO_4^{3-}. The exceptional 6-coordination of Si in SiP_2O_7 seems similarly to be incidental to the 4-coordination of the P atoms in the P_2O_7 groups. It is of interest in this connexion to notice that PCl_5, which in the vapour state exists as trigonal bipyramidal molecules, consists in the crystalline state of $[PCl_4]^+$ and $[PCl_6]^-$ ions.

We were led to this discussion of 5-coordination because the usual 'explanation' of the condensation of BO_3, SiO_4, and other ions to form complex oxy-ions does not account for the similar behaviour of the oxy-ions of the fifth group elements. If it appears that this discussion has little to do with the chemistry of the elements, we would point out that our knowledge of the oxygen chemistry of many elements must be derived largely from studies of their complex oxy-compounds, many of which exist only in the solid state.

We set out below the observed oxygen coordination numbers of the elements in which we are interested, the broken lines separating the regions of different coordination numbers. The elements B, Si, and Te (printed in heavy type) are those for which the oxygen coordination number is equal to the number of valency electrons in the atom. The coordination numbers of the elements of the later groups are those found in complex ions, i.e. they are those of the element exhibiting its 'group valency', viz. Cr^6, Mn^7, etc. Many transition metals form stable ions of lower charge, and these ions have different coordination numbers, e.g. Mn^{3+} in Mn_2O_3 and Mn^{4+} in MnO_2 are both surrounded by six oxygen neighbours. We have seen that certain elements in the neighbourhood of Si are also found in 4-coordination, notably B (3 and 4), Al (4 and 6), P and As (4). These are distinguished as a group in the diagram because they are often found in structures which may be regarded as derived from a simpler Si—O structure by replacing Si atoms by atoms of these elements (see p. 337).

TABLE 20



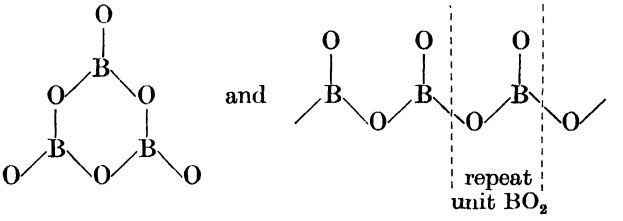
We have now to consider the types of complex oxy-ion which arise. Little is known of complex oxy-compounds of phosphorus, but phosphates derived from the PO_4 group will present the same geometrical possibilities as the silicates. We need therefore deal only with the linking of planar BO_3, tetrahedral SiO_4, and octahedral WO_6 groups, and we shall examine the possibilities systematically according to the number of O atoms of each coordination group which are shared with other groups. In this connexion we may remind the reader of the restrictions on the sharing of edges and faces of polyhedra already mentioned in Chapter III under Pauling's 'rules' governing the structures of ionic crystals. The relevant

facts are that BO_3 groups share only corners, SiO_4 groups share only corners, but WO_6 groups may share corners and/or edges. (The sharing of opposite faces of octahedral groups is known in the W_2Cl_9 and similar ions.)

(*a*) If every O atom of every coordination group is shared with other groups the neutral oxides B_2O_3, SiO_2, and WO_3 arise. The finite molecules P_4O_6, As_4O_6, and Sb_4O_6 may be regarded as arising in a similar way by the sharing of all corners of pyramidal PO_3, etc., groups. For the structures of SiO_2 and WO_3 see pp. 463 and 331.

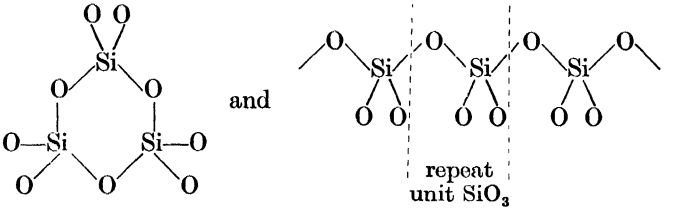
(*b*) When some of the O atoms are shared and some unshared, complex ions arise. For BO_3 groups there is only the one possibility:

(1) *BO_3 groups sharing two corners*, leading to rings or infinite chains, all of empirical composition $(BO_2)_n^{n-}$, e.g.



For tetrahedra there are two possibilities:

(1) *SiO_4 sharing two corners*, giving rings or chains of empirical formula $(SiO_3)_n^{2n-}$,



The PO_4 group may form similar complex ions, but the only one known so far is the ring complex P_4O_{12} in aluminium metaphosphate. The above two classes of compounds are the so-called meta-salts, of metaboric, metasilicic, and metaphosphoric acids. Below are given the empirical formulae of certain meta-salts and the formulae indicating the types of complex ion actually found in the crystals.

$NaBO_2$—$Na_3(B_3O_6)$	Ring complex ion
$Ca(BO_2)_2$—$Ca_n(BO_2)_{2n}$	Infinite chain ion
$BaTi(SiO_3)_3$—$BaTi(Si_3O_9)$	Ring complex ion
$Be_3Al_2(SiO_3)_6$—$Be_3Al_2(Si_6O_{18})$	,, ,,
$CaSiO_3$—$Ca_3(Si_3O_9)$	,, ,,
$CaMg(SiO_3)_2$—$Ca_nMg_n(SiO_3)_{2n}$	Infinite chain ion
$AlPO_3$—$Al_4(P_4O_{12})$	Ring complex ion

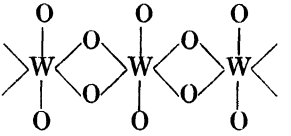
(2) *SiO_4 sharing three corners.* The infinite layers of silicon-oxygen tetrahedra characteristic of the structures of the micas and clay minerals

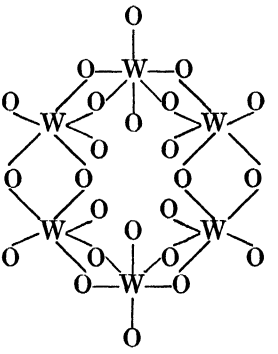
have, ideally, the composition $(Si_2O_5)_n^{2n-}$. These and other silicates are described in more detail in Chapter XIV.

The sharing of corners and edges of octahedra naturally gives rise to a greater variety of complex ions. We shall mention here only three simple possibilities.

(1) *WO_6 sharing two opposite corners.* Chains and rings could arise in this way as in the meta-ions described above.

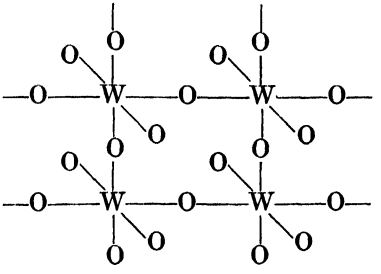
(2) *WO_6 sharing four corners (two opposite edges).* The linking of WO_6 octahedra into chains or rings of the types shown below has not been observed.





It is possible (see below) that sharing of edges between WO_6 octahedra will not take place owing to the large charge on the W^{6+} ion, assuming the bonds in the groups to be essentially ionic. Another simple arrangement (3) is apparently preferred.

(3) *WO_6 sharing four corners with four surrounding octahedra.* In this way an infinite 2-dimensional complex may be formed, shown diagrammatically below. This is not known as a layer ion, but WO_6 octahedra linked up in exactly the same way form the basis of the closed basket-like ions of certain poly-acids. This is the logical place in which to describe the iso- and hetero-poly acids, but to avoid interrupting our survey of complex oxides we postpone any further discussion of these compounds until a later section.



Before leaving the complex oxy-ions we should remark that we have not mentioned specifically the various finite ions which may be regarded as formed by the linking up, as outlined above, of limited numbers of

groups into *finite* chains or portions of infinite 2-dimensional nets. Apart from the pyro-ions formed by tetrahedrally coordinated atoms such ions are rare, presumably because the process goes to its logical conclusion, the formation of the infinite ion.

The Crystal Structures of some Complex Oxides

We shall recognize two types of complex oxides—those in which no definite groups A_mO_n can be distinguished, and those in which complex ions, finite or infinite, exist. It is relevant to inquire by what criteria we decide that certain groups of atoms should be regarded as complex ions. In defining a complex ion as a charged group of atoms for each atom of which the forces attaching it to the group are greater than the forces attaching it to other atoms, no mention was made of the nature of the bonds within the complex ion. It might appear logical to extend the concept of electrostatic bond strength to provide the basis for a classification of oxides. For any observed coordination group A^aO_n we may say that the strength of the bonds A—O is a/n where a is the positive charge on the central ion A. The charge on the O^{2-} ion is -2, so that if a/n is greater than unity then the O ion is more firmly attached to A than to any other atoms in the structure. Accordingly three cases may be distinguished, depending on whether a/n is greater than, equal to, or less than 1. Only in the first case is the group AO_n regarded as a complex ion. In the second the AO_n groups can condense to form infinite ions (as in borates and silicates), and in the third case the O ions cannot be regarded as attached to the A atoms rather than to any other positive ions in the crystal.

We have already pointed out two objections to any such electrostatic treatment. In ions such as SO_4^{2-} the S—O bonds are not essentially ionic, for such highly charged ions as S^{6+} are not physical realities, and difficulties arise when the treatment is applied to the fifth Periodic Group. We shall also find that some complex oxides exist in two forms, a low-temperature form in which there are recognizable complex ions, and a high-temperature modification in which such an ion may no longer be distinguished. Finally the similarity in structure between such pairs of compounds as Al_2BeO_4 and Mg_2SiO_4 would not be expected if the structures were determined simply by the charges on the ions. It is probably better merely to relate, in a general way, the behaviour of atoms in oxide structures to their respective electronegativities—e.g. Be and Si are approximately equally electronegative. Since the electronegativity of the atoms in Table 20 decreases from right to left and also from top to bottom of a given column, we shall merely draw a diagonal line across the table passing through B, Si, and Te. Atoms to the left of this line, i.e. those of the earlier groups with small charges, form essentially ionic bonds with O and the structures may be treated as aggregates of ions, the coordination numbers of the ions being determined by their relative sizes. To the right of this line are the elements forming complex ions, in which the bonds have appreciable amounts of covalent character. Atoms on and around

the dividing line behave in both ways, B and Si being notable for the variety of complex ions they form. On account of the intermediate position of Si, the classification of silicates in terms of discrete SiO_4 groups or more complex Si_xO_y ions is not always very satisfactory, though this method is usually adopted and is discussed in more detail in Chapter XIV. In many cases there is little doubt as to whether a particular group of atoms should be regarded as a complex ion or not, e.g. CO_3^{2-}, SO_4^{2-}, etc., but in doubtful cases interatomic distances, bond angles, and coordination numbers must be taken into consideration.

(*a*) *Structures without Complex Ions.* These structures consist of aggregates of O^{2-} ions with positive ions of various kinds, the number of O^{2-} ions surrounding a given ion being determined by the ratio of the radii of the ions and the O^{2-} ion. For reference purposes the crystal radii of some ions are repeated below.

TABLE 21

O^{2-} 1·40 A.

+1	+2	+3	+4				
Li	Be			*Ions of transition metals*			
0·60	0·31						
Na	Mg	Al	(Si)	Mn^{2+}	0·80	Ti^{3+}	0·69
0·95	0·65	0·50	0·41				
K	Ca	Sc	Ti	Fe^{2+}	0·75	V^{3+}	0·66
1·33	0·99	0·81	0·68				
NH_4^+	Rb	Sr	Y	Zr	Co^{2+}	0·72	Cr^{3+}	0·64
1·48	1·48	1·13	0·93	0·80			
Tl^+	Cs	Ba	La	Ce	Ni^{2+}	0·70	Mn^{3+}	0·62
1·44	1·69	1·35	1·15	1·01			Fe^{3+}	0·60

The first point to be observed is that few ions approach in size the O^{2-} ion. The above radii are those for 6-coordination; for higher coordination numbers they should be increased—by 4 per cent. for 8-coordination and by about 10 per cent. for 12-coordination. Only the ions to the left of the diagonal line are found with coordination numbers as high as 12. We accordingly find that many complex oxide structures may be regarded as assemblies of O^{2-} ions in close packing (in which each has twelve nearest neighbours) with the smaller positive ions occupying the interstices between them. For the very large positive ions, however, there is the alternative that they and the O^{2-} ions together form a close-packed arrangement, the smaller positive ions still occupying the spaces between four or six O^{2-} ions. Thus two compounds may have the same type of empirical formula and yet differ in this important respect—compare, for example, the structures of $FeTiO_3$ and $CaTiO_3$. In the oxides with close-packed O^{2-} ions the latter form a rigid lattice which will not collapse if some of the small ions are absent, provided that the structure is electrically neutral. Considerable variation in composition is therefore often found in this type of oxide structure, electrical neutrality being maintained by changes in valency. When the number of small positive ions in the

structure is much smaller than the number of positions available they are often distributed statistically—see, for example, the structure of γ-Fe_2O_3.

Some of the simpler complex oxide structures are listed below. They are named after minerals with the particular structure.

Perovskite . . .	ABO_3
Ilmenite . . .	ABO_3
Spinel . . .	AB_2O_4
Pseudobrookite . .	A_2BO_5
Columbite . . .	AB_2O_6

We shall describe the perovskite structure as an example of one in which A and O ions are close-packed, and the ilmenite and spinel structures as examples of those containing close-packed O^{2-} ions.

The Perovskite Structure is an example of a structure in which large A ions and O^{2-} ions together form a close-packed arrangement with the smaller B ions in some of the interstices. We have already seen that in close-packed arrangements there are two types of hole—between 4 and 6 atoms respectively. In the perovskite structure the B ions occupy the latter positions and are surrounded octahedrally by six O^{2-} ions. For the 'ideal' structure there must therefore be a definite relation between the radii of the A, B, and O^{2-} ions which is

$$r_A + r_O = \sqrt{2}(r_B + r_O).$$

Actually the cubic perovskite structure or slightly deformed variants of it are found for ions which do not obey this relation exactly and we find a certain degree of tolerance, expressed by

$$r_A + r_O = t\sqrt{2}(r_B + r_O),$$

where t has values from about 0·8 to 1·0. Provided that the ionic sizes are approximately right, the only other condition to be fulfilled is that the structure is electrically neutral, i.e. that the sum of the valencies of A and B is 6. Among the compounds crystallizing with this structure are the following:

$NaNbO_3$	$CaTiO_3$	$YAlO_3$	and also	$KMgF_3$
$KNbO_3$	$SrTiO_3$	$LaAlO_3$		$KNiF_3$
KIO_3	$CaZrO_3$	$LaGaO_3$		$KZnF_3$
$RbIO_3$	$CuSnO_3$			

The close-packing of the K^+ and F^- ions in the 'double fluorides' may be compared with that of Cs^+ and Cl^- in $Cs_3Tl_2Cl_9$ and $Cs_3As_2Cl_9$ (see the section on complex halides). The absence of discrete IO_3 ions in the iodates of K and Rb should be noted—compare the structures of the corresponding bromates and chlorates in which there are discrete BrO_3^- and ClO_3^- ions—and also the absence of any finite complex ions in the 'niobates', 'titanates', and 'aluminates' listed above.

We have said that the sum of the valencies of the A and B ions in the perovskite structure must be 6. It is interesting to examine the relation

of this structure, Fig. 85 (*a*), to that of the trioxides of hexavalent electropositive elements, since by removal of the 12-coordinated A ions we obtain a possible structure for such oxides $B^{6+}O_3$. The oxide ReO_3 has this structure (Fig. 85 (*b*)), but the Group VI trioxides have less symmetrical structures to which reference has already been made. That of WO_3 is

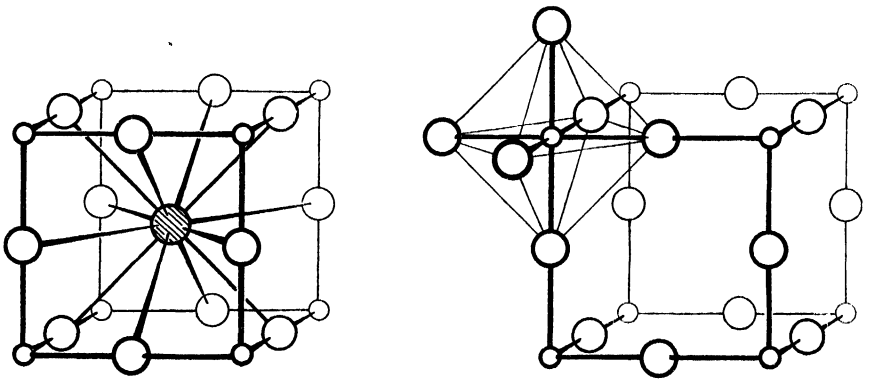


FIG. 85. (*a*) The perovskite structure for compounds ABO_3 (or ABX_3). Large open circles represent O (or F) ions, the shaded circle A, and the small circles B ions. (*b*) The crystal structure of ReO_3.

apparently a slightly distorted form of the ReO_3 structure. Now tungsten can form both W^{5+} and W^{6+} ions, so that we might expect to find compounds such as $NaW^{5+}O_3$ with the perovskite structure. The tungsten bronzes are intermediate between the compound $NaWO_3$ and the oxide WO_3. They are obtained either by heating a mixture of Na_2WO_4, WO_3, and WO_2 *in vacuo* or by reducing Na_2WO_4 by hydrogen or molten zinc. They may be represented by the formula Na_xWO_3, where x has a value between 0 and 1. They have metallic lustre, colours ranging from golden yellow ($x \sim 1$) through red ($x \sim 0{\cdot}6$) to deep violet ($x \sim 0{\cdot}3$), and are quite good conductors of electricity. The phases from $Na_{0{\cdot}32}WO_3$ to $Na_{0{\cdot}93}WO_3$ are all cubic with the perovskite structure, the cell size varying regularly with the Na content. When the latter falls below about 0·3 the cubic structure collapses to a less symmetrical arrangement which has not been investigated in detail. In these tungsten bronzes there is a random arrangement of the Na^+ ions and for every Na^+ ion there must be one W^{5+} ion, the rest of the tungsten being in the form of W^{6+} ions, so that we may write the formula $Na_xW^{5+}_xW^{6+}_{1-x}O_3$.

A number of 'lower oxides' of W have been described such as W_4O_{11}, W_8O_{23}, and $W_4O_{10}(OH)_2$. The empirical formulae of such compounds are difficult to determine and they may be tungsten bronzes containing hydrogen. Their structures appear to be closely related to that of WO_3.

The Ilmenite Structure requires little description. Corundum (α-Al_2O_3)

and haematite (α-Fe_2O_3) have the same structure, in which the metal atoms occupy two-thirds of the octahedral holes in a hexagonal close-packed oxygen lattice. Ilmenite, $FeTiO_3$, is strictly isomorphous with Fe_2O_3, one-half of the Fe atoms being replaced by Ti. Further replacement of Fe by Mg often occurs, many ilmenites having the composition (Fe, Mg)TiO_3, and $MgTiO_3$ itself is isomorphous with Fe_2O_3 as also are the following: $MnTiO_3$, $CoTiO_3$, $NiTiO_3$, and the low-temperature form of $CdTiO_3$—the high-temperature form has the perovskite structure. It will be apparent that there is no reason for calling such compounds 'titanates'. Pseudobrookite, Fe_2TiO_5, has a somewhat similar structure in which Fe and Ti are each surrounded by six O as in ilmenite.

In the *Spinel Structure* the O^{2-} ions are arranged in cubic close-packing, the A atoms occupying tetrahedral holes and the B atoms positions of octahedral coordination. Structures of the types we are now considering, with close-packed oxygen ions, are not conveniently represented by the ordinary perspective view of a unit cell on account of the large number of atoms therein. We have, however, already seen (p. 109) that close-packed atoms are arranged in layers and that the differences between the various kinds of close-packing arise from the way in which the layers are stacked together. The small metal ions are found between the layers, surrounded by either four or six oxygen ions. We may therefore show the relation of such structures to one another by imagining that the layers of oxygen ions are taken apart, leaving associated with each layer the metal ions immediately in contact with its upper surface. If we apply this process to the structure of BeO we find that it is made up of identical layers, one of which is illustrated in Fig. 86 (*a*). Successive layers pack together in such a way that an oxygen atom comes vertically above every Be atom so that these atoms are surrounded tetrahedrally by four oxygen atoms. In the resulting (wurtzite) structure the O atoms are in hexagonal close-packing. If similar layers, with Mg instead of Be ions, are arranged so as to surround every Mg with six O ions, the result is the structure of MgO (rock-salt structure) with cubic close-packed oxygen atoms. If one-third of the positive ions are removed in a regular way from the layer of Fig. 86 (*a*) we have the corundum (Al_2O_3) layer, shown in (*b*). The structure of ilmenite, $FeTiO_3$, is obtained by superposing layers of this kind, substituting Fe and Ti for Al between alternate layers of oxygen atoms. The spinel structure may be regarded as built up of alternate layers of two kinds, Fig. 86 (*c*) and (*d*), superposed to give every A atom four and every B atom six oxygen neighbours. In the resulting structure the oxygen atoms are cubic close-packed. The numbers of layers which are obtained by dissecting a close-packed structure in this way must not be confused with the numbers of layers which constitute a crystallographic 'repeat unit' of the structure, viz. 2 for hexagonal, 3 for cubic close-packing, etc. This should be clear from the fact that the layers of Fig. 86 (*a*) may be packed to give either hexagonal or cubic close-packing of the O atoms in BeO or MgO respectively. The actual type of packing

which results is determined by the particular way in which the successive layers are superposed.

The crystallographic unit cell of the spinel structure contains thirty-two oxygen atoms and there are equivalent positions in this cell for eight atoms surrounded tetrahedrally by four O atoms and for sixteen atoms

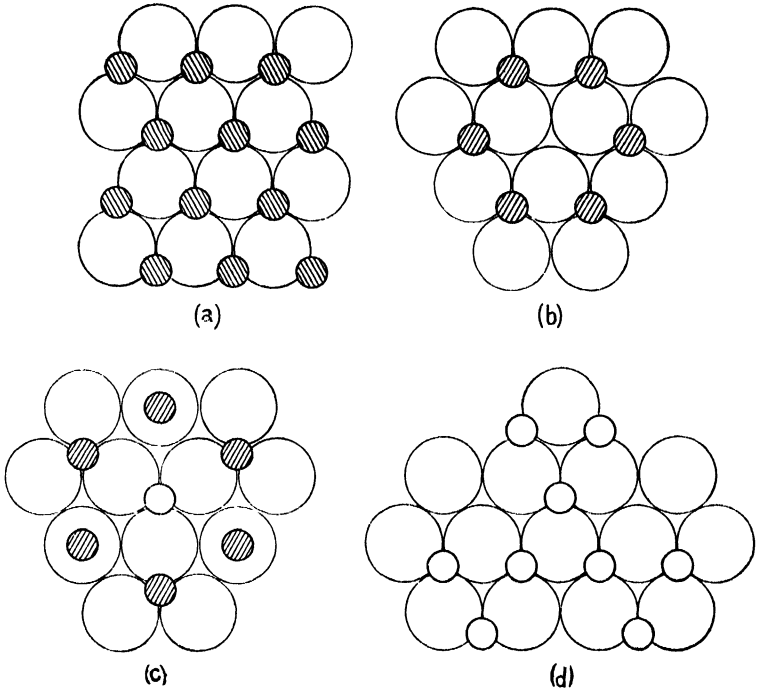


FIG. 86. Layers of close-packed oxygen atoms with the metal atoms immediately in contact with their upper surfaces resulting from the dissection of (*a*) BeO or MgO, (*b*) Al_2O_3, corundum, (*c*) and (*d*) a spinel, AB_2O_4. In the latter structure layers (*c*) and (*d*) alternate (A atoms shaded).

surrounded octahedrally by six O atoms. Since there are eight A atoms and sixteen B atoms to place in the unit cell (which contains eight AB_2O_4), it was natural to place the A atoms in the positions of tetrahedral and the B atoms in those of octahedral coordination. The spinels MAl_2O_4 (where M is Fe, Co, Ni, Mn, and Zn) have this structure, but in certain other spinels the A and B atoms are arranged differently. In these the eight tetrahedral positions are occupied, not by the eight A atoms, but by one-half of the B atoms, the rest of which together with the A atoms are arranged at random among the sixteen octahedral positions. These are therefore best represented $B(AB)O_4$ to differentiate them from those of the first type, AB_2O_4. Examples include $FeMgFeO_4$, $FeTiFeO_4$, and $ZnSnZnO_4$. These compounds are often described as ferrites, zincates, aluminates, etc., but in view of their structures such nomenclature should be abandoned.

The spinel structure has been considered in some detail because of its importance in connexion with the oxides of iron and aluminium. The oxides M_2O_3 (and also the hydroxides $M(OH)_3$ and the oxy-hydroxides MO(OH), which are dealt with later) of these elements exist in two forms, distinguished as the α- and γ-forms. (For β-alumina see below, p. 335.) The structure of the isomorphous α forms, corundum and haematite, has already been described. The γ forms have spinel-like structures with a deficiency of metal ions. We have seen that there are thirty-two oxygen atoms in the unit cell of the spinel structure and twenty-four positive ions. Magnetite, Fe_3O_4, has the spinel structure (as also has Co_3O_4) with the full complement of positive ions, of which one-third are Fe^{2+} and the remainder Fe^{3+}—$Fe^{2+}Fe^{3+}_2O_4$. In γ-Fe_2O_3, however, there are on the average only $21\frac{2}{3}$ Fe atoms per unit cell distributed at random over the eight tetrahedral and sixteen octahedral positions. Accordingly γ-Fe_2O_3 and Fe_3O_4 are easily interconvertible. Careful oxidation of Fe_3O_4 yields γ-Fe_2O_3 which is converted back into Fe_3O_4 by heating *in vacuo* at 250° C. The relation of FeO to γ-Fe_2O_3 and Fe_3O_4 is of interest in this connexion. FeO has, ideally, the rock-salt structure with $4Fe^{2+}$ and $4O^{2-}$ per unit cell, but it is always deficient in iron. The length of the side of the unit cell varies, approximately linearly, with the composition, and typical values are: $a = 4{\cdot}3010$ A. for 48·56 atomic per cent. Fe and 4·2816 A. for 47·68 per cent. Fe. Fe_3O_4 has the spinel structure ($a = 8{\cdot}37$ A.) with eight Fe^{2+}, sixteen Fe^{3+}, and thirty-two O^2 ions in the unit cell. The arrangement of oxygen ions is therefore the same (cubic close-packed) in FeO, γ-Fe_2O_3, and Fe_3O_4. If we double the above spacing for iron-deficient specimens of FeO (viz. 8·6020 for 48·56 per cent. and 8·5632 A. for 47·68 per cent.) and plot them against composition we find that the line passes through the points for Fe_3O_4 and γ-Fe_2O_3 (viz. *c.* 8·37 A., 42·86 per cent. Fe, and *c.* 8·30 A., 40 per cent. Fe). The relation between these structures is therefore as follows. A cube with edge about 8·6 A. containing thirty-two oxygen ions can accommodate thirty-two Fe^{2+} ions in the octahedral holes between the cubic close-packed oxygen ions. This would give the ideal structure of stoichiometric FeO. If we remove a small proportion of these Fe^{2+} ions and replace them by two-thirds their number of Fe^{3+} ions, so maintaining electrical neutrality, we have FeO deficient in iron, alternatively (but incorrectly) described as FeO containing excess oxygen (see also FeS, p. 388). If this process be continued until we have only twenty-four iron atoms in the volume containing thirty-two oxygen ions, we have Fe_3O_4. Further removal of iron gives γ-Fe_2O_3, with an average of $21\frac{2}{3}$ iron atoms in the same volume. We have now a physical picture of the oxidation of $FeO \rightarrow Fe_3O_4 \rightarrow \gamma$-$Fe_2O_3$. The oxygen lattice of FeO is extended by the addition of more oxygen, added as new layers of close-packed oxygen atoms. Into these iron atoms migrate, resulting in a continuous decrease in the concentration of iron atoms in a given volume of the oxygen lattice. The defect γ structures are stabilized by the presence of ions such as Li, the compounds containing a little Li being intermediate

between the trioxides and compounds such as $LiAl_5O_8$, which also has the spinel structure.

The system Mn_xO_y also shows continuous variation in composition between α-Mn_2O_3 and Mn_3O_4 which are probably related in the same way as γ-Fe_2O_3 and magnetite (β-Mn_2O_3 has a different type of structure). Other defect oxide structures include the so-called γ'-Al_2O_3 formed by surface oxidation, in which there appears to be random distribution of $21\frac{2}{3}$ Al atoms per unit cell over thirty-two positions, so that since the arrangement of the thirty-two O atoms in the spinel structure is the same as that of the Cl^- ions in the rock-salt structure, this may be described as a defect rock-salt structure and written $Al_{\frac{2}{3}}O$. The lithium 'titanate', Li_2TiO_3, is similar, with 2Li+Ti randomly arranged in a rock-salt structure, and is fully miscible with both MgO and $LiFeO_2$. In the latter, Li and Fe are statistically distributed in a lattice of the rock-salt type. It is interesting to summarize here the structures of some 'titanates' and 'ferrites', since this will emphasize a point which is stressed throughout this book—that deductions concerning the structures of solids must not be based merely on similarity in empirical formulae.

		Structure type
'Titanates'	$CaTiO_3$, $SrTiO_3$	Perovskite
	$MgTiO_3$	Ilmenite
	Li_2TiO_3	Rock-salt (defect)
'Ferrites'	$MgFe_2O_4$	Spinel $B(AB)O_4$ type
	$LiFeO_2$	Rock-salt (defect)
	$K_2Fe_2O_4$	Cristobalite (see below)

The ability of a spinel such as $MgAl_2O_4$ to dissolve considerable amounts of Al_2O_3 is simply accounted for by the fact that both $MgAl_2O_4$ and γ-Al_2O_3 crystallize with the spinel structure. Certain other oxides, notably those of the alkali metals, the alkaline earths, and lead, form well-defined 'aluminates' and 'ferrites' containing many 'molecules' of Al_2O_3 or Fe_2O_3 in the general formulae $MO.nAl_2O_3$ or $MO.nFe_2O_3$. Examples are:

$Na_2O.11Al_2O_3$,	also formed by		K
$K_2O.11Fe_2O_3$,	,,	,,	Rb
$CaO.6Al_2O_3$,	,,	,,	Sr and Ba
$SrO.6Fe_2O_3$,	,,	,,	Ba and Pb

The first of these, $Na_2O.11Al_2O_3$, was originally thought to be a form of Al_2O_3, hence its name—β-alumina. X-ray investigation, however, showed it to have a definite structure closely related to that of spinel, no less than 100 of the 116 atoms in the unit cell being arranged in exactly the same way as in the spinel structure. The large Na or K ions are situated between large blocks of spinel structure and their presence is essential to the stability of the structure.

The structure of magneto-plumbite, $PbO.6Fe_2O_3$, is similarly built up of large portions of the magnetite (Fe_3O_4) structure, between which are

found the large Pb ions. These examples of complex oxide structures are included here to show that compounds with such extraordinary

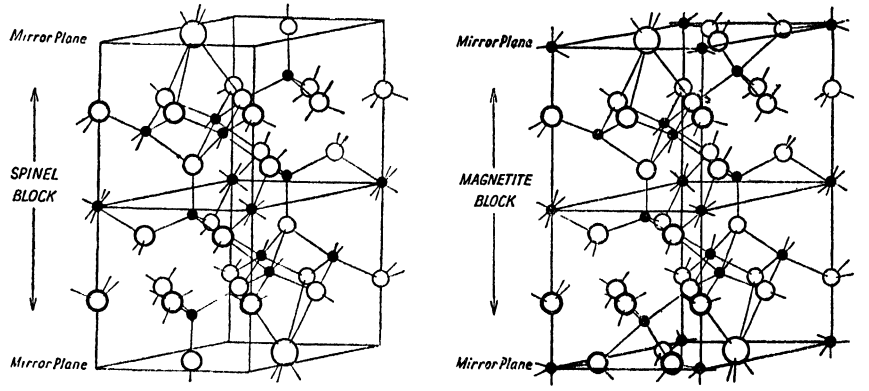


FIG. 87. (*a*) The relation of the structure of β-alumina, $Na_2O.11Al_2O_3$, to that of spinel (after Beevers and Ross). Large circles represent Na, small ones O, and black circles Al. (*b*) The relation of the structure of magneto-plumbite, $PbO.6Fe_2O_3$, to that of magnetite, Fe_3O_4 (after Adelsköld). Large circles represent Pb, small ones O, and black circles Fe.

formulae as $Na_2Al_{22}O_{34}$ and $CaAl_{12}O_{19}$ may be related in quite a simple way to γ-Al_2O_3 itself and to $MgAl_2O_4$.

Before leaving the complex oxides we may mention a number of compounds the structures of which are closely related to those of the forms of silica. Of the three* forms of crystalline silica, quartz, tridymite, and cristobalite, the former is relatively closely packed compared with the latter high-temperature forms, in which there are comparatively large holes in the open silicon-oxygen framework. These holes are large enough to accommodate ions of alkali metals, so that we find a compound like $NaAlSiO_4$ with a structure closely related to that of cristobalite. Replacement of Si by Al in half of the SiO_4 tetrahedra is accompanied by the introduction of positive ions to maintain electrical neutrality. Moreover, this compound, like SiO_2 itself, also exists with a tridymite-like structure, but further collapse to a quartz-like structure is impossible because the holes in the structure are occupied by ions. If alternate Si atoms are replaced by Ca instead of Al, then two monovalent ions must be introduced and the silicate Na_2CaSiO_4 results. This has the cristobalite structure, and since all the available holes in the structure are occupied by Na ions, only the cristobalite structure is possible. Instead of substituting Ca^{2+} for one-half of the Si^{4+} we may replace all the silicon by

* Each of these exists in two forms, α and β, but whereas the α-β change involves only a rearrangement of the atoms without breaking and re-forming any Si—O—Si bonds, the SiO_4 tetrahedra are differently linked together in quartz, tridymite, and cristobalite, and the conversion of one of these forms into another involves the rupture of Si—O—Si bonds. (See Chapter XIV.)

Al^{3+} or Fe^{3+} giving 'aluminates' or 'ferrites' of the type $K_2Al_2O_4$ or $K_2Fe_2O_4$, again with the cristobalite structure. Finally the silicon atoms may be replaced alternately by atoms of higher and lower valency ($M^{3+}M^{5+}O_4$), and since no additional ions are introduced into the lattice compounds of this type may have any one of the three structures, quartz, tridymite, or cristobalite. These examples are summarized below:

	Type of structure		
	Quartz	*Tridymite*	*Cristobalite*
(*a*)	$AlPO_4$		BPO_4
	$AlAsO_4$		$BAsO_4$
(*b*)		$NaAlSiO_4$ (nepheline)	$NaAlSiO_4$ (carnegieite)
(*c*)			$K_2Al_2O_4$
			$K_2Fe_2O_4$
			Na_2CaSiO_4

The relation of the perovskite structure of $Na^+Ta^{5+}O_3$ to that of $Re^{6+}O_3$ has already been mentioned, and other examples of structures of complex compounds which are related in a similar way to simpler structures will be found in other chapters. They are summarized on p. 151.

(*b*) *Structures containing Complex Ions.* We have seen that a compound with the formula ABO_n may form an ionic lattice in which we cannot distinguish any grouping BO_n as a structural unit or, on the other hand, the O and B atoms may be associated as finite or infinite complex ions. In this book we shall not be much concerned with the structures of crystals containing complex ions, since the packing together of the ions in such crystals is determined largely by the size and shape of the ions. For example, compounds with a certain type of empirical formula such as ABO_4 have many different crystal structures and the changes from one structure type to another may be related to the sizes of the ions. The relation between the calcite and aragonite structures has already been given (p. 105) as an example of the use of the concept of radius ratio. From the chemical point of view, however, we are more interested in the structures of the complex ions themselves, and the complex oxy-ions of boron and silicon are described in the chapters devoted to those elements. We shall merely note here two general points.

The first is that the structures of certain oxy-salts $A(BO_n)$ containing complex ions are related in a simple way to the structures of compounds AX. The structure of calcite may be regarded as derived from that of rock-salt by replacing Na^+ by Ca^{2+} and Cl^- by CO_3^{2-}, there being, of course, some distortion of the structure owing to the fact that the CO_3^{2-} ion is far from spherical in shape. It is interesting that KSH crystallizes with both the calcite structure (low-temperature form) and the rock-salt structure (high-temperature form). The aragonite structure bears a rather similar relation to that of NiAs.

The second point is that a series of compounds with similar empirical formulae may be of entirely different structural types, as is well illustrated

by compounds ABO_3. The simple ionic structures of several 'titanates' have already been described. In these there are no complex ions. The group BO_3 may, on the other hand, be a finite planar ion as in $CaCO_3$ or it may be a finite ring ion or an infinite chain ion formed by tetrahedral BO_4 groups each sharing two corners. Thus the following four compounds, all with the same type of empirical formula, have completely different structures:

ABO_3	*Type of complex ion*	*Oxygen coordination number of* B
$CaCO_3$	CO_3 (finite)	3
$CaSiO_3$	Si_3O_9 (finite)	4
$MgSiO_3$	$(SiO_3)_n$ (infinite)	4
$CaTiO_3$	None	6

CHAPTER X

OXYGEN AND SULPHUR (*continued*)

ISO- AND HETERO- POLYACIDS

TUNGSTEN, molybdenum, and to a lesser extent vanadium are notable for their complex oxy-salts and oxy-acids. Comparatively little is known of the detailed structure of these compounds, for complete structure determinations have been made of only three tungsten compounds. We shall confine our attention to the polyacids of tungsten, as these are typical of these compounds as a whole and will serve to illustrate the principles determining their structures. Whereas sulphates all contain the SO_4^{2-} ion, or the pyrosulphates the less stable $S_2O_7^{2-}$ ion, tungstates may be prepared in which the ratio y/x in the complex ion W_xO_y has various values. Acids containing such complex ions are termed iso-polyacids. The following classes of tungstates are distinguished on chemical grounds: normal and ditungstates (M_2WO_4 and $M_2W_2O_7$), paratungstates, and metatungstates.

On acidifying a hot solution of a normal or paratungstate, yellow tungstic acid is precipitated, to which the empirical formula H_2WO_4 is assigned. In cold solutions a voluminous white precipitate is formed. Both these modifications easily form sols, and the latter also a gel. Acidification of a solution of a metatungstate gives the soluble metatungstic acid which may be extracted with ether and forms large colourless crystals. Salts of the first class, such as Na_2WO_4 or $Na_2W_2O_7$, are prepared by fusing together the constituent oxides, but para- and meta-tungstates cannot be made in this way, for their empirical formulae are of the type $(M_2O)_x(WO_3)_y(H_2O)_z$. The para-compounds result from neutralizing a solution of a normal tungstate, which is alkaline, and crystallizing by evaporation, and the meta-compounds by boiling a solution of a paratungstate with yellow tungstic acid. The alkali paratungstates were originally formulated $5R_2O.12WO_3.nH_2O$ or $3R_2O.7WO_3.mH_2O$, it being difficult to decide between these two possibilities by chemical analysis, and the metatungstates, $R_2O.4WO_3.pH_2O$. It is now known, however, that ammonium paramolybdate is $(NH_4)_6Mo_7O_{24}.4H_2O$ and the paratungstates can be formulated in a similar way. The meta-compounds are known to contain the same type of complex ion as the 12-heteropolyacids, the structure of which is described below. The simple ratio of basic to acidic oxide in these metatungstates gives little idea of their complex structure.

The heteropolyacids are compounds containing in the empirical formula usually one atom of P, Si, B, or As, together with atoms of a second element (usually Mo or W) and a relatively large number of atoms of oxygen. The general formula of the phosphotungstic acids is therefore $H_mP_xW_yO_z.nH_2O$, the formation of hydrates with many molecules of

water of crystallization being an interesting feature of these acids and of their salts. The compounds which have been most studied are those with the ratio $y:x = 12$, and they are conveniently referred to as the 12-acids. We cannot describe here in any detail the methods by which these compounds may be prepared. The following are typical of the numerous methods. The well-known ammonium phosphomolybdate is precipitated from a solution containing a phosphate, ammonium molybdate, and nitric acid. Alternatively alkali phosphomolybdates (e.g. $Na_3PW_{12}O_{40}.nH_2O$) result from boiling a solution of the alkali phosphate with WO_3. The heteropolyacids are very soluble in water and ether and crystallize very well, often with large numbers of molecules of water of crystallization. For example, hydrates of $H_3PW_{12}O_{40}$ are described with 5, 14, 21, 24, and 29 H_2O. These acids have the remarkable property of forming insoluble precipitates with many complex organic compounds such as albumen and various alkaloids. Both the acids and salts possess considerable stability towards acids, but are readily reduced by sulphur dioxide and other reducing agents.

The general formulae of the complex ions of the heteropolyacids may be written $(P_xW_yO_z)^{n-}$, it being understood that P may be replaced in this formula by As, Si, B, etc., and W by Mo. Compounds are known in which

$$(a)\ y/x = 6$$
$$(b)\ 6 < y/x < 12$$
$$(c)\ y/x = 12.$$

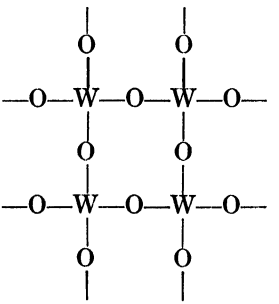
For many years these compounds were classified according to the Miolati-Rosenheim scheme, which was based on Werner's coordination theory. For the 'saturated' acids, classes (a) and (c), typical constitutional formulae were $H[As(MoO_4)_6]^{7-}$ and $[P(W_2O_7)_6]^{7-}$. The paratungstates and paramolybdates were formulated in a similar way to the 6-heteroacids of class (a), H_2 replacing the P atom in the general formula above. For example, the ammonium salt was written $(NH_4)_5H_5[H_2(MoO_4)_6]$. The determination of the cell dimensions and density of this compound gives the mass of material in one unit cell of the crystal structure, and this must be an integral multiple of the molecular weight. In this way it was found that the above formula must be rejected and that $(NH_4)_6[Mo(Mo_6O_{24})]4H_2O$ is consistent with the crystallographic data. The formulation of the 12-acids as $H_7P(W_2O_7)_6.nH_2O$ and $H_8[Si(W_2O_7)_6].nH_2O$, which was apparently supported by titration experiments, was a backward step, as earlier work showed the formulae of the completely dehydrated acids to be $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$, which we now know to be correct.

The intermediate compounds presented more difficulty. For example, the salt with the empirical formula $K_6H_6As_2Mo_{16}O_{65}$ (prepared from a solution of potassium arsenite saturated with molybdic acid) had to be written as a polynuclear compound:

$$K_6H_6\left[\begin{matrix} O & & O \\ & As-Mo_2O_7-As & \\ (Mo_2O_7)_4 & & (Mo_2O_7)_4 \end{matrix}\right]$$

in order to preserve the 6-coordination of the arsenic atoms. An important step in elucidating the constitution of these compounds was made by Pauling in 1929. He accepted the formulation of the 6-ions as a central AsO_6 octahedron surrounded by, and sharing corners with, six WO_4 tetrahedra. There is an alternative structure for these ions which consists of a ring of six WO_6 octahedra each sharing two edges. The As or other atom would then occupy the octahedral hole at the centre of the ring (compare the layer structures of $Mg(OH)_2$ and $Al(OH)_3$). It may be, however, that only corners and not edges of tungsten-oxygen polyhedra will be shared. This is certainly so in the 12-acids, for the ions of which Pauling suggested a 3-dimensional structure in which a central PO_4 tetrahedron was surrounded by a polyhedral shell of composition $W_{12}O_{18}$, in which every W atom was joined to three others via O atoms. The octahedra around the W atoms were completed by OH groups outside the shell, the composition of the whole being $[PO_4W_{12}O_{18}(OH)_{36}]^{3-}$. Although this structure was very near to the true one, which we describe below, it clearly could not represent the structure of the ion in the anhydrous acid or in the lower hydrates, since it contains thirty-six H atoms.

The structures of the heteropolyacid ions are best understood if we concentrate our attention on the way in which the W atoms are linked together by O atoms to form a large polyhedral closed basket. When discussing complex oxy-ions we saw that WO_6 octahedra might share corners in various ways. If each corner of every octahedron is shared with another octahedron we have the structure of WO_3, extending indefinitely in three dimensions, but if only four corners are shared we obtain a planar network of the type shown below. (The unshared O atoms above and below the W atoms are not shown.) Octahedra linked in this way can also form a closed basket, which may be regarded as a portion of plane net joined up, with suitable adjustment of the —O— bond angles.



X-ray study of the pentahydrate of 12-phosphotungstic acid showed that the complex ion has the structure shown, in idealized form, in Fig. 88 (*b*). If we imagine W atoms at the corners of a cubo-octahedron (Fig. 88 (*a*)) and O atoms at the mid-points of the edges, we obtain a closed polyhedral group of composition $W_{12}O_{24}$. These O atoms may now be moved outwards from the centre of the complex until each W atom is surrounded by four O atoms in a plane. The octahedra of O atoms around the W

atoms may now be completed by the addition of sixteen O atoms, four within the complex (shown in black) and twelve outside (dotted circles). The four atoms inside the shell form a tetrahedron, at the centre of which

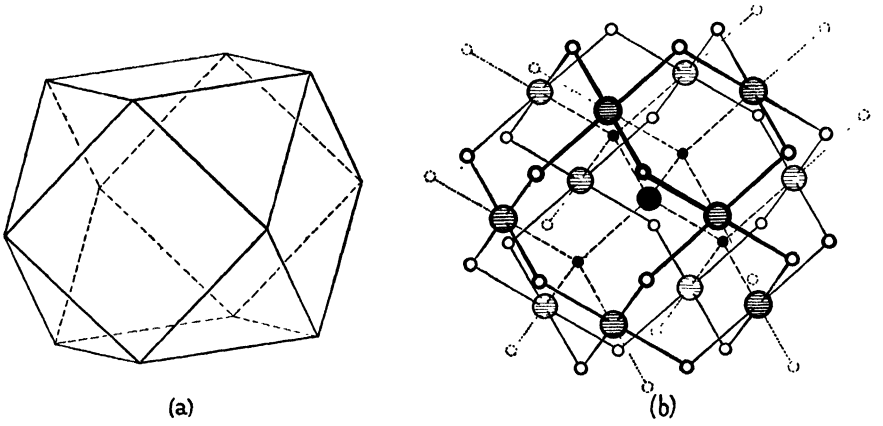


FIG. 88. (*a*) Cubo-octahedron, (*b*) the ion $[PW_{12}O_{40}]^{3-}$. The W atoms (shaded circles) are at the vertices of a cubo-octahedron. The oxygen atoms outside the polyhedral shell are shown as small dotted circles, those inside as small black circles. The latter form a tetrahedral group around the central P atom (large black circle).

an atom of P is placed, the result being the complex ion $[PW_{12}O_{40}]^{3-}$. The five water molecules are arranged between these large negative ions so that the water molecules, and the three H^+ ions associated with them, are responsible for the cohesion of those ions. The pentahydrates of $H_5BW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and of metatungstic acid, $H_6[H_2W_{12}O_{40}]$ are all isomorphous with $H_3PW_{12}O_{40}.5H_2O$.

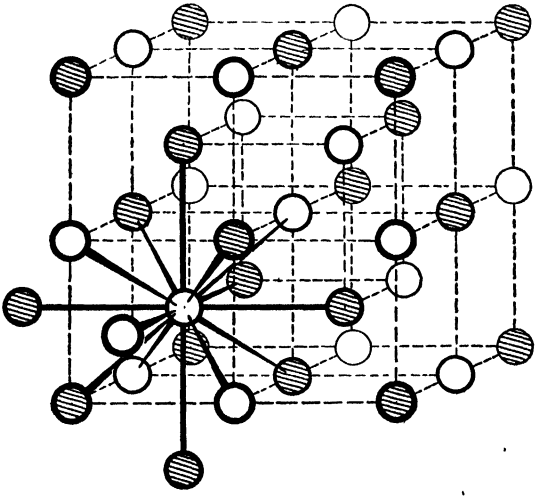


FIG. 89. The arrangement of $[PW_{12}O_{40}]^{3-}$ and $[H_3.29H_2O]^{3+}$ complexes in a crystal of $H_3PW_{12}O_{40}.29H_2O$. Shaded circles represent $[H_3.29H_2O]^{3+}$ complexes.

The crystal structure of $H_3PW_{12}O_{40}.29H_2O$ also has been determined. It may be described most simply as an aggregate of units $PW_{12}O_{40}^{3-}$ and $H_3^+.29H_2O$, arranged as shown in Fig. 89. Comparison with the structure of diamond (p. 431) will show that this structure may be regarded as two interpenetrating diamond lattices. If we examine in more detail how the polyacid ions and the water molecules are linked together, we find that the large complex ions are bound together by the water molecules, there being no direct linkage between one $PW_{12}O_{40}^{3-}$ ion and another. Of the twenty-nine H_2O molecules seventeen are linked together into a well-defined group, but the other twelve are not directly bonded to any of these seventeen or to one another. The outer six of this group of seventeen H_2O and the other twelve are responsible for linking together the anions.

Basicity of the Polyacids and the Formulae of their Salts

In the isomorphous pentahydrates of the acids $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_5BW_{12}O_{40}$, and $H_6[H_2W_{12}O_{40}]$ there are respectively 3, 4, 5, and 6 H^+ ions which we might expect to be replaced by metal ions in their salts. Let us consider the silicotungstates, as X-ray investigations have established the numbers of metal ions in the empirical formulae of these salts. The smaller alkali metals form salts with large numbers of molecules of water of crystallization, e.g. $Li_2H_2SiW_{12}O_{40}.26H_2O$, $Li_3HSiW_{12}O_{40}.24H_2O$, and $K_4SiW_{12}O_{40}.18H_2O$, but caesium apparently forms only the salt $Cs_3HSiW_{12}O_{40}.0$ or $2H_2O$, no matter what proportions of caesium salt and acid are mixed. This latter salt has a structure similar to that of $H_4SiW_{12}O_{40}.5H_2O$, the positions of three of the water molecules being occupied by the large Cs^+ ions; it is uncertain whether the other two H_2O are present or not. The acids $H_5BW_{12}O_{40}$, $H_6[H_2W_{12}O_{40}]$, and $H_3PW_{12}O_{40}$ all give similar tri-caesium salts in spite of their different apparent basicities. It would therefore appear that the primary consideration is the packing of the large complex ions rather than the number of H^+ ions in the acid. Only the pentahydrate type of structure is possible for the large Cs^+ ions and also for Rb^+ and Tl^+, and there is room in the structure for only three such ions, but for the K salt a structure containing many molecules of H_2O leads to a more satisfactory packing and in the structure there is room for the full complement of four K^+ ions. The salts of di- and tetravalent metals are also normal with larger water contents, e.g. $Ba_2SiW_{12}O_{40}.24H_2O$, and $ThSiW_{12}O_{40}.30H_2O$. The salts of trivalent metals are more interesting. The normal salts would have formulae such as $Al_4(SiW_{12}O_{40})_3.87H_2O$, but determinations of cell size and density show that this salt is actually $AlHSiW_{12}O_{40}.28H_2O$ (see p. 201). The silicotungstates of trivalent metals appear to have no less than four highly hydrated forms, with 20, 24, 28, and 30 H_2O, and the cell dimensions show that the structures of all four hydrates are very similar and closely related to that of $H_3PW_{12}O_{40}.29H_2O$.

The determination of the formulae of these salts by the packing of the constituent ions in the crystal rather than by the number of replaceable

H^+ ions in the acid may be compared with the formation of acid salts such as $(NH_4)_2H_3IO_6$ and KH_2PO_4 which we have already described (p. 260).

The 'Unsaturated Acids'

Unsaturated acids, class (*b*), appear to exist in which the ratio of W to P atoms has the values 8, $8\frac{1}{2}$, 9, 10, $10\frac{1}{2}$, and 11, or—doubling these

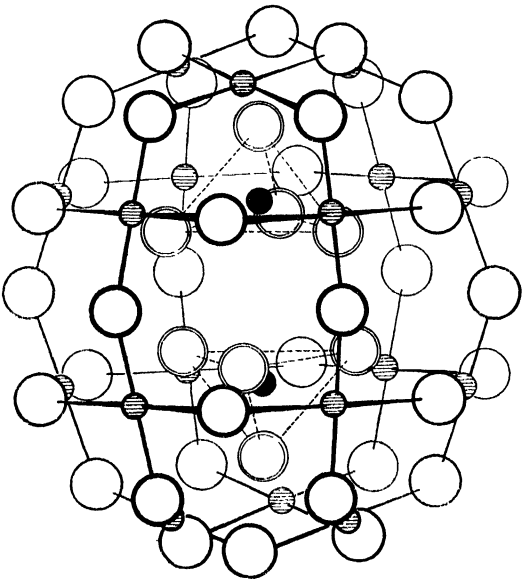


FIG. 90. A possible structure for the nucleus of the ion $[P_2W_{18}O_{62}]^{6-}$, the 18 oxygen atoms outside the polyhedral shell being omitted. The P atoms within the PO_4 tetrahedra are shown as black, and the W atoms as shaded circles.

values—P_2W_{16} to P_2W_{22}. Pauling suggested that these might arise from the combination of two or more 12-anions, and he derived for the P_2W_{18} anion the formula $[(PO_4)_2W_{18}O_{30}(OH)_{48}]^{6-}$ or $[P_2W_{18}O_{62}.24H_2O]^{6-}$. In view of what has been said about the 12-acids, it will be seen that such formulae are now unacceptable. It is possible that these higher acids are based on larger polyhedra of the same type as the cubo-octahedron but containing two PO_4 tetrahedra instead of one. On this scheme the general formulae of these higher acids would be $[P_2W_pO_{3p+8}]^{6-}$, for example, $H_6[P_2W_{18}O_{62}]$, and this ion is illustrated in Fig. 90.

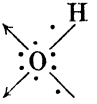
Our general picture of the heteropolyacids is therefore as follows. After the 4- and 6-ions, based presumably on PO_4 and WO_4 or WO_6 groups, there is a gap until we reach a polyhedral group large enough to contain one PO_4 tetrahedron at $PW_{12}O_{40}$. There is then a further interval until there is room for two PO_4 tetrahedra, apparently at $P_2W_{16}O_{56}$. The isopolyacids have similar structures in which W (or Mo) or H occupy the central positions occupied by P, Si, etc., in the heteropolyacid ions.

The formulae of the main types of iso- and hetero-polyacid ions are set out below.

Isopolyacids	*Heteropolyacids*
(Simple ions WO_4^{2-}, $W_2O_7^{2-}$)	6-acids $[AsW_6O_{24}]^{7-}$, etc.
Paratungstic $[W(W_6O_{24})]^{6-}$	12-acids $[PW_{12}O_{40}]^{3-}$, etc.
Metatungstic $[H_2W_{12}O_{40}]^{6-}$	Higher acids $[P_2W_{16}O_{56}]^{6-}$, etc.

HYDROXIDES

Oxygen may complete its octet by forming two electron-pair bonds as in compounds containing covalently bound hydroxyl groups, where we have —O—H, or it may reach the same stable configuration by forming one such bond and acquiring one electron, as in the hydroxyl ion, OH^-. If we adopt the simple picture of purely covalent single bonds, then further bond formation is possible making use of the remaining orbitals of the oxygen atom, just as the halogens can form up to four tetrahedral bonds.



The hydroxyl ion is isoelectronic with F^-, and in structures in which it is behaving as a spherical ion has an effective radius intermediate between those of F^- and Cl^-. The SH^- ion has about the same size as Br^- and is isoelectronic with Cl^-. We should therefore expect to find that hydroxides and hydrosulphides have structures similar to those of halides, and we do in fact find many points of resemblance between these compounds. In the previous chapter we saw that in some halides (e.g. the alkali halides) the halogen behaves as a spherical ion; in others the R—X bonds have more covalent character and various kinds of layer lattice are formed. We find hydroxides and hydrosulphides with the rock-salt structure, and certain hydroxides $M(OH)_2$ have the same kind of crystal structure as many halides MX_2.

We shall see, however, that the resemblance between hydroxides and halides is limited and there are significant differences between the structures of the two sets of compounds. Typical of these differences are the following. Whereas KCl has the simple ionic rock-salt structure to be expected for spherical ions, KOH and KSH have this structure only at higher temperatures. The structure of KOH at ordinary temperatures is not known, but the less symmetrical structure of the low-temperature form of KSH will be described below. The packing of the OH groups in certain metallic hydroxides with layer structures is quite different from that of the halogen atoms in halides of similar formula type, suggesting directed forces between adjacent OH groups bound to different metal atoms. Similar differences are found between oxyhydroxides MO.OH and oxychlorides MO.Cl. We shall be largely concerned with these differences in the following account.

The simple hydroxides $R(OH)_n$ range from the strongly basic compounds of the alkali metals through the so-called amphoteric hydroxides of Zn, Al, and other metals to the hydroxy-acids of B, Te, P, etc. The distinction between the extreme types rests on the fact that they ionize in quite different ways. A basic hydroxide ionizes in the following way:

$$R(OH)_n \rightleftharpoons R^{n+} + n(OH)^-$$

yielding hydroxyl ions, whereas a hydroxy-acid gives up H^+ ions, the oxygen remaining with the atom R in a complex ion:

$$R(OH)_n \rightleftharpoons RO_n^{n-} + nH^+.$$

This is analogous to the complete ionization of an oxyacid $H_mRO_n (m \neq n)$

$$H_mRO_n \rightleftharpoons RO_n^{m-} + mH^+.$$

The general method of preparing the less soluble metallic hydroxides is therefore to add OH^- ions to a solution of the metallic salt, though in some cases the oxide instead of the hydroxide is obtained in this way. The hydroxy-acids, on the other hand, are obtained by acidifying a solution containing the oxy-ion RO_n.

The intermediate amphoteric hydroxides are said to be capable of ionizing in both the ways, viz.

$$Zn(OH)_2 \rightleftharpoons Zn^{2+} + 2OH^-$$

and

$$H_2ZnO_2 \rightleftharpoons ZnO_2^{2-} + 2H^+,$$

but we shall have more to say about these compounds later. We shall first consider some of the properties of these three groups of hydroxides:

(1) (*a*) Hydroxides of Na, K, Rb, Cs, and Tl^I.
    (*b*) Hydroxides of Li and the alkaline earths (excluding Be).
(2) Other metallic hydroxides, including the amphoteric hydroxides.
(3) Hydroxy-acids.

(1) The Hydroxides (and Hydrosulphides) of the more Electropositive Metals

All the alkali and alkaline-earth hydroxides may be prepared by the action of water on the metal or oxide, the reaction with the metal being very energetic in the case of the alkali metals. Lithium in many ways resembles the alkaline-earths rather than the other alkali metals. For example, when burnt in excess oxygen the metal forms the normal oxide Li_2O, whereas the other alkali metals give Na_2O_2, KO_2, RbO_2, and CsO_2 respectively. Furthermore, LiOH decomposes to the oxide at red heat (compare Ca, etc.) whereas NaOH and the other alkali hydroxides can be volatilized without loss of water. Lithium hydroxide dissolves in water only to the extent of about 4 moles/litre at 10° C. whereas the corresponding figure for NaOH is about 12 moles/litre. Just as LiOH resembles in many ways the alkaline-earth hydroxides, so beryllium hydroxide has many properties in common with $Al(OH)_3$, and for this reason is placed in the second rather than in the first group. It is precipitated by addition

of alkali hydroxide to a solution of a beryllium salt in a gelatinous form which redissolves in excess of alkali. Both of these properties are characteristic of a considerable number of hydroxides in group (2). Magnesium hydroxide also tends to form a rather slimy precipitate, but the hydroxides of Ca, Sr, and Ba may easily be obtained crystalline. The hydroxides of Mg, Ca, Sr, and Ba are far less soluble than those of the alkali metals, the solubilities ranging from $3{\cdot}5 \times 10^{-4}$ moles/litre at 10° C. for $Mg(OH)_2$, to about 0·15 moles/litre for $Ba(OH)_2$. We shall see later that the structural analogy with halides is confined to the simple ionic hydroxides of the alkali metals (excluding Li) and certain hydroxides with layer lattices such as those of the alkaline-earths and Mg.

Only the most electropositive metals form hydrosulphides, so that only the hydrosulphides of the alkali and alkaline-earth metals are known. We shall see later that this is associated with the inability of sulphur to form hydrogen bonds. The structures of the alkaline-earth hydrosulphides have not been studied and LiSH does not appear to be stable under ordinary conditions. Ammonium hydrosulphide has the same structure as PH_4I and the tetramethylammonium halides, $N(CH_3)_4X$. In crystals of these salts the ions are arranged in a similar way to the Pb and O atoms in PbO (see Fig. 159, p. 518). The structures of the remaining alkali compounds are of some interest. With the exception of NaSH they may be prepared by the action of gaseous H_2S on the metal. In the case of sodium this reaction gives a mixture of NaSH and Na_2S, and the pure hydrosulphide is conveniently prepared from the metal and liquid H_2S. Only one crystalline form of CsSH has been prepared, and this has the CsCl structure in common with the following caesium salts: CsCl, CsBr, CsI, CsCN, $CsNO_3$ (at 200° C.). The cell dimensions of CsSH are the same as those of CsBr, so that the SH^- ion is behaving as a spherically symmetrical ion with the same radius as Br^-. The Na, K, and Rb compounds all exist in two crystalline forms and are isodimorphous. Above their respective transition points they crystallize with the NaCl structure (6:6 coordination), but at room temperature they form rhombohedral crystals. In this calcite-like structure the SH^- ion has lower symmetry than in the high-temperature forms and appears to behave like a planar group. It is probable that the proton rotates around the sulphur atom in a plane, forming an anisotropic group like the planar NO_3^- and CO_3^{2-} ions in $NaNO_3$ and calcite, which have similar rhombohedral structures.

	NaSH	KSH	RbSH	CsSH
Low-temperature form	Rhombohedral structure			CsCl
Transition temperature	90°	160–170°	?	structure
High-temperature form	Rock-salt structure			

(2) Other Metallic Hydroxides

Comparatively little is known of the structures of other metallic hydroxides, and for this reason we group together in this class all other

hydroxides. We have placed thallous hydroxide with the alkali compounds since like them it is obtained by the action of water on the metal and is comparatively soluble, whereas the hydroxides of this group are notable for their insolubility in water. Unlike the alkali hydroxides, however, TlOH may be converted into the oxide *in vacuo* at room temperature, the easy dehydration of the hydroxides being characteristic of many of the heavy metals. Many hydroxides of this group are precipitated from solutions of their salts in a gelatinous form which dries to a horny mass with conchoidal fracture, but some may be obtained crystalline by slow precipitation. The difficulty of obtaining these compounds in a crystalline form suitable for X-ray examination is the chief reason for our ignorance of their structures, for only the structures of those which occur crystalline as minerals have been investigated.

Hydrolysis of metallic salt solutions often yields colloidal solutions of the hydroxides. For example, by boiling ferric acetate solution or by adding excess NaOH to ferric chloride solution until the precipitated $Fe(OH)_3$ redissolves, clear brown colloidal solutions of $Fe(OH)_3$ are obtained. Among the hydroxides which easily form colloids are those of Fe^3, Al^3, Cr^3, Sn^2, Mn^2, and the elements of the fourth Periodic Group, Si, Ge, Sn^4, Ti, Zr, and Th. It is unlikely that the tetrahydroxides of these latter elements are present in such solutions, for the water content in gels $MO_2.xH_2O$ is very variable.

Certain hydroxides are easily 'dehydrated' to the corresponding oxide. Lead hydroxide, $Pb(OH)_2$, may be precipitated in cold solution, but the addition of strong boiling NaOH to a solution of a lead salt leads to precipitation of PbO. Other hydroxides which are converted into the corresponding oxides in boiling solution include $Cu(OH)_2$, $Tl(OH)_3$, and $Sn(OH)_2$. The following hydroxides are not known: CuOH, $Pb(OH)_4$, AgOH, and $Hg(OH)_2$. In other cases the dehydration may be stopped at an intermediate stage. Thus if $Au(OH)_3$ is dehydrated over P_2O_5 the compound AuO.OH is formed, which dissolves in KOH to form the meta-aurate, $AuO.OK.3H_2O$. Other oxy-hydroxides include AlO.OH, FeO.OH, MnO.OH, and GaO.OH, the structures of some of which will be described below.

Amphoteric Hydroxides

Many hydroxides when precipitated by NaOH redissolve if excess alkali is added, e.g. $Be(OH)_2$, $Al(OH)_3$, $Zn(OH)_2$, $Pb(OH)_2$, and others (e.g. $Cu(OH)_2$ and $Cr(OH)_3$) show the same behaviour but redeposit the hydroxide on standing. Such hydroxides, which dissolve in alkali as well as in acids, are termed amphoteric since the solubility in alkali was taken to indicate that the hydroxide had acidic properties, ionizing to produce H^+ ions in the one case and OH^- ions in the other (see above). In many cases, however, the conductivities of such solutions are equal to those of alkali in the same concentration, suggesting that the 'solubility' of the hydroxides is more probably due to the formation of sols which are

stabilized by the OH^- ions. There is no evidence for the existence of complex ions in these solutions. The existence of mixed oxides such as K_2ZnO_2, $NaAlO_2$, Ca_2PbO_4, etc., is not inconsistent with this view of the constitution of the alkaline solutions of the amphoteric hydroxides. Most of these compounds can be made only by fusion of a mixture of the constituent oxides, and we have seen that they are essentially ionic crystals—often with structures closely related to those of the simple oxides. In the case of Al and Zn compounds such as $NaAlO_2$ and K_2ZnO_2 may be crystallized from solutions of the hydroxides containing excess alkali hydroxide—after adding alcohol. These compounds are hydrolysed by water and their structures have not been determined, but there is no more reason for regarding K_2ZnO_2 as derived from $Zn(OH)_2$ acting as an acid (H_2ZnO_2) than for considering the spinel $MgAl_2O_4$ as a salt of $H_2Al_2O_4$.

(3) Hydroxy-acids

This is a small group of compounds, and only in one case has a structure been determined in detail (H_3BO_3, p. 355). The relation of these compounds to the other hydroxides is discussed below.

We must emphasize that our picture of the structural chemistry of hydroxides is very incomplete. Though many of the higher hydroxides do not appear to be stable under ordinary conditions, nevertheless compounds like $Ni(OH)_3$, $Mn(OH)_4$, $U(OH)_4$, $Ru(OH)_4$, etc., are described in the literature and a knowledge of their structures would be of great interest. Some may not be simple hydroxides—e.g. $Pt(OH)_4.2H_2O$ may be $H_2[Pt(OH)_6]$. The first step in clearing up this field will be to ascertain which of the alleged hydroxides are in fact compounds of the type $R(OH)_n$. Apart from the metallic hydroxides there are compounds such as H_3PO_3 and H_2SO_2 still awaiting examination.

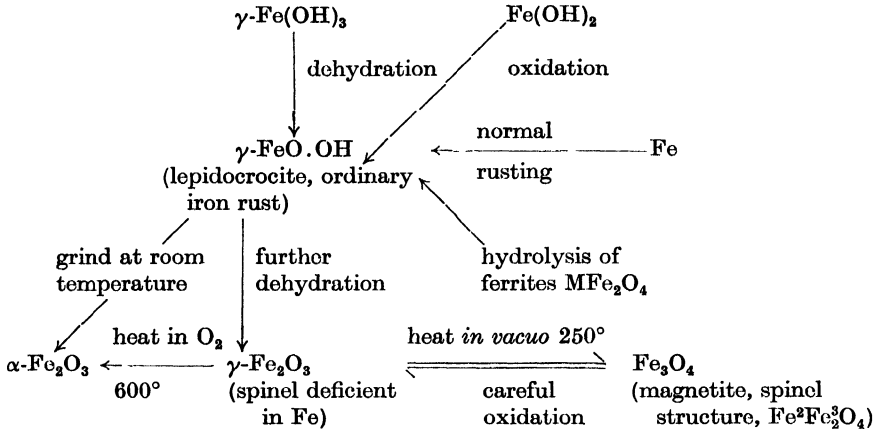
The Oxy-hydroxides

A few elements are known to form compounds intermediate between the oxides and hydroxides, e.g. AlO.OH, FeO.OH, MnO.OH. The iron and aluminium compounds exist in two crystalline forms, as do the trioxides and trihydroxides of these elements, the compounds of the α series being more stable than the γ compounds. The names of these compounds, most of which occur as minerals, and the inter-relations of the iron compounds are set out below.

	α series	*γ series*
$Al(OH)_3$	(Structures unknown)	Hydrargillite
$Fe(OH)_3$		γ-$Fe(OH)_3$ (structure unknown)
AlO.OH	Diaspore	Boehmite
FeO.OH	Goethite	Lepidocrocite
Al_2O_3	Corundum	γ-Al_2O_3
Fe_2O_3	Haematite	γ-Fe_2O_3

(The so-called β-alumina has been referred to on p. 335.)

The Relations between the Iron Compounds



We have dealt with the structures of the α and γ oxides and of Fe_3O_4. The structures of the γ hydroxides and of the hydroxy-oxides will be described in a later section.

The Crystal Structures of Hydroxides—the Hydroxyl Bond

We saw in a previous chapter that the abnormally short O—O distances in certain acid salts arise from the presence of a H atom between the two oxygen atoms and that such short hydrogen bonds —O—H—O—, of length about 2·55 A., are symmetrical owing to resonance between the extremes, —O—H · · O— and —O · H—O— which are states of equal energy (see, however, p. 253). The H atom is not attached preferentially to either of the O atoms, as shown by the infra-red absorption spectra. The absorption band at 3 μ characteristic of the OH group is absent in the spectrum of H_2SO_4 and of compounds with intramolecular H bonds such as salicylaldehyde. It was also pointed out that bonds of a somewhat similar nature are formed by hydroxyl groups. In this case, as distinct from the above, there is a H atom attached to each O atom and we saw that, in some cases at least, there is good evidence that the H atoms of these longer 'hydroxyl' bonds remain associated with their own O atoms. In other words, the hydroxyl group retains its identity when forming a hydroxyl bond.

It has been mentioned that the packing of the OH groups in certain hydroxides indicates that directed bonds are formed between OH groups attached to different metal atoms, leading to a more open packing of these groups than is found for the halogen atoms in the corresponding halides. Since the OH groups concerned are attached on one side to metal atoms, the bond between the OH groups cannot be any simple dipole attraction since similar ends of the dipoles would be in contact. Bernal therefore suggested that in a suitable environment the oxygen atom of the OH group develops the same tetrahedral character as in the water

molecule (see p. 361). In the OH group the H atom lies about 1 A. from the centre of the O atom, the effective radius of which ranges from 1·3 to 1·8 A., and we may assume a similar position for the H in the OH^- ion. The O—H bond is polar so that we may picture the OH^- ion as a dipole with a charge of about $-1{\cdot}5e$ near the centre of the O atom and a charge

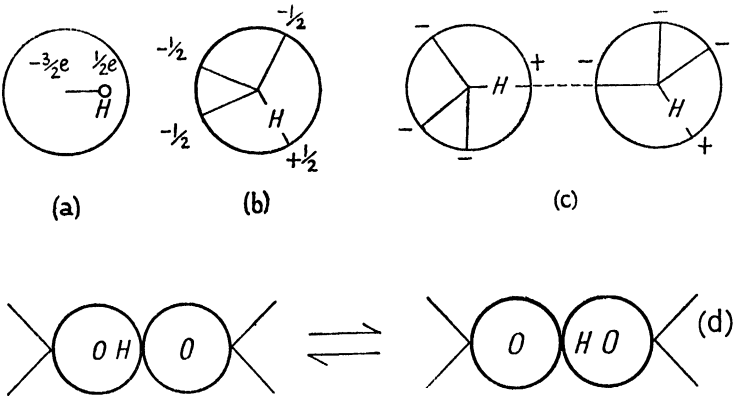


FIG. 91. (*a*) and (*b*) the hydroxyl group with cylindrical and tetrahedral symmetry of charge distribution. (*c*) and (*d*) O—H—O bonds.

of $+\frac{1}{2}e$ at the H atom, Fig. 91 (*a*). This ion has cylindrical polar symmetry. In the cubic high-temperature form of KOH the OH^- ion may become spherically symmetrical by rotation, or the cubic symmetry may arise from the special way in which the OH dipoles are oriented.

In the vicinity of more highly charged positive ions, however, the electron distribution is distorted and Bernal suggests that the OH^- ion passes through the following stages. If the polarization is small the group retains its cylindrical symmetry and merely increases its dipole moment. Further distortion leads to a separation of charges arranged tetrahedrally as shown at (*b*). The negative charge on one O can attract the H atoms attached to another forming a hydroxyl bond, Fig. 91 (*c*). With this may be compared the behaviour of the water molecule with its analogous tetrahedral charge distribution. With still further polarization the H atom can leave the O and migrate to a neighbouring O atom (*d*). This corresponds to our picture of the short H bond, for the two states of the system have identical energies and the H may be regarded as belonging equally to both atoms. This final stage in the polarization of the OH group will occur only in oxy-acids and acid salts. In hydroxides $R(OH)_n$ such a transfer of H would lead to the formation of a water molecule



unless the OH groups formed an infinite array and the H atoms were all assumed to move simultaneously in the same direction.

The evidence in support of this view of the behaviour of the OH^- ion in hydroxides comes from the geometrical nature of their crystal structures and the interatomic distances therein. Let us consider first the interatomic distances. The distance in which we are interested is that between two OH groups attached to different metal atoms, since this will be smaller the greater the interaction between these groups. In KOH there is no contact between OH ions of different coordination polyhedra and we can give only the effective radius of OH as $d_{K-OH}-r_K = 1{\cdot}53$ A. Since we wish to associate the interaction between OH groups with the polarization of the group we need some measure of this latter quantity. We shall simply give the electrostatic strength of the bond R—OH, which is equal to the charge on R (assumed to be an ion) divided by the number of OH groups surrounding it in the crystal.

	Electrostatic strength of bond R—OH	OH—OH	
KOH	$\frac{1}{6}$	..	
LiOH	$\frac{1}{4}$	3·60 A.	
$Ca(OH)_2$	$\frac{1}{3}$	3·36	No OH bonds
$Mg(OH)_2$	$\frac{1}{3}$	3·22	
$Zn(OH)_2$	$\frac{1}{2}$	2·82	
$Al(OH)_3$	$\frac{1}{2}$	2·78	
$Te(OH)_6$	1*	2·76	OH bonds
$B(OH)_3$	1	2·70	
H_2O (ice)	..	O—H—O 2·76 A.	
$NaHCO_3$	$\frac{4}{3}$†	2·54	H bonds
KH_2PO_4	$\frac{5}{4}$†	2·54	

* The justification for applying the concept of electrostatic bond strength to such coordination groups, implying the existence of highly charged ions such as Te^{6+}, has already been discussed. It is used here because there is no other convenient way of comparing the polarization of the OH groups in these compounds.

† The distances O—H—O in two acid salts are included in the table for comparison purposes. They are the lengths of the short symmetrical H bonds.

We see that there is a relation between the polarization of the OH groups and the extent of the interaction between different groups. In structures where the electrostatic bond strength is one-half or more the OH groups of different coordination polyhedra approach to within 2·7–2·8 A. of one another, and the crystal structures of these compounds become intelligible only if we postulate the formation of directed hydroxyl bonds between such hydroxyl groups. The structures of some of these hydroxides will now be described.

Lithium Hydroxide. This compound forms a layer lattice in which every Li is surrounded tetrahedrally by four OH. A hydroxyl group is attached

on one side to four Li and on the other to four OH of the next layer. A portion of a layer is shown in Fig. 92.

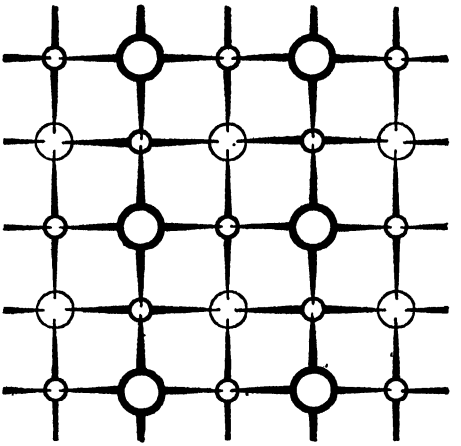
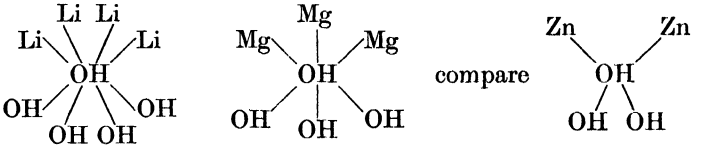


FIG. 92. Portion of one layer in a crystal of LiOH. Small circles represent Li atoms in the plane of the paper and large circles OH groups lying in planes above and below that of the Li atoms.

Magnesium Hydroxide. This compound, and also the dihydroxides of Ca, Cd, Mn, Fe, Co, and Ni, crystallize with the CdI_2 layer structure (see p. 101) in which every Mg is surrounded by six OH. Every OH forms three bonds to Mg atoms in its own layer and is in contact with three OH of the adjacent layer. The environments of OH in LiOH and $Mg(OH)_2$ show that there are no OH bonds in these structures. We now come to structures involving hydroxyl bonds.



Zinc Hydroxide. In this structure, which is built up of $Zn(OH)_4$ tetrahedra sharing OH groups, every OH is surrounded—approximately tetrahedrally—by two Zn and two OH. This arrangement, and the short OH—OH distances (2·83 A.), show that hydroxyl bonds are formed.

Aluminium Hydroxide. This is still one of the best examples of structures involving hydroxyl bonds. It is built up of double layers of hydroxyl groups, the Al atoms occupying two-thirds of the octahedral holes between the two layers. An idealized plan of one such double layer is shown in Fig. 93. The actual arrangement is a slightly distorted version of this. This arrangement of OH groups is exactly the same as in the dihydroxides such as $Mg(OH)_2$, though in these all the octahedral holes are occupied by metal atoms. The way in which these double layers pack together is, however, quite different in the two structures. In $Mg(OH)_2$ they pack so

that each OH group on the underside of a layer fits into the depression between three such groups on the top of the next layer below. As a result, all the OH groups throughout the structure are close-packed. In

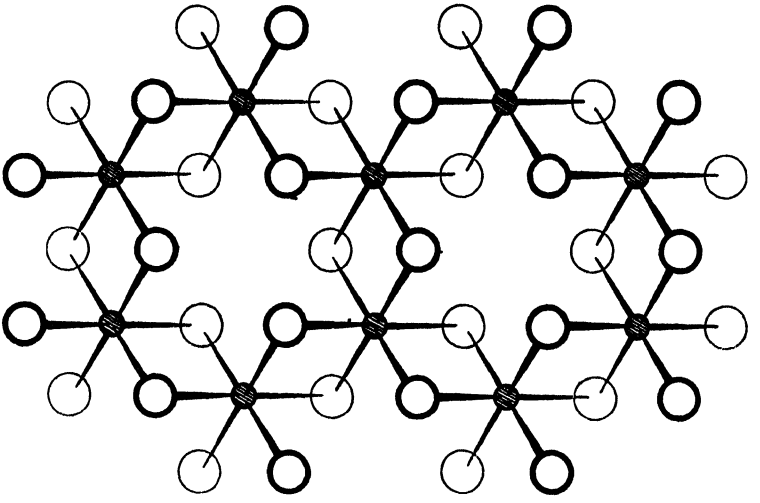


FIG. 93. Part of a layer of $Al(OH)_3$ (idealized). The heavy and light open circles represent OH groups above and below the plane of the Al atoms (shaded).

hydrargillite, on the other hand, the OH groups on the underside of one layer rest on the groups of the layer below, as shown in elevation in Fig. 94. This unusual arrangement is due to, and in fact led to the idea of, directed

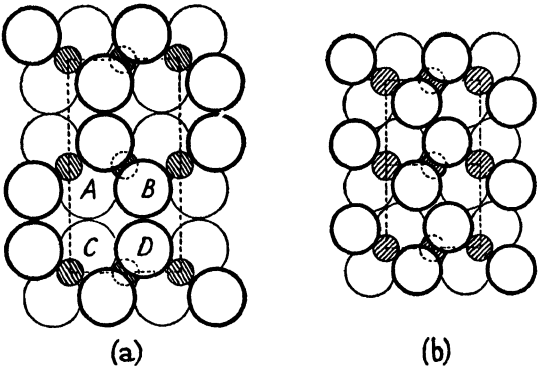


FIG. 94. The structures of (*a*) $Al(OH)_3$ and (*b*) $Mg(OH)_2$, viewed in a direction parallel to the layers, to illustrate the difference in packing of OH groups of different layers.

hydroxyl bonds between OH groups of adjacent layers, instead of the non-directional forces operating in $Mg(OH)_2$ and similar crystals. Since it is not possible to locate the actual H atoms by X-ray methods, their positions can only be inferred from the interatomic distances. In Fig. 94 the atoms A, B, C, D, and B′ and D′ behind B and D form a somewhat

distorted trigonal prism, the lengths of the edges of which are shown in Fig. 95. It is reasonable to place the H atoms as indicated so that the hydroxyl bonds account for the shorter OH—OH distances. It will be noticed that the hydroxyl bonds in the planes of the OH groups are all longer than those between the layers. The reason for this is that the former are the unshared edges of $Al(OH)_6$ octahedra which are lengthened owing to the shortening of the shared edges, and on these OH—OH distances the formation of hydroxyl bonds has only a second-order effect.

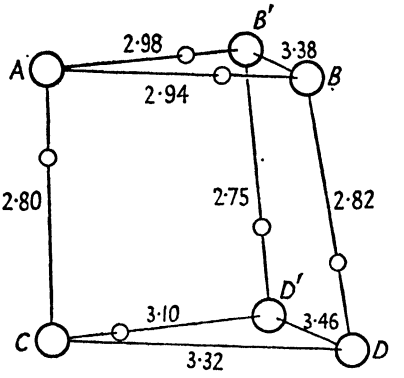


FIG. 95. Arrangement of hydroxyl bonds in and between the layers of $Al(OH)_3$ (after Bernal and Megaw).

The Hydroxy-acids

Two have been studied by the methods of X-ray crystallography, H_3BO_3 and H_6TeO_6, but only for the former has a complete structure been deduced. Telluric acid is dimorphous and the cubic form can probably best be described as consisting of octahedral $Te(OH)_6$ groups held together by hydroxyl bonds. Boric acid has an elegant layer structure (accounting for its perfect basal cleavage), the B and O atoms in any layer being arranged as shown in Fig. 96. A characteristic of these hydroxy-acids is

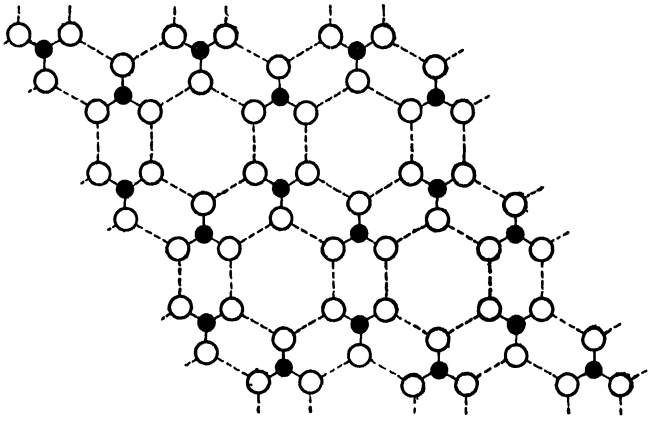


FIG. 96. Portion of a layer of H_3BO_3. Broken lines indicate O—H—O bonds.

that they consist of molecules $A(OH)_n$ linked by hydroxyl bonds so that the oxygen coordination number of A is that shown in the empirical formula, in contrast to all the hydroxides described above in which the coordination number of the metal atom is 4 or 6 for values of $n = 1, 2$, or 3.

The arrangement of the BO_3 groups relative to one another and the short distances between O atoms of adjacent groups clearly indicate some

fairly strong binding between these pairs of atoms. Each O atom is bound to two others in this way. These bonds were originally regarded as symmetrical H bonds, but it appears preferable to describe them as hydroxyl bonds, both because of their length ($2{\cdot}71 \pm 0{\cdot}05$ A.) and also because each O atom forms two such bonds. In the acid salts where there are short hydrogen bonds (2·55 A.) only one such bond is formed by each O atom (see p. 260).

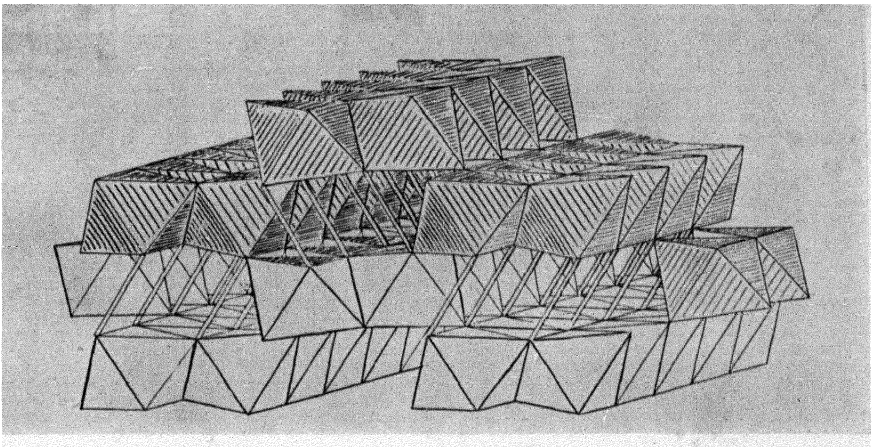
The Oxy-hydroxides

Certain trivalent metals form compounds of the type MO.OH intermediate in composition between the trihydroxide $M(OH)_3$ and the oxide M_2O_3. The oxy-hydroxides of Al, Fe, and Mn have been studied, and as already stated AlO(OH) and FeO.OH are isodimorphous, the names of the naturally occurring forms being

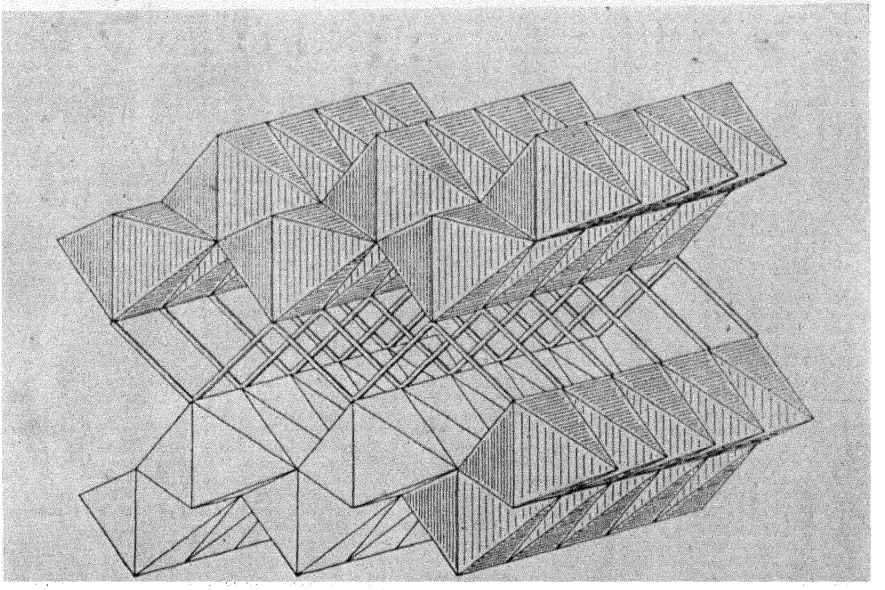
α-AlO.OH	diaspore	α-FeO.OH	goethite
γ-AlO.OH	boehmite	γ-FeO.OH	lepidocrocite

Goethite has the same type of structure as diaspore and boehmite as lepidocrocite, and since diaspore and lepidocrocite have been studied in detail we shall describe their structures.

We saw in Chapter VIII how in a close-packed assembly of atoms complexes of different kinds may be distinguished according to the arrangement of the metal atoms in the interstices. The structure of diaspore provides a good illustration of this point. Neglecting the H atoms, it consists essentially of close-packed oxygen atoms with atoms of Al in certain of the octahedral holes, and it may be regarded as built up of infinite strips of the brucite ($Mg(OH)_2$) type of structure linked by sharing O atoms at the corners of AlO_6 octahedra. This aspect of the structure is well brought out in Fig. 97 (*a*), due to Ewing. The distance between certain pairs of O atoms of different 'strips' is only $2{\cdot}71 \pm 0{\cdot}05$ A., indicating strong interaction between these atoms. It is reasonable to place the hydrogen atoms between such pairs of O atoms, the bonds between which are distinguished in Fig. 97 (*a*) as double lines. The view has been expressed that these are symmetrical hydrogen bonds but it seems more probable that they are hydroxyl bonds, and to discuss this point it is necessary to consider the structure in rather more detail. Although the O atoms are approximately close-packed, they are not all equivalent in the sense that they have the same environment. This can be seen from the plan (on the plane (100)) shown in Fig. 98 (*a*), where the heights of the atoms (in terms of the *a* dimension of the unit cell) above the plane of the paper are as indicated. It will be seen that the O atom marked A has two Al neighbours above and one below, the O atom lying almost in the plane of these three Al—a plane which is, of course, inclined to that of the paper. The atom B, on the other hand, has three Al neighbours all lying above it and, like A, three O atoms below. Each of the bonds involving H atoms is between an atom of type A and one of type B.



(*a*)



(*b*)

FIG. 97. The structures of (*a*) diaspore, AlO(OH), and (*b*) lepidocrocite, FeO(OH) (after Ewing). Oxygen atoms are to be imagined at the corners of each octahedron and an Al (or Fe) atom at its centre. The double lines indicate O—H—O bonds.

It seems likely that the H atoms are associated with the B atoms and not symmetrically placed with respect to the atoms A and B which have different environments. The existence of OH groups rather than symmetrical O—H—O bonds is supported by the presence in the infra-red absorption spectrum of a band at 3 μ (see Chapter VII).

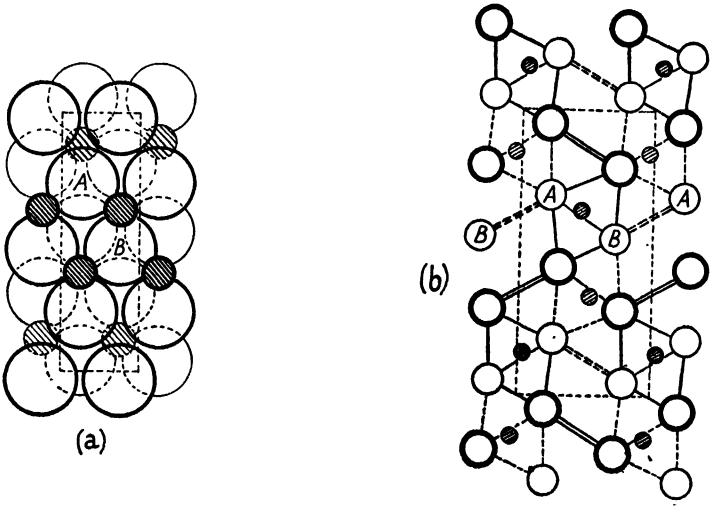


FIG. 98. Projections of the structure of diaspore, on two perpendicular planes: (*a*) on the (100) and (*b*) on the (001) plane. The smaller shaded circles represent Al atoms; H atoms are omitted. Atoms at different heights are indicated by light and heavy circles. The double lines in (*b*) indicate O—H—O bonds.

The structure of lepidocrocite, FeO.OH, is shown as a perspective drawing in Fig. 97 (*b*). In the elevation of this structure, Fig. 99, the broken circles indicate atoms $c/2$ (1·53 A.) above and below the plane of

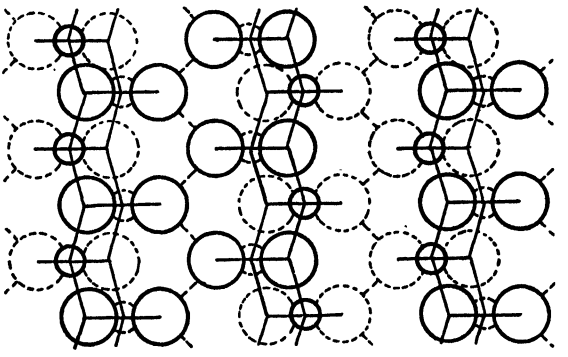


FIG. 99. Elevation of the structure of lepidocrocite, FeO(OH). The broken lines indicate O—H—O bonds.

the full circles, which themselves repeat at c (3·06 A.) above and below their own plane. From this it may be seen that each Fe atom (small

circle) is surrounded by a distorted octahedral group of O atoms (large circles), and these octahedral groups are linked together to form complex layers as shown in Fig. 97 (*b*).

From the environments of the O atoms it is easy to see with which the H atoms are associated, i.e. which are OH groups. The O atoms within the layers are nearly equidistant from four Fe atoms (there are actually two neighbours at 1·93 and two more at 2·13 A.), whereas the atoms on the bounding surfaces of the layers are bonded to two Fe atoms only (at 2·05 A.). Also, the distance between the O atoms of different layers is only 2·72 A., so that there are clearly OH groups on the outer surface of each layer. The formation of directed hydroxyl bonds between the OH groups of different layers accounts for the fact that the O atoms of adjacent layers are not packed together in the most compact way. As may be seen from Figs. 97 (*b*) and 99, a hydroxyl group lies in the same plane as those of the next layer with which it is in contact. The corresponding oxychloride FeOCl is built up of layers of exactly the same kind as in FeO.OH, but the layers pack together so that the chlorine atoms on the outsides of adjacent layers are close-packed. This interesting difference between the structures of FeOCl and FeO.OH is quite comparable with that between $Mg(OH)_2$ and $Al(OH)_3$, being due to the formation of hydroxyl bonds between the layers.

Review of Hydroxides

In the light of our present knowledge of the structures of solid hydroxides we may say that the structural differences between these compounds bear out the ordinary chemical classification into the following groups:

I. Hydroxides without hydroxyl bonds

(*a*) Typical ionic structures, the OH^- ion having spherical symmetry or possibly lower symmetry in the low-temperature forms (compare the hydrosulphides).

NaOH	RbOH
KOH	CsOH

(*b*) OH^- ion with cylindrical symmetry. Layer lattices similar to those of the corresponding chlorides, except in the case of LiOH.

LiOH	$Co(OH)_2$
$Mg(OH)_2$	$Ni(OH)_2$
$Ca(OH)_2$	$Fe(OH)_2$
$Mn(OH)_2$	$Cd(OH)_2$

II. Hydroxides with hydroxyl bonds

(*a*) Coordination groups $M(OH)_4$ or $M(OH)_6$ sharing OH groups. These are the 'amphoteric' hydroxides, so called because they may be dissolved by excess of strong alkali. The formation of clear colloidal solutions is presumably to be associated with the possibility of the formation of $M(OH)_4$ or $M(OH)_6$ complexes in solution which can

form hydroxyl bonds to one another or to water molecules, just as the SO_4^{2-} ions in concentrated H_2SO_4 are held together by hydrogen bonds. The formation of solid compounds such as 'aluminates', etc., is not to be interpreted as evidence of acidic properties, as we see from the structures of such solids.

$Zn(OH)_2$ $Al(OH)_3$
$Be(OH)_2$ $Fe(OH)_3$

(*b*) The oxy-hydroxides, with coordination groups $M(OH)_mO_n$, also contain hydroxyl bonds.

III. The Hydroxy-acids

These consist of discrete molecules $R(OH)_n$ held together by hydroxyl bonds. In contrast to all the above hydroxides no O atoms are shared between the $R(OH)_n$ coordination groups. The structures of the acids of the more electronegative elements which are formally of this type are not known and may be structurally quite different (e.g. $P(OH)_3$, $Cl(OH)$).

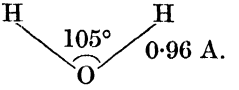
$B(OH)_3$ $Te(OH)_6$

CHAPTER XI

OXYGEN AND SULPHUR (*concluded*)

THE STRUCTURES OF ICE AND WATER

THE problem of finding the structure of a condensed phase consisting of discrete molecules may be resolved into two parts: the structure of the individual molecules and the arrangement of these molecules relative to one another. The structure of the individual H_2O molecule is accurately known from spectroscopic studies, but we have seen that compounds



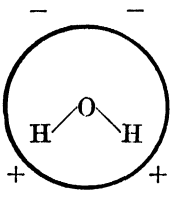
containing hydrogen are often abnormal owing to the formation of hydrogen bonds, and therefore it may not be assumed that the structural unit in ice, for example, is the single molecule H_2O. Some of the abnormal properties of water as compared with other hydrides have been mentioned in Chapter VII. It has been customary to postulate the existence of various polymers in water, for example, $(H_2O)_2$ and $(H_2O)_3$, in proportions varying with the temperature. The double molecules were also suggested in certain crystalline hydrates to make, for example, dodecahydrates conform with Werner's coordination theory (see p. 366). The practical approach to the structures of ice and water, however, is rather different owing to the fact that only the oxygen atoms can be located by X-ray methods. Other evidence from physical properties then has to be utilized in order to place the H atoms in the most probable positions, and only when this has been done can we say whether discrete H_2O molecules (or polymers) exist in water or in ice. It is convenient to discuss the structure of ice before that of water because we can obtain by X-ray methods much more information about the structure of a solid than in the case of a liquid. In a liquid there is continual rearrangement of neighbours and we can determine only the mean environment, i.e. number and spatial arrangement of nearest neighbours, of a molecule. The only X-ray data obtainable from a liquid at a given temperature is the scattering curve, and the interpretation of the various maxima in terms of nearest, next nearest neighbours, and so on is a matter of some difficulty.

Ice

We shall be speaking here of ordinary ice (ice I). If distilled water is frozen from the surface in open air ordinary ice I is formed between 0° and −8° C., but below this latter temperature rhombohedral (β) ice is produced. There are also other varieties of ice stable only under high pressures, ice II and ice III. In both of these, which have higher densities

(1·2 and 1·105 g./c.c. respectively) than ice I, the immediate environment of an oxygen atom is the same as in ordinary ice—four tetrahedral neighbours at 2·71 A.—but the linking of these tetrahedral groups is distorted, bringing the next nearest neighbours to 3·4 A. as compared with 4·47 A. in ice I.

In ice I the O atoms occupy the positions of the Zn and S atoms in the wurtzite structure, or alternatively those of the Si atoms in tridymite, one of the forms of silica (p. 464)—compare the relation of diamond to zinc-blende. Every O atom is therefore surrounded tetrahedrally by four others and the O—O distance is 2·76 A. This structure may be contrasted with the close-packed structure of H_2S, in which every molecule has twelve equidistant nearest neighbours. As to the positions of the H atoms, three suggestions have been made. Barnes derived a structure, based on a unit cell containing only three molecules, in which the H atoms lay midway between the pairs of O atoms. However, there is good reason to believe that the bonds O—H—O are not symmetrical. There is only a small difference between the vibrational frequencies involving the stretching of the O—H bonds for ice and water vapour, much less than would be expected if the O—H distance had changed from 0·96 A. in the vapour to 1·38 A. (half O—H—O) in the crystal. In the structure of Bernal and Fowler, therefore, the bonds between O atoms are assumed to be hydroxyl bonds, with H about 1 A. from an O atom, two H atoms being closely associated with each O atom. The tetrahedral environment of each water molecule indicates that the H_2O molecule behaves as if it has a tetrahedral distribution of two positive and two negative charges. The assignment of the H atoms to particular positions adjacent to O atoms in the Bernal-Fowler structure of ice necessitated the adoption of a larger unit cell containing twelve molecules. This view of the structure of ice is not



accepted by Pauling. The unsymmetrical positions of the H atoms are not disputed, but it is suggested that the O—H bonds are not permanently oriented towards the same neighbours. Above about 200° K. the dielectric constant of ice is of the same order of magnitude as that of water, showing that the molecules can change their orientation quite easily in an electric field. Furthermore, a value of the residual entropy of ice, agreeing well with the experimental value, can be calculated if we assume merely that two of the four H atoms surrounding each O atom are nearer to that atom than the other two and directed approximately towards two of the four surrounding O atoms but not necessarily always towards the same two. On this view a crystal of ice can assume any one of a large number of

configurations, distinguished by different arrangements of the H atoms, either by rotating some of the H_2O molecules or by movement of some of the H atoms from positions about 1 A. from one O atom to a similar position near the other O atom of the bond.

Water

The fact that water is liquid at ordinary temperatures whereas all the hydrides CH_4, NH_3, HF, PH_3, SH_2, and HCl of elements near to oxygen in the Periodic Table are gases, indicates interaction of an exceptional kind between neighbouring molecules. That these interactions are definitely directed towards a small number of neighbours is shown by the low density of the liquid compared with the value (1·84) calculated for a close-packed liquid with molecules of similar size, assuming a radius of 1·38 A. as in ice. This is confirmed by the X-ray diffraction effects, which show that every O atom is surrounded by an average of four neighbours. The similarity between the dielectric constants of ice and water, which are practically the same for low frequencies, supports the idea that water has the same general type of structure as ice, allowance being made for greater disorder in the liquid than in the solid. Various arrangements of water molecules are possible if the only condition is that each is surrounded tetrahedrally by its four neighbours. Ordinary ice crystallizes with the same type of structure as tridymite, which may be regarded as built up of tetrahedral SiO_4 groups sharing all their corners with other similar groups. The structures of the other two polymorphic forms of silica, quartz and cristobalite, represent alternative ways of grouping these tetrahedral groups into an infinite 3-dimensional array. The densities of these forms are: quartz, 2·655, tridymite, 2·30, cristobalite, 2·27 g./c.c. Since water is more dense than ice we need only consider the quartz structure, and for the same reason any model for the structure of water based on a disordered tridymite-like structure may be ruled out since it would have a density less than that of ice.

Bernal and Fowler therefore suggested that over the ordinary temperature and pressure ranges the molecules in water are packed in a rather similar way to the SiO_4 groups in quartz, and the experimentally determined X-ray diffraction curve for water is very similar in general form to that calculated for this quartz-like model. It is suggested that this pseudocrystalline structure extends over small regions in the liquid containing from tens to hundreds of molecules, there being constant rearrangement so that a given group exists only for an extremely short time. It is necessary to assume the existence of these groups, each of which would have an appreciable electric moment, in order to account for the high dielectric constant of water which, as we have already said, is almost the same as that of ice for low frequencies. Our picture of water would then be as follows.

At low temperatures, particularly in supercooled water, the packing of the water molecules is predominantly tridymite-like. The anomalous con-

traction between 0° and 4° C. may be attributed to the breaking down of this relatively open structure to form the more compact quartz-like structure, the resulting change in volume being greater than that due to the normal thermal expansion of the latter. Under ordinary conditions the quartz-like structure is retained, but at high temperatures the X-ray

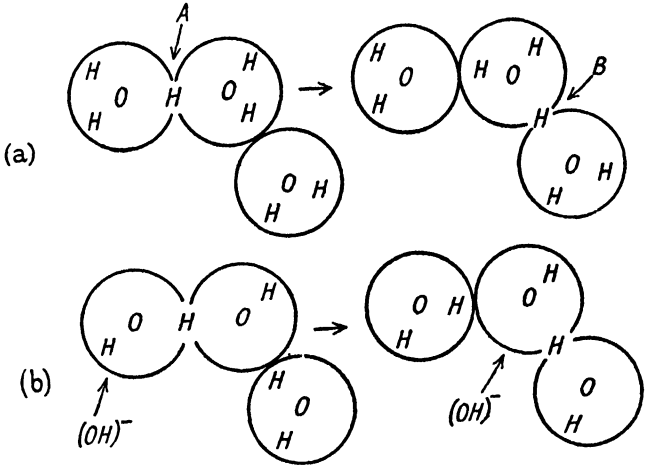


FIG. 100. The effective movement of (*a*) H^+ ion and (*b*) OH^- ion resulting from small shifts of protons (after Bernal and Fowler).

diffraction effects begin to resemble those of a close-packed liquid. Bernal and Fowler suggest a further gradual change towards a close-packed structure. There is no question of the existence of definite polymers as had been suggested earlier. Instead, each water molecule tends to surround itself tetrahedrally with four neighbours, and although in water the regular arrangement extends only over comparatively small groups of molecules and for a given group persists only for a short time, in ice this tetrahedral coordination extends throughout the whole crystal. This theory of the structure of water suggests an explanation of the extraordinary mobility of the H^+ and OH^- ions. The mobilities of these ions are respectively 32·5 and $17{\cdot}8 \times 10^{-4}$ cm./sec. for an applied field of 1 volt/cm., whereas the values for other ions are of the order of 6×10^{-4} cm./sec. Calculations show that very little energy is required to remove a proton from one water molecule, to which it is attached as $(H_3O)^+$, to another, for the states H_3O, $H_2O \rightleftharpoons H_2O$, H_3O have the same energy. If we assume that the H^+ ion acts as a bond between two molecules, then the process shown diagrammatically in Fig. 100 (*a*) results in the movement of H^+ from A to B. The analogous mechanism for the effective movement of OH^- ions through water is illustrated in Fig. 100 (*b*). Whereas other ions have to move bodily through the water, the H^+ and OH^- ions move by what Bernal terms a kind of relay race, small shifts of protons only being necessary.

HYDRATES

One of the simplest ways of purifying a compound is to recrystallize it from a suitable solvent. The crystals separating from the solution may consist of the pure compound or they may contain 'solvent of crystallization'. For most salts water is a convenient solvent, so that crystals containing water—hydrates—have been known from the earliest days of chemistry, and many inorganic compounds are normally obtained as hydrates. Certain other compounds, apart from salts, acids, and bases, form hydrates, among them being methyl and ethyl halides, methane, and the inert gases. Many of these hydrates contain $6H_2O$ for every molecule of solute. The hydrates of the gaseous substances are formed only under pressure and are extremely unstable, and the melting-points are usually close to 0° C. Such hydrates are presumably related structurally to ice itself, in the structure of which there is room for 'interstitial' atoms or molecules.

A characteristic of all the above hydrates is that removal of water from the crystals leads to collapse of the lattice, the structure of the anhydrous material bearing no simple relation to that of the hydrate. On the other hand, there are certain crystals which have the remarkable property of absorbing water, and this water may be subsequently removed without radically altering the crystal. This is possible in crystals of several different geometrical types. If the anhydrous crystal consists of a rigid framework in which there are cavities or tunnels sufficiently large to accommodate water molecules, then reversible hydration and dehydration may take place as in the zeolites, the structures of which are described in another chapter (p. 482). In such a case little or no alteration in the size of the unit cell is found. Other possibilities are the taking up of water between infinite chain or layer complexes or between large finite molecules. The swelling of some of the clay minerals (p. 476) is due to the introduction of water between the $Al_xSi_yO_z$ layers, so that the crystal expands in one direction only, while the proteins provide examples of crystals in which expansion takes place in three, two, or only one direction when they take up water.

We see therefore that there are different effects on dehydration, ranging from the complete breakdown of the crystal in the case of a salt hydrate through the intermediate examples such as clay minerals and certain proteins, where removal of water merely brings the structural units closer together with continuous changes in one or more of the cell dimensions, to the 'framework' crystal which may be reversibly hydrated without appreciable alteration of the structure of the anhydrous crystal. We shall confine our attention here to the hydrates of salts, acids, and bases.

The term hydrate should be used only for compounds in the crystals of which discrete water molecules may be distinguished. In practice, since we cannot locate H atoms by X-ray methods, this means that there must be certain oxygen atoms the environment of which indicates that they

are the O atoms of H_2O molecules (or H_3O^+, see below). Formulae such as $Na_2O.SnO_2.3H_2O$ for $Na_2[Sn(OH)_6]$ are relics of the days when sulphuric acid was written $H_2O.SO_3$ or sulphurous acid $H_2O.SO_2$, and must be abandoned. There still remains a tendency to refer to such compounds as containing 'water of constitution'. The correct formulation of solid compounds is often possible only when their crystal structures are known, and this applies particularly to hydrates. As further examples of the revision of formulae we may give: the antimonates $[M^{II}(H_2O)_6][Sb(OH)_6]_2$, previously written $M(SbO_3)_2.12H_2O$, and potassium 'pentaborate', $KH_2B_5O_{10}(H_3O)_2$, formerly considered to be a tetrahydrate, $KB_5O_8.4H_2O$. The structure of the latter compound is described later as an example of a hydrated acid salt. The problem of the constitution of salt hydrates is closely related to the hydration of ions in aqueous solution. In crystalline $NiSO_4.6H_2O$ every Ni^{2+} ion is surrounded by six water molecules, and in $BeSO_4.4H_2O$ every Be^{2+} ion is found at the centre of a tetrahedral group of four water molecules. In a sufficiently dilute solution of any salt each ion is surrounded entirely by water molecules, but not all ions are hydrated in solution. An ion is said to be hydrated only if the water molecules surrounding it are oriented with respect to the ion. Calculations of the 'effective ionic volume in solution' show that all positive ions except the largest univalent ions (e.g. Rb^+, Cs^+, NH_4^+) are hydrated in solution and that the environment of, for example, Ni^{2+} and Be^{2+} in solution is the same as in the hydrated salts mentioned above. In solution, however, we may assume that the Ni^{2+} ion is not surrounded permanently by the same six water molecules as is the case in the crystalline hydrate.

We may mention here the so-called 'aquo-ions', taking the hydrates of $CrCl_3$ as an example. There are three compounds with the empirical formula $CrCl_3.6H_2O$, one forming violet and the other two green crystals. Measurements of equivalent conductivity and of the weight of AgCl precipitated by equal weights of the three forms show that the formulae of these compounds should be written $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$, and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$, the 'aquo-ions' (enclosed in square brackets) retaining their identity in solution. Many such ions containing water firmly attached to the central atom are known; see, for example, p. 521. In order to distinguish five of the water molecules in the second of these compounds from the sixth we could call the compound a monohydrate. Crystallographically the water molecules would be of two types (the crystal structure of this particular compound is not known), and there is a similar difference between six of the water molecules and the seventh in $NiSO_4.7H_2O$.

Earlier Ideas on the Constitution of Hydrates

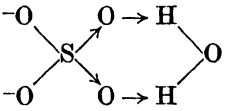
Before proceeding to the detailed structures of hydrates it is worth while considering what contributions have been made by classical chemistry to this problem of the constitution of hydrates. These compounds have long attracted interest both because of their varied formulae and because they

are the forms in which many salts are normally handled. Werner naturally emphasized the analogy between hydrates and the more stable coordination compounds such as cobalt- and chrom-ammines. The very large number of hydrates containing $6H_2O$ per formula-weight of the salt suggested that water could play a role similar to that of NH_3 in metal ammines. Sidgwick in his *Electronic Theory of Valency* attempted to show that the constitution of hydrates is determined by the same rules as those governing the formation of other coordination compounds. He pointed out that all the water molecules in hydrates need not necessarily be linked directly to anion or cation but suggested that this would generally be the case and that as a rule the water could be regarded as attached to the positive ion by coordinate links from the oxygen or hydrogen atoms of the water molecules. He concluded:

(*a*) The tendency of an ion to hydrate would be greater (1) the greater its charge, (2) the greater its size, if an anion, and (3) the smaller its size if a cation, in accordance with Fajans's principles. It is difficult to generalize about hydrates, but the salts of the larger monovalent ions, K, Rb, Cs, Ag, Au, Tl, and NH_4, are almost invariably anhydrous, whereas many of those of the smaller Li and Na are hydrated. Many salts of the small Be^{2+} ion are tetrahydrated. As examples of the effect of ionic charge CsCl (anhydrous), $BaCl_2$ (1 and $2H_2O$), and $LaCl_3$ (6 and $7H_2O$) are quoted.

(*b*) The hydration of positive ions is limited by the 'covalency rule'. Where the permissible maximum is exceeded Werner's original suggestion of double water molecules (occupying one coordination position) was adopted. This appeared to be supported by the fact that in many cases of 'excessive hydration' the number of water molecules is 8 or 12, i.e. twice 4 or 6, e.g. $[Be(H_2O)_8]PtCl_6$, $[Ca(H_2O)_8]O_2$, and $MgX.12H_2O$, where X is Cl_2, Br_2, $PtCl_6$, SO_4, or $(ClO_3)_2$.

(*c*) Sidgwick concluded that the hydration of negative ions is exceptional but well established in certain cases and that it accounts, for example, for the existence of hydrated sulphates with odd numbers (1, 5, 7) of water molecules. Examples of such hydrates are: $Li_2SO_4.H_2O$, $Na_2SO_4.7H_2O$, $M^{2+}SO_4.7H_2O$ (M = Mg, Zn, Cd, Co, Ni, Mn, Cr, V), $CuSO_4.5H_2O$, etc. It was assumed that one water molecule is definitely associated with a SO_4^{2-} ion:



It is now known that this is not the case and the actual arrangement of bonds to the 'odd' water molecule in $CuSO_4.5H_2O$ is shown on p. 379.

The formation of hydrates by the alkali metal hydroxides was taken to indicate hydration of the hydroxyl ion. It was difficult to account for the existence of hydrated fluorides ($KF.2H_2O$, $AgF.2$ and $4\ H_2O$) of elements which normally form anhydrous salts on the assumption of

covalent linking of the water molecules to the metal, and Sidgwick suggested hydration of the F^- ion, $[F—H.OH]^-$.

We now have to see how these ideas, which are important as an attempt to bring the formulation of hydrates into line with the behaviour of elements in their other compounds, fit in with our knowledge of the structures of hydrated salts. On any coordination theory it is difficult to explain the existence of hydrates with numbers of H_2O other than (3), 4, 6, and 8, particularly if the number of water molecules per molecular weight is small. Also, many salts form a number of hydrates, so that the analogy with the stable cobaltammines is not very close.

The Crystal Structures of Hydrates

We have seen that the properties of water and ice indicate that the H_2O molecule behaves as if there were a tetrahedral distribution of two

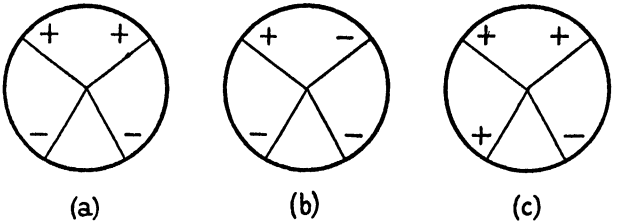
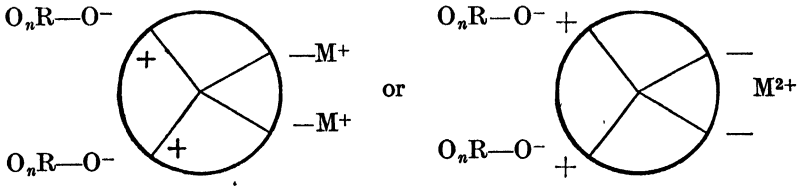


FIG. 101. The tetrahedral charge distributions of (*a*) H_2O, (*b*) OH^-, and (*c*) H_3O^+.

positive and two negative charges (*a*), with which may be compared the hydroxyl ion (*b*) and the H_3O^+ ion (*c*) found in crystalline hydrates of acid salts (see p. 375). By examining the environments of water molecules in crystalline hydrates we shall find that in many cases the arrangement of the nearest neighbours is consistent with this tetrahedral character of the H_2O molecule. We commonly find, for example, a water molecule attached on the one side to two O atoms of an oxy-ion and on the other to two univalent positive ions or to one divalent ion thus:



The neighbours of a water molecule may equally well be other water molecules suitably oriented so that oppositely charged regions are adjacent. In this way groups of water molecules may be held together as in $H_3PW_{12}O_{40}.29H_2O$, and water molecules in excess of those immediately surrounding the metal ions may be present, as in $NiSO_4.7H_2O$, which may be written $[Ni(H_2O)_6]H_2O.SO_4$. In our discussion of the structures of hydroxides we saw that in suitable environments the OH group is

polarized to the stage where a hydroxyl bond is formed, and in hydrates we find an analogous effect. In hydrated oxy-salts and hydroxides the short distances (2·7–2·9 A.) between O atoms of water molecules and those of the oxy-ions are similar to those found in certain hydroxides and oxy-hydroxides, and indicate the formation of hydroxyl bonds. In hydrated fluorides also there are probably O—H—F bonds of considerable strength, but as yet little is known of the structures of these compounds. In simple hydrated chlorides containing Cl^- ions the two positive regions of the water molecule are directed towards two Cl^- ions, but in hydrates containing complex chloro-ions (e.g. $NiSnCl_6.H_2O$) where the charge is spread over a large ion ($SnCl_6^{2-}$) the water molecule is surrounded by more than two halogen atoms and is therefore not exhibiting its tetrahedral nature. In both sets of compounds, however, the O–Cl distance is about the same, suggesting that chlorine does not form strong bonds O—H—Cl. More evidence of this is given later in comparing hydrates with ammines. The third group of hydrates of which we shall give examples comprises acid salts in which H^+ ions are associated with some or all of the water molecules forming H_3O^+ which can form bonds to three O atoms of oxy-ions.

(a) Hydrates of Oxy-salts and Hydroxides, containing O—H—O *bonds*

The general formula of these compounds may be written $M_mR_n.xH_2O$, where R is an oxy-ion, SO_4^{2-}, CO_3^{2-}, O_2^{2-}, OH^-, etc. The number of O atoms which may be accommodated around the ion M is determined by the radius ratio $r_M:r_O$, and since the bonds M—O are essentially electrostatic in nature the coordinated oxygen atoms, usually four or six in number, are arranged tetrahedrally or octahedrally around the metal ion. The coordination group around the metal ion is formed as far as possible by water molecules, for these do not arrange themselves around the negatively charged oxy-ions. The simplest structures are therefore those with x equal to the oxygen coordination number of M, so that the number of water molecules is just sufficient to form complete coordination groups around all the metal ions as in $[Be(H_2O)_4]SO_4$, $[Ni(H_2O)_6]SO_4$, alums $[K(H_2O)_6][Al(H_2O)_6](SO_4)_2$, $[Sr(H_2O)_8](OH)_2$, etc. There are clearly two other possible types of hydrate. On the one hand, the number of water molecules may be less than the coordination number of M, in which case M is surrounded partly by H_2O molecules and partly by O atoms of oxy-ions, e.g.

Hydrate	*C.N. of* M	*Actual environment of* M *in crystal*
$Li_2SO_4.H_2O$	4	H_2O, 3O, or 4O*
$CuSO_4.5H_2O$	6	$4H_2O$, 2O
$CdSO_4.8/3H_2O$	6	$2H_2O$, 4O
$CaSO_4.2H_2O$	8	$2H_2O$, 6O

O represents oxygen atom of oxy-ion.

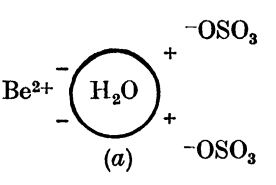
* There are two sets of Li atoms in the crystal, with different environments.

On the other hand, the number of water molecules may be greater than the coordination number of M. An example of this type of hydrate is $NiSO_4.7H_2O$, in which six of the water molecules form an octahedral group around the Ni^{2+} ion and the seventh is linked only to oxy-ions and other water molecules. The fifth water molecule in $CuSO_4.5H_2O$ differs in a similar way from the other four and, as we have seen above, there is the further complication in this case that the total number of water molecules is less than the coordination number of Cu^{2+}, so that the co-ordination group around the metal ion is made up of four H_2O and two O atoms of SO_4^{2-} ions. The structures of highly hydrated compounds such as $Zn(ClO_3)_2.12H_2O$ and $MgCl_2.12H_2O$ are of great interest, but they have not yet been studied.

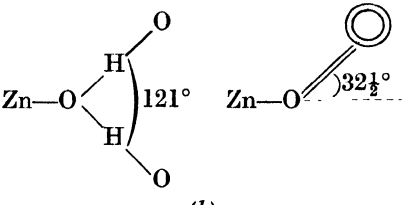
So far we have assumed that the groups $[M(H_2O)_n]$ are separate units in the crystal and not sharing water molecules with one another. However, just as we may have infinite complex ions or molecules arising from coordination groups sharing corners, edges, or faces, so we find infinite $[M(H_2O)_n]$ groups in the trihydrates of certain lithium salts. These are described below. We shall now note some points of interest of the structures of the following hydrates, selected as examples of the various types already mentioned:

I. x = C.N. of M: $BeSO_4.4H_2O$, $Zn(BrO_3)_2.6H_2O$.
II. $x >$ C.N. of M: $NiSO_4.7H_2O$.
III. $x <$ C.N. of M: $CaSO_4.2H_2O$, $LiClO_4.3H_2O$.

I. $BeSO_4.4H_2O$. This structure consists of tetrahedral $[Be(H_2O)_4]^{2+}$ and SO_4^{2-} ions arranged in approximately the same way as the ions in the CsCl structure. Each water molecule makes two external contacts, to O atoms of SO_4^{2-} ions, its environment thus being consistent with our picture of the water molecule (*a*):



(*a*)

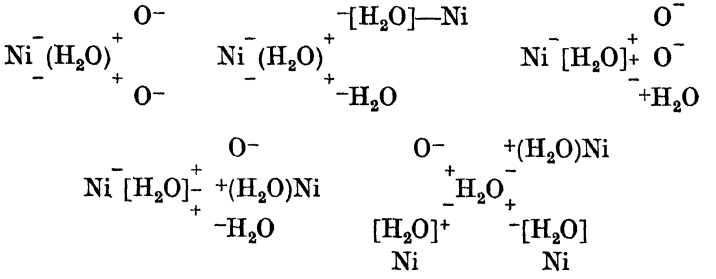


(*b*)

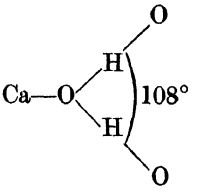
$Zn(BrO_3)_2.6H_2O$. In this hydrate the $[Zn(H_2O)_6]$ complexes are joined to the surrounding BrO_3^- ions by O—H—O bonds of length about 2·7 A., every H_2O forming two such bonds. The three bonds from each water molecule are not quite coplanar, (*b*), and in general the environment of any given atom in a crystal only approximates to the ideal since it represents a compromise between the requirements of all the atoms in the structure.

II. $NiSO_4.7H_2O$. Here we find octahedral groups $[Ni(H_2O)_6]^{2+}$ as in the hexahydrate $NiSO_4.6H_2O$ and the seventh water molecule held between these groups and the SO_4^{2-} ions. On account of the presence of

this odd water molecule the structure is more complex than in the case of $Zn(BrO_3)_2.6H_2O$, for example, and all the six water molecules of a $[Ni(H_2O)_6]^{2+}$ group have not the same environment. Of these six water molecules four, distinguished below as (H_2O), make two contacts outside the group, these bonds being roughly coplanar with the third bond to the Ni atom. The other two water molecules, $[H_2O]$, make three external contacts, these three bonds and the fourth to the Ni atom being arranged tetrahedrally. The bonds from the seventh water molecule, H_2O, are also approximately tetrahedral. The environments of the different types of water molecules are shown in the accompanying diagrams, in which an oxygen atom of a SO_4^{2-} ion is shown as O.



III. $CaSO_4.2H_2O$ (gypsum) has been chosen as an example of a hydrate of type III since it is a well-known mineral and has interesting physical properties. It has a rather complex layer structure in which the layers are bound together by bonds from water molecules. Each water molecule is joined to a Ca^{2+} and to a sulphate O of one layer and to an O atom (of a SO_4^{2-} ion) of an adjacent layer, so that its environment is similar to that of a water molecule in $BeSO_4.4H_2O$ or $Zn(BrO_3)_2.6H_2O$. These O—H—O bonds are the weakest in the structure, thus accounting for its



good cleavage (Fig. 102) and the marked anisotropy in thermal expansion, which is far greater normal to the layers than in any direction in the plane of the layers.

$LiClO_4.3H_2O$ *and Related Compounds.* A considerable number of lithium salts form trihydrates, $LiR.3H_2O$ (R = Cl, Br, I, ClO_3, ClO_4, MnO_4, NO_3, BF_4). The fluoborate and perchlorate also form monohydrates, as do the corresponding salts of silver. The structure of $LiClO_4.3H_2O$ is closely related to that of a large group of isomorphous hexahydrates $R(MX_4)_2.6H_2O$, where R is Mg, Mn, Fe, Co, Ni, or Zn and the complex ion is BF_4^- or ClO_4^-. The isomorphism of hydrated fluoborates and perchlorates is of some interest and is referred to later.

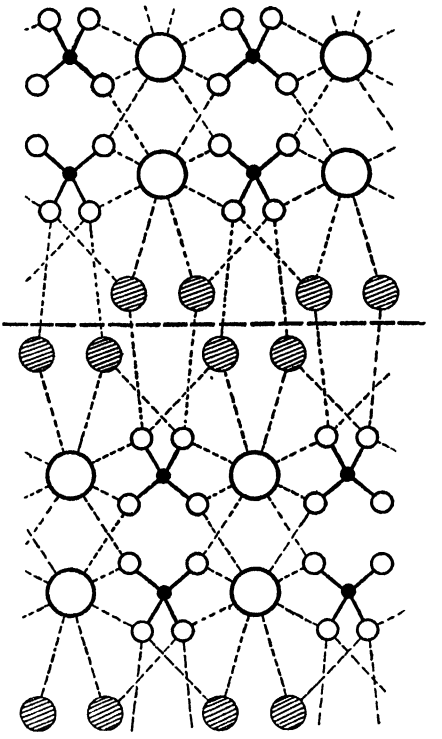


FIG. 102. Section through the crystal structure of gypsum perpendicular to the layers (diagrammatic). The layers are composed of SO_4^{2-} and Ca^{2+} ions (large open circles) with H_2O molecules on their outer surfaces (shaded). The heavy broken line indicates the cleavage, which breaks only O—H—O bonds.

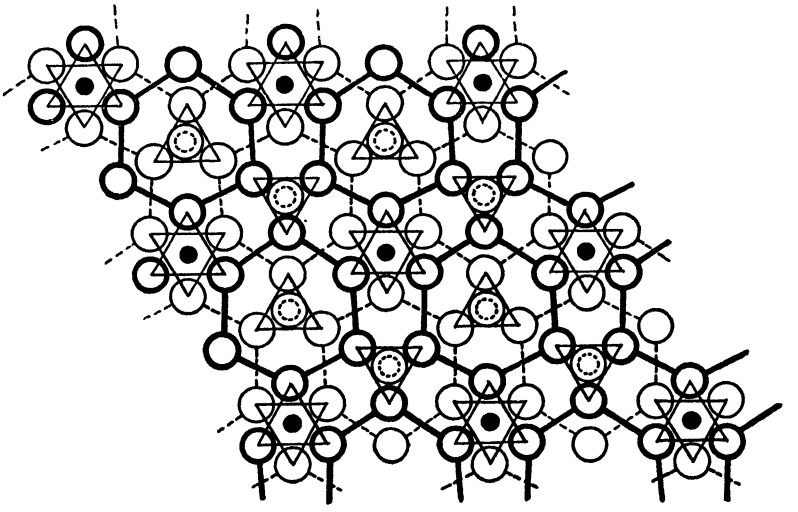
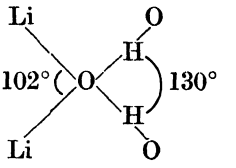


FIG. 103. Plan of the structure of $LiClO_4.3H_2O$. The full and dotted lines indicate O—H—O bonds between H_2O molecules and oxygen atoms (of ClO_4^- ions) which are approximately coplanar. These bonds thus link together the columns of $[Li(H_2O)_6]$ octahedra, which share opposite faces, and the ClO_4^- ions. The small black circles represent Li^+ ions in planes midway between the successive groups of $3H_2O$.

In crystals of $LiClO_4.3H_2O$ the water molecules are arranged in groups of three around lines perpendicular to the plane of the paper, Fig. 103, successive groups along these lines being related to one another by a rotation through 60°. The distance between these groups is one-half the length of the c-axis of the crystal. The Li^+ ions lie between the groups at heights $c/4$ and $3c/4$ and are therefore surrounded octahedrally by six H_2O molecules. The sequence $3H_2O$—Li—$3H_2O$—Li— gives the ratio Li:$3H_2O$ in the empirical formula. The tetrahedral ClO_4^- ions are packed between these columns, of composition $[Li(H_2O)_3]_n$, with their central Cl atoms at heights 0 and $c/2$. Since the water molecules also lie at heights 0 and $c/2$, one-half of these molecules and three of the perchlorate O atoms in each unit cell are approximately in the same plane parallel to that of the paper, and are shown as heavier circles. Let us consider the environment of a water molecule (Fig. 103). It is approximately equidistant from two Li^+ ions (Li—H_2O = 3·14 A.) and also from its two closest perchlorate oxygen neighbours (at 2·94 A.), the Li—H_2O—Li and the O—H_2O—O bonds lying in perpendicular planes. These neighbours of the H_2O molecule are thus arranged approximately tetrahedrally. The H atoms of the H_2O molecule must be directed towards the negatively charged perchlorate O atoms as shown in the accompanying sketch. If we draw in these O—H—O bonds between the O and H_2O



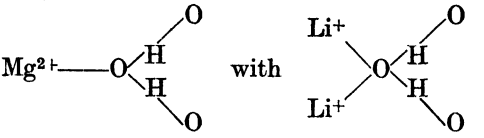
which lie at approximately the same height above the plane of the paper in Fig. 103, we find that they form slightly puckered hexagonal rings, rather like the plane rings of short H bonds in H_3BO_3. In this way the ClO_4^- ions are held in position between the infinite $[Li(H_2O)_3]$ columns.

The hexahydrates of $Mg(ClO_4)_2$, etc., are related in a simple way to $LiClO_4.3H_2O$. The unit cell of the latter contains $2LiClO_4.3H_2O$, i.e. $Li_2(ClO_4)_2.6H_2O$. If one-half of the Li positions are unoccupied we obtain possible structures for the compounds $M(ClO_4)_2.6H_2O$ of divalent metals. The two simplest possibilities are shown in Fig. 104. The rhombus represents the plan of the unit cell of the lithium salt with Li ions at the heights indicated in (*a*). By omitting alternate ions along a vertical line in the manner shown at (*b*), we derive the structure of $Mg(ClO_4)_2.6H_2O$ and isomorphous hydrates. The alternative possibility shown at (*c*) is found in $Cd(ClO_4)_2.6H_2O$. In both cases we now have the sequence

$$-3H_2O.3H_2O-M-3H_2O.3H_2O-M-3H_2O.3H_2O-$$

alternate positions at the centres of octahedra of H_2O molecules being unoccupied. By comparison with $LiClO_4.3H_2O$ it will be clear that,

instead of two Li^+ neighbours, each H_2O in $Mg(ClO_4)_2.6H_2O$ has only one Mg^{2+} neighbour; compare



Few hydrated hydroxides have been examined in any detail. Hydroxyl bonds can be formed between the H_2O molecules and the OH^- ions, as

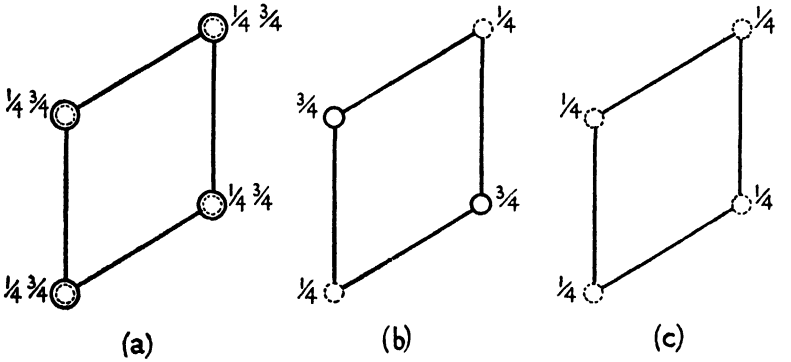


FIG. 104. The positions of the metal ions in the structures of three related hydrates (*a*) $LiClO_4.3H_2O$, (*b*) $Mg(ClO_4)_2.6H_2O$, and (*c*) $Cd(ClO_4)_2.6H_2O$.

is the case in $LiOH.H_2O$. Here each Li^+ ion is surrounded tetrahedrally by two OH^- and two H_2O, and these coordination tetrahedra share edges to form infinite chains of composition $LiOH.H_2O$. These chains are held together by lateral hydroxyl bonds between OH^- ions and H_2O molecules of different chains.

The above examples are sufficient to substantiate our picture of the water molecule with its tetrahedral charge distribution, forming, in the hydrated oxy-salts, hydroxyl bonds to O atoms of neighbouring oxy-ions. We now come to the hydrated halides in which we shall find water behaving rather differently.

(*b*) *Hydrated Halides*

In Chapter VIII we saw that, although there are general group relationships between the halogens, there are rather large differences between the properties of fluorine and its compounds and those of the remaining halogens. This we associated with the extreme electronegativity of fluorine, and we found that the more ionic character of M—F bonds compared with M—Cl, M—Br, and M—I bonds was reflected in the difference between the structures of crystalline fluorides as compared with the corresponding chlorides, bromides, and iodides. Whereas, for example, in CaF_2 the F^- ion is surrounded tetrahedrally by four Ca^{2+} ions, in $CaCl_2$ each Cl atom is attached to only three Ca atoms, all of which lie to one side of it.

The fluorides also differ from the other halides in the extent to which

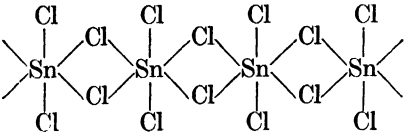
they form hydrates. In some cases the fluoride is anhydrous while the other halides of the metal form hydrates (compare CaF_2 with $CaCl_2.6H_2O$, etc.), and in others the fluoride is the only hydrated halide (e.g. $KF.2H_2O$, $AgF.2$ and $4\ H_2O$, other halides anhydrous). In these hydrated fluorides and in such complex fluorides as $K_2TiF_6.H_2O$ and $K_2WO_2F_4.H_2O$ it may be assumed that F—H—O bonds are formed, and of the halogens only fluorine is sufficiently electronegative to form such bonds. This is supported by the isomorphism of many hydrated fluoborates and perchlorates. Since we do not know the detailed structure of any hydrated fluoride we shall not discuss these compounds further. The rest of this section will be devoted to chlorides. In some cases analogous bromides have been shown to have the same structures as the chlorides, but hydrated iodides have been little studied.

The first point we notice is that the formulae of hydrated chlorides seldom, if ever, contain odd numbers of water molecules—contrast the sulphates. The reason for this is that Cl does not, like O, form strong bonds X—H—O by which the odd water molecule could be held in the structure. We shall return to this question of odd and even numbers of water molecules in the section in which we compare hydrates with ammines, and we shall see that structurally many hydrated chlorides are more closely related to ammino-chlorides than to hydrated oxy-salts. The simplest type of hydrated chloride is that in which the number of water molecules is equal to the coordination number of M, as in $MgCl_2.6H_2O$ or $AlCl_3.6H_2O$. If the only factor determining the structure were the relative sizes of $[Mg(H_2O)_6]^{2-}$ and Cl^-, then $MgCl_2.6H_2O$ could have the fluorite structure, but this would mean that each H_2O molecule would be in contact with four Cl^- ions. Actually the corresponding ammine, $MgCl_2.6NH_3$, does crystallize with the fluorite structure, but $MgCl_2.6H_2O$ has a less symmetrical monoclinic structure in which each water molecule is in contact with only two Cl^- ions. Similarly the ammine $Al(NH_3)_6Cl_3$ has the YF_3 structure, but $Al(H_2O)_6Cl_3$ has a much more complex rhombohedral structure in which again every H_2O molecule is adjacent to only two Cl^- ions. It is clear therefore that in these chlorides containing discrete Cl^- ions the H_2O molecule is exhibiting its tetrahedral character, but the fact that the distances H_2O—Cl are about the same in these crystals as in $NiSnCl_6.6H_2O$, where the Cl has very little effective negative charge, shows that there is no stronger binding between H_2O and Cl in $MgCl_2.6H_2O$ than in the hydrated complex chlorides. On the basis of the environment of the H_2O molecules we may distinguish the hydrates of simple halides, in which there are discrete Cl^- ions, from those of complex halides. The term complex halide will be applied here to any halide in the structure of which separate Cl^- ions cannot be distinguished. As examples we shall take $CuCl_2.2H_2O$, $K_2SnCl_4.H_2O$ (and the isomorphous $K_2HgCl_4.H_2O$), and $NiSnCl_6.6H_2O$.

The nearest neighbours of a water molecule in crystals of these compounds are as follows:

	$CuCl_2.2H_2O$	$K_2SnCl_4.H_2O$ *and* $K_2HgCl_4.H_2O$	$NiSnCl_6.6H_2O$
Nearest neighbours of H_2O molecule	1 Cu at 2·01 4 Cl ,, 3·06	2 K at 3·20 4 Cl ,, 3·30	1 Ni at 2·4 A. 4 Cl ,, 3·25 A.

In the first of these structures there are finite groups $CuCl_2(H_2O)_2$ consisting of a Cu atom surrounded by two Cl and two H_2O approximately at the corners of a square. These groups (with the trans-configuration) are packed together in much the same way as the non-polar molecules $C_{10}H_8$ in a crystal of naphthalene. The structure of $CuCl_2.2H_2O$ is shown, in plan and elevation, in Fig. 36 (p. 149). In $K_2SnCl_4.H_2O$ there are infinite chain ions of composition $[SnCl_4]^{2-}$ formed by $SnCl_6$ octahedra sharing two opposite edges, and the K ions and H_2O molecules fit in



between these parallel chains. A plan of the unit cell of $K_2SnCl_4.H_2O$ is shown in Fig. 39 (p. 150). The third example, $NiSnCl_6.6H_2O$, consists of octahedral groups $[Ni(H_2O)_6]^{2+}$ and $[SnCl_6]^{2-}$ arranged rather similarly to the Cs^+ and Cl^- ions in CsCl. In all of these compounds therefore the chlorine atoms are incorporated in complex groups, the bonds M—Cl having considerable covalent character, and in such compounds where there is little or no effective charge on the Cl atoms the environment of a water molecule is not determined by the same conditions as in the hydrates of simple halides or oxy-salts.

(c) *Hydrated Acids and Acid Salts*

Very little work has as yet been done on these compounds, so that anything in the nature of a general survey is not possible. These hydrates are of interest because some or all of the H^+ ions are likely to be associated with the water molecules as H_3O^+ ions, leading to the possibility of three hydrogen or hydroxyl bonds from the O atom of the water molecule to surrounding ions. To illustrate this we shall consider briefly two structures, those of the compound usually called potassium pentaborate tetrahydrate and of oxalic acid dihydrate.

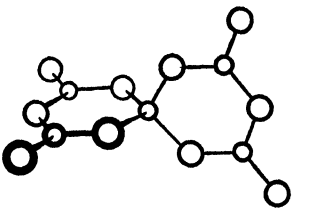


FIG. 105. The configuration of the $[B_5O_{10}]^{5-}$ ion. The smaller circles represent B atoms.

The compound with empirical formula $KB_5O_8.4H_2O$ contains complex ions $[B_5O_{10}]^{5-}$, with the configuration shown in Fig. 105, in which the central B atom forms four tetrahedral bonds (so that the planes of the two 6-rings are perpendicular) and the remaining B atoms each form three coplanar

bonds. These $[B_5O_{10}]^{5-}$ ions are linked together by short hydrogen bonds (of length 2·52 A.) forming an 'acid-salt' network of composition $[H_2B_5O_{10}]^{3-}$. The K^+ ions are surrounded by eight O atoms and are, of course, also essential to the stability of the structure, but we are more interested here in the function of the H^+ ions and of the water molecules.

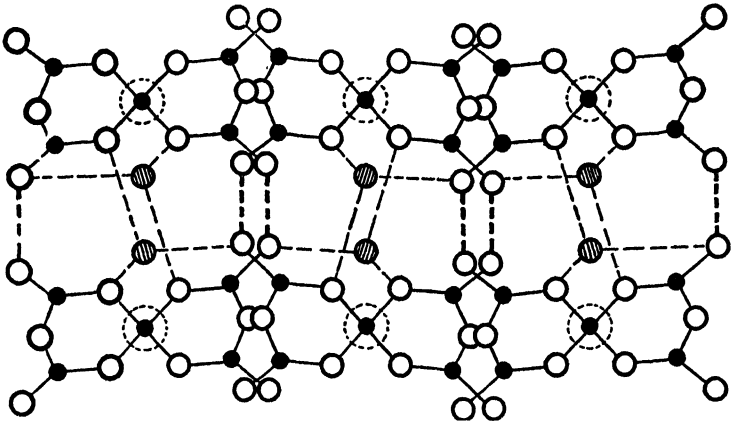
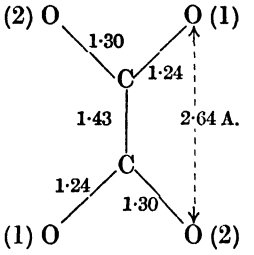


FIG. 106. Projection of the structure of $KH_2(H_3O)_2B_5O_{10}$ showing the probable mode of linking of the B_5O_{10} ions by short and long O—H—O bonds (heavy and light broken lines respectively). Boron atoms are shown as small black circles, H_3O^+ shaded, and K^+ ions as dotted circles. The latter lie between the complex ions, surrounded by 8 O atoms. Certain O atoms have been shifted slightly to avoid superposition.

The latter are surrounded by three O atoms of $[B_5O_{10}]^{5-}$ ions and by one K^+ ion, showing that they are H_3O^+ ions, rather than simple H_2O molecules, forming three hydroxyl bonds. The lengths of these bonds are 2·68, 2·77, and 2·93 A., mean 2·79 A., considerably greater than 2·52 A., the length of the short hydrogen bonds. These bonds and the short O—H—O bonds are distinguished in Fig. 106 as heavy and light broken lines respectively. The correct formulation of the compound is therefore $KH_2(H_3O)_2B_5O_{10}$.

In the dihydrate of oxalic acid also the water molecules are linked to three O atoms of the acid radical. One of the three bonds is a short hydrogen bond, of length 2·52 A., but the other two are longer (2·84, 2·87 A.) and are presumably hydroxyl bonds. The projection of the structure is shown in Fig. 107. It should be noted that the hydrogen and hydroxyl bonds do not link the oxalic acid molecules together in sheets as might appear to be the case, for the system of bonds marked *a* is not a closed circuit, and if we start from any particular atom in the ring and follow the bonds we arrive back, not at the same atom, but at a similar atom vertically above the starting-point. In the oxalic acid molecule the slightly different C—O distances suggest that one O is the carbonyl and the other the hydroxyl O atom, and this appears to be supported by the

fact that the former O atom (1) is attached to only one H_2O molecule (at a distance of 2·52 A.). The other O, (2), is linked to two water molecules (at 2·84 and 2·87 A.). A possible disposition of the H atoms may



be made if we assume internal hydroxyl bonds, which is not unreasonable in view of the intramolecular O—O separation of 2·64 A.

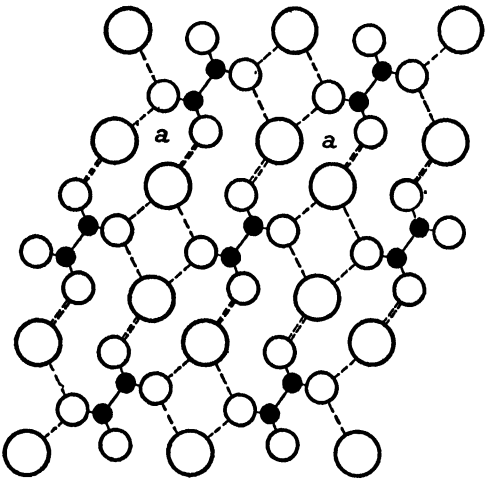


FIG. 107. Projection of the structure of oxalic acid dihydrate (along the *b* axis) showing the linking of H_2O and $(COOH)_2$ molecules by hydrogen bonds. Short hydrogen bonds are shown as double broken lines and long (hydroxyl) bonds as single broken lines. Large open circles represent H_2O molecules.

We have now considered a number of hydrates of different kinds and have seen that the behaviour of the water molecules in these structures can be accounted for quite satisfactorily. The effect of surrounding small positive ions with a layer of H_2O molecules does not lead to structures as simple as might be expected, whereas the corresponding ammines usually have the simple structures predicted from the radius ratio. The structural differences between hydrates and ammines are due to the fact that the neighbours of NH_3 do not, as do those of H_2O, have to conform with any tetrahedral nature of the molecule. We shall conclude this section with a few remarks on ammines and their relation to hydrates.

Ammines and Hydrates

Ammines are prepared by the action of ammonia on the salt, using either the gas or liquid and the anhydrous salt, or crystallizing the salt from ammoniacal solution. In preparing ammines of trivalent cobalt from cobaltous salts, oxidation of the cobalt to the trivalent state must accompany the action of ammonia, and this may be accomplished by passing air through the ammoniacal solution. No general statement can be made about the stability of ammines as compared with hydrates, for, as we shall see, the term ammine covers a very large number of compounds which differ greatly in constitution and stability. As extremes we may cite the very unstable ammines of lithium halides and the stable cobalt- and chrom-ammines.

A comparison of the empirical formulae of hydrates and ammines leads to the following conclusions:

(*a*) *Oxy-salts*

Many sulphates crystallize with odd numbers of molecules of water of crystallization, e.g. the vitriols $MSO_4.7H_2O$ (M = Fe, Co, Ni, Mn, Mg, etc.), $MnSO_4.5H_2O$, and $CuSO_4.5H_2O$, $MgSO_4.H_2O$, and many others. Dehydration of these hepta- and penta-hydrates to the monohydrate stage is easy, but the last molecule of water is not removed until temperatures between 200° and 300° C. are reached (e.g. for $NiSO_4.H_2O$, $CuSO_4.H_2O$) and $MgSO_4.H_2O$ occurs as the mineral kieserite. The structures of these monohydrates are not known. The ammines of these salts contain even numbers of NH_3 molecules, usually 4 or 6, e.g. $NiSO_4.6NH_3$. The hexahydrates, of course, also exist in many cases, but the heptahydrate is usually obtained by evaporation of aqueous solution at ordinary temperatures. The ammine of copper sulphate is interesting. Its formula is $Cu(NH_3)_4SO_4.H_2O$ (compare $Cu(H_2O)_4SO_4.H_2O$), and not $Cu(NH_3)_4SO_4.NH_3$. The reason for the non-existence of ammines with odd numbers of molecules of NH_3 in excess of the coordination number of the metal is that such odd NH_3 molecules would have to be accommodated between the $[M(NH_3)_n]$ groups and the SO_4^{2-} ions, and no strong bonds are formed between NH_3 and NH_3. The odd water molecule in $CuSO_4.5H_2O$ or $NiSO_4.7H_2O$, however, is held by hydroxyl bonds between H_2O molecules coordinated to metal atoms and O atoms of SO_4^{2-} ions. Part of the plan of the structure of $CuSO_4.5H_2O$ is shown in Fig. 108 to show the environment of the 'odd' water molecule.

The nitrates of many divalent metals crystallize with $6H_2O$ (Fe, Mn, Mg, etc.), but a few nitrates have odd numbers of water molecules, e.g. $Fe(NO_3)_3.9$ (and 6) H_2O, $Cu(NO_3)_2.3H_2O$. Where the corresponding ammine is known it has an even number of NH_3, as in $Cu(NH_3)_4(NO_3)_2$. There are many other series of hexahydrated salts—perchlorates, sulphites, bromates, etc.—and although in such cases the ammines often contain $6NH_3$, the structures of ammine and hydrate are quite different—

compare, for example, the structure of $[Co(H_2O)_6](ClO_4)_2$, described above, with the simple fluorite structure of $[Co(NH_3)_6](ClO_4)_2$.

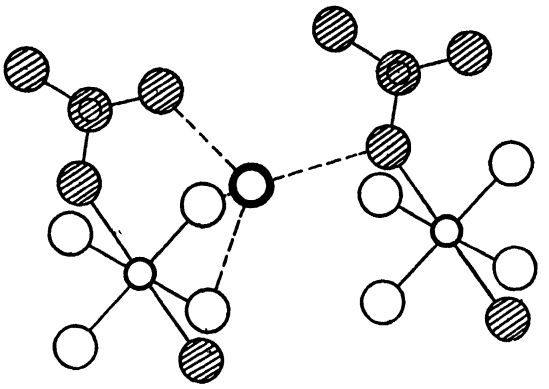


FIG. 108. The environment of the fifth H_2O molecule (centre) in $CuSO_4.5H_2O$. The octahedral coordination group around a copper atom is composed of 4 H_2O molecules and 2 oxygen atoms of SO_4^{2-} ions (shaded circles).

(*b*) *Halides*

In contrast to the oxy-salts, halides rarely crystallize with an odd number of water molecules. When they do, the number is never greater than the coordination number of the metal ($BiCl_3.H_2O$, $LiCl.3H_2O$, $ZnCl.H_2O$), for additional water molecules cannot be held between $[M(H_2O)_n]$ groups and Cl^- any more than additional NH_3 between $[M(NH_3)_n]$ and an oxy-ion, since strong hydrogen bonds are not formed between O and Cl. Moreover, the ammines of these exceptional halides contain even numbers of NH_3 molecules, e.g. $ZnCl_2.H_2O$ but $ZnCl_2.2NH_3$. Although the ammines and hydrates of halides usually contain the same numbers of molecules of NH_3 and H_2O respectively:

$NiCl_2.6H_2O$,	$NiCl_2.6NH_3$	$NiSO_4\begin{cases}7H_2O\\6H_2O\end{cases}$ but	$6NH_3$
	contrast		
$CuBr_2.4H_2O$,	$CuBr_2.4NH_3$	$CuSO_4.5H_2O$	$4NH_3.H_2O$
$CuCl_2.2H_2O$,	$CuCl_2.2$, 4, or $6NH_3$, ($CuCl_2.4NH_3.2H_2O$ from solution)	$Cu(NO_3)_2.3H_2O$	$4NH_3$

the crystal structures of the two sets of compounds are different, as has already been pointed out for the pairs $Al(NH_3)_6Cl_3$ and $Al(H_2O)_6Cl_3$, and $Mg(NH_3)_6Cl_2$ and $Mg(H_2O)_6Cl_2$.

From this brief survey we see that the ammines $MX_x.nNH_3$ with n greater than the coordination number of M are likely to be rare and that n is commonly 4 or 6, depending on the nature of the metal M. In these ammines the NH_3 molecules form a group around M, and these groups $M(NH_3)_n$ often pack with the anions into a simple crystal structure. The

linking of the NH_3 to M in the ammines of the more electropositive elements such as Al and Mg is essentially electrostatic in nature. This has also been established for Ni^2 and Cu^2 by measurements of the magnetic moments of such complexes. The stability of these compounds is of quite a different order from that of the very stable ammines of trivalent cobalt and chromium. The reason for the extraordinary stability of octahedral Co^3 complexes as compared with octahedral Co^2 complexes is discussed in Chapter XVI. Magnetic measurements show that in the ammine complexes of Co^3 (and also of Ir^3, Pd^4, Pt^4) the bonds M—NH_3 are predominantly covalent, and we shall shortly see that in the earlier Periodic Groups the more covalent ammines of the B sub-group metals are more stable than, and quite different in structure from, the ammines of the A sub-group metals. We may conclude therefore that the formal similarity between hydrates and ammines is limited to those ammines in which the M—NH_3 bonds are essentially electrostatic, and that even in these cases there are significant differences between the crystal structures of the two compounds $MX.nNH_3$ and $MX.nH_2O$. This latter point has already been dealt with; the former is best illustrated by a comparison of the ammines and hydrates of the salts of the metals of Groups I and II of the Periodic Table.

Of the alkali metal chlorides only those of Li and Na form ammines, $MX.yNH_3$ ($y_{max.} = 6$), and these are very unstable. Similarly LiCl forms a trihydrate, NaCl a dihydrate (stable only below 0° C.), while KCl, RbCl, and CsCl crystallize without water of crystallization. The formation of ammines thus runs parallel with the formation of hydrates. As the size of the ion increases, from Li to Cs, the charge remaining constant, the ability to polarize H_2O or NH_3 molecules and so attach them by polar bonds decreases. In the B sub-group we find an altogether different relation between hydrates and ammines. Ammino-compounds are commonly formed by salts which form no hydrates and they resemble in many ways the cyanido- and other covalent complexes. The only halide of silver which forms a hydrate is the fluoride, but AgCl and the other halides form ammines. Again, the nitrate and sulphate are anhydrous but form ammines, $AgNO_3.2NH_3$ and $Ag_2SO_4.4NH_3$ respectively. In the latter, the structure of which has been determined, and presumably also in the former, there are linear ions $[NH_3—Ag—NH_3]^+$ exactly analogous to the ion $[NC—Ag—CN]^-$ in $KAg(CN)_2$. Gold also forms ammines, e.g. $[Au(NH_3)_4](NO_3)_3$, and several of the ammines of copper salts have already been mentioned.

In the second Periodic Group we find a similar difference between the stability and constitution of ammines in the A and B sub-groups. Magnesium forms a number of ammines, but the tendency to form ammines falls off rapidly in the alkaline earths. The compound $CaCl_2.8NH_3$, for example, readily loses ammonia. The degree of hydration of salts also decreases from Ca to Ba except for the octahydrates of the peroxides and hydroxides ($SrO_2.8H_2O$, $Ba(OH)_2.8H_2O$), which presumably owe their

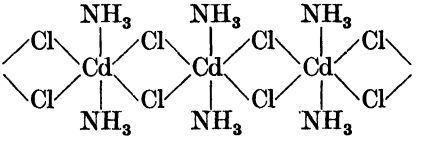
stability to hydroxyl bond formation between the O_2^{2-} or OH^- ions and the water molecules. In the B sub-group, however, as in I B, the ammines and hydrates are structurally unrelated. We find

	$ZnCl_2.H_2O$	but	$ZnCl_2.2NH_3$
and	$CdCl_2.2H_2O$	and	$CdCl_2.2NH_3$

but these two diamminodichlorides have quite different structures, in which the bonds M—NH_3 must possess appreciable covalent character. In $ZnCl_2.2NH_3$ we find discrete molecules $Zn(NH_3)_2Cl_2$ with tetrahedral configuration which may be compared with the planar groups $Cu(H_2O)_2Cl_2$, the configuration of which emphasizes the essentially covalent nature of the bonds from the copper atom.



In $Cd(NH_3)_2Cl_2$ there are infinite chain molecules in which each Cd atom is surrounded octahedrally by four halogen atoms and two NH_3 molecules thus:



the bonds between neighbouring chains being only of the van der Waals type. With this chain molecule may be compared the structure of the infinite $SnCl_4^{2-}$ ion in $K_2SnCl_4.H_2O$ described on p. 288. The ammines of certain other elements, notably cobalt and palladium, are discussed in Chapters VI and XVI.

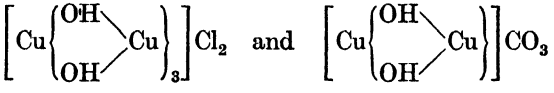
BASIC SALTS

The term 'basic salt' is applied to a variety of compounds—the basic chlorides and oxy-salts of the less electropositive metals, more particularly of the B sub-groups, the oxyhalides and such compounds as basic beryllium acetate. It has been usual to describe as a basic salt any compound intermediate between the normal salt and the hydroxide or oxide, but we shall restrict the term to hydroxy-salts. The oxychlorides, which contain no hydrogen, have much simpler structures, which have already been described with the halides in Chapter VIII. For 'basic beryllium acetate' see p. 307. Although there is no possibility of hydroxyl bond formation in hydroxy-chlorides, they will be included here in order to keep all hydroxy-compounds together in the same chapter. It is possible that the very stable mono-hydrates of certain sulphates (e.g. Cu, Ni, Mn) which do not lose water until they are heated to a temperature above 200° C. are really hydroxy-salts, e.g. $Cu(OH)(SO_4H)$ instead of $CuSO_4.H_2O$—

compare $MgCO_3.H_2O$ below. This change in formulation would not imply any radical change in the constitution of the compound, since if the H atoms are disregarded the structural units in the crystal would in both cases be Cu, O, and SO_4 ions. The distinction would lie in the nature of the bonds between O and SO_4, whether hydroxyl or hydrogen bonds. We shall expect to find differences between the structures of hydroxy-halides (hydroxy-fluorides are not known) and of hydroxy-oxy-salts similar to those between hydrated halides (other than fluorides) and hydrated oxy-salts. In the halides, hydroxyl bonds are not formed between OH^- or H_2O and Cl, Br, or I, but in the oxy-salts O—H—O bonds can be formed between O atoms of OH or H_2O and those of the oxy-ions.

Basic salts may be prepared in various ways, which usually involve—directly or indirectly—hydrolysis of a normal salt. The hydrolysis may be carried out indirectly by heating a hydrated salt, and many compounds described as basic salts are formed in this way in place of the anhydrous normal salts, e.g. $Cu(NO_3)_2.3Cu(OH)_2$ by heating hydrated copper nitrate, basic magnesium chloride, and so on. The precipitates obtained by adding sodium carbonate solution to metallic salt solutions are in many cases described as basic carbonates. Some metals do not form normal carbonates (e.g. Cu); others such as Pb, Zn, Co, and Mg form normal or basic carbonates according to the conditions of precipitation. Lead, for example, forms $2PbCO_3.Pb(OH)_2$ and $Pb(OH)_2.PbCO_3$, both of which occur as minerals, and cobalt, $CoCO_3.3Co(OH)_2$ in addition to the normal salts. The 'basic magnesium carbonates' may contain hydroxy-carbonates, for if a solution of magnesium bicarbonate is crystallized at 50° C., crystals of the empirical composition $MgCO_3.3H_2O$ separate. On heating to 100° C. two molecules of water only are lost, and further heating results in loss of CO_2 and formation of the hydroxide, so that these compounds are possibly $Mg(OH)(CO_3H).2H_2O$ and $Mg(OH)(CO_3H)$.

Before describing the structures of a few hydroxy-salts we should mention that 'structural formulae' have been assigned to some of these compounds on the supposition that they are Werner coordination compounds. We may instance:



for atacamite, $CuCl_2.3Cu(OH)_2$, and malachite, $CuCO_3.Cu(OH)_2$, respectively. Such formulae are quite erroneous, for these compounds do not contain large complex ions with a central copper atom. Malachite, for example, consists of an infinite array in three dimensions of Cu^{2+}, CO_3^{2-}, and OH^- ions, the structure being determined, as in the case of simple oxy-salts, by the packing of these ions with allowance for the formation of hydroxyl bonds, the formation of which has some influence on the environment of the OH^- ions.

Hydroxy-halides

From what is known of the structures of the hydroxy-halides they appear to be closely related to the corresponding hydroxides and halides. Various rather ill-defined products of the incomplete precipitation of $CoCl_2$ and $NiCl_2$ solutions by NaOH have been described. Some may have structures consisting of interleaved portions of $Co(OH)_2$ and $CoCl_2$, in the

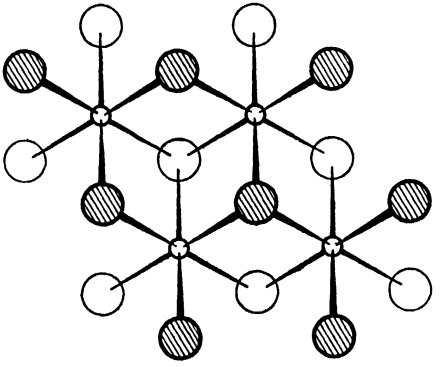
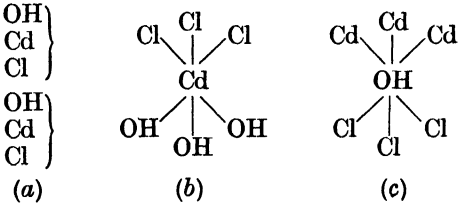


FIG. 109. Portion of one layer of Cd(OH)Cl. The OH groups (shaded) lie above, and the Cl atoms below, the plane of the metal atoms.

case of the cobalt compounds, and hydroxy-chlorides of the type M(OH)Cl have also been described. The latter may be analogous to Cd(OH)Cl, which is described below. The basic chlorides $MCl_2.3M(OH)_2$ seem to be characteristic products which can be prepared in various ways. The cell dimensions are very similar to those of the hydroxides, and it is suggested that they consist of $M(OH)_2$ layers in which one-quarter of the OH groups are replaced by Cl atoms.

The structure of Cd(OH)Cl has been determined. As in $Cd(OH)_2$ and $CdCl_2$ the structure consists of layers, and every Cd atom is surrounded octahedrally by three Cl and three OH. The sequence of layers is shown at (*a*) and the environment of Cd and OH at (*b*) and (*c*) respectively. The fact that OH is surrounded on the one side by three Cd and on the other



by three Cl shows that there is no question of hydroxyl bond formation—compare $Cd(OH)_2$, p. 353, and hydrated chlorides, p. 379. Fig. 109 shows, in plan, a layer of the structure. Regarding the Cd atoms as lying in the plane of the paper, then the OH groups lie in a plane above and the Cl atoms in a plane below that of the Cd atoms.

Hydroxy-oxy-salts

We can mention here only a few examples of the many types of hydroxy-oxy-salts. Copper is notable for forming such compounds, many of them occurring as minerals, e.g.

$Cu_4(OH)_6SO_4$ or	$CuSO_4.3Cu(OH)_2$,	brochantite
$Cu_4(OH)_6Cl_2$	$CuCl_2.3Cu(OH)_2$,	atacamite
$Cu_4(OH)_6(NO_3)_2$	$Cu(NO_3)_2.3Cu(OH)_2$,	
$Cu_2(OH)PO_4$	$Cu_3(PO_4)_2Cu(OH)_2$,	libethenite
$Cu_2(OH)AsO_4$	$Cu_3(AsO_4)_2Cu(OH)_2$,	olivenite
$Cu_2(OH)_2CO_3$	$CuCO_3.Cu(OH)_2$,	malachite

Zinc forms many similar compounds, e.g. $Zn_2(OH)AsO_4$, isomorphous with the copper compound. We have already said that these salts consist of the constituent ions packed together in much the same way as in normal

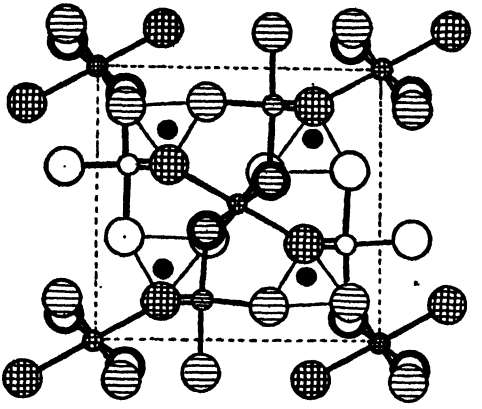


FIG. 110. Plan of the structure of $Cu_2(OH)AsO_4$ (olivenite). Large circles represent O (light) or OH (heavy), small shaded circles Cu, and small black circles As. Shading indicates height above the plane of the paper; unshaded atoms are at height 0, those shaded horizontally at height $c/2$, and those shaded horizontally and vertically at heights $c/4$ and $3c/4$. The 6-coordinated Cu atoms are those at the corners and centre of the unit cell.

oxy-salts, with the possibility of hydroxyl bond formation between OH and O of the oxy-ions. The formation of such bonds does not greatly affect the packing of the ions since their length is about the same as the normal distance between O^{2-} ions. Hence we find $Cu_2(OH)PO_4$, $Cu_2(OH)AsO_4$, and $Zn_2(OH)AsO_4$ all with essentially the same structure as andalusite, Al_2OSiO_4 (or Al_2SiO_5). Also, since the radius of the F^- ion is very nearly the same as that of O^{2-}, hydroxyl groups may be replaced by F^- without appreciable alteration in structure. Hydroxy-apatite, $Ca_5(OH)(PO_4)_3$, is isomorphous with $Ca_5F(PO_4)_3$, and the structural units are Ca^{2+}, OH^-, and PO_4^{3-} ions. Although it is not easy to appreciate the geometry of a complicated crystal structure from a simple diagram, the plan of the structure of $Cu_2(OH)AsO_4$ is given above as it illustrates at

least the general nature of these hydroxy-salts. It will be seen that one-half of the Cu atoms are surrounded, approximately octahedrally, by four arsenate O atoms and two OH^- ions, and the other half by by four O atoms and one OH^- ion. This peculiar coordination group of five atoms forming a deformed trigonal bipyramid has already been noted as occurring in andalusite (pp. 324 and 471). In malachite we find a similar difference in the environments of the Cu atoms, some being surrounded by two O and four OH and others by three O and two OH. The similarity between the oxygen chemistry of phosphorus and arsenic and that of silicon is dealt with at greater length when we come to the elements of the fifth Periodic Group, in Chapter XII.

SULPHIDES

The section on the structure of oxides was prefaced by a comparison of oxides and sulphides. The essential points brought out may be summarized as follows. A bond M—S is more covalent in character than the bond M—O, and accordingly while there is often a structural resemblance between oxides and fluorides, the sulphides tend to crystallize with the same types of structures as chlorides, bromides, and iodides of corresponding formula type—compare MgF_2, MnF_2, TiO_2, and SnO_2 with the ionic rutile structure, but $MgCl_2$, $MnCl_2$, TiS_2, and SnS_2 with the $CdCl_2$ layer structure. Layer lattices are rare in oxides and fluorides, but are commonly found in sulphides and the other halides. The only essentially ionic sulphides are the water-soluble compounds of the alkalis and alkaline-earths which are isomorphous with the corresponding oxides. A number of important structure types are found in sulphides which have no counterpart among oxide structures, notably the layer structures, pyrites, marcasite, and NiAs structures. Further, many sulphides, particularly of the transition elements, behave like alloys, the resemblance being shown by their formulae (in which the elements do not exhibit their normal chemical valencies—e.g. Co_9S_8 and Co_3S_4), their variable composition, and their extraordinary physical properties—metallic lustre, reflectivity, and conductivity. The resemblance to alloys is even more marked in some selenides and tellurides, and the compounds CoTe and $CoTe_2$ are described later to illustrate this point. We therefore find that the sulphides and oxides of many metals do not have similar formulae, compare

FeO, Fe_2O_3, and Fe_3O_4 with FeS and FeS_2,

and PbO, PbO_2, and Pb_3O_4 with PbS (the only sulphide of Pb).

Except in the case of the most electropositive metals the structure types possible for oxides and sulphides correspond to different empirical formulae, and an oxide of a given type can exist where the corresponding sulphide cannot and vice versa. In cases where the oxide and sulphide of the same formula type do exist they generally have quite different structures, and often that of the sulphide is much more complex. Compare, for example, the following pairs: CuO and CuS, Cu_2O and Cu_2S,

NiO and NiS, PbO and PbS. The structures of all these oxides have been referred to in Chapter IX, and in each case they are different from those of the sulphides, which will be described below.

TABLE 22

The Crystal Structures of some Sulphides

Type of structure	*Coordination numbers of* M *and* S	*Name of structure*	*Examples*
Infinite 3-dimensional complexes	4:8	Antifluorite	Li_2S, Na_2S, K_2S, Rb_2S
	6:6	Rock-salt	MgS, CaS, SrS, BaS, MnS, PbS
	6:6	Nickel arsenide	FeS, CoS, NiS*
	6:6†	Pyrites or Marcasite	FeS_2, CoS_2, NiS_2, MnS_2, OsS_2, RuS_2
	4:4	Zinc-blende	BeS, ZnS, CdS, HgS‡
		Wurtzite	ZnS, CdS, MnS
	4:4	Cooperite	PtS
Layer structures	6:3	Cadmium iodide	TiS_2, ZrS_2, SnS_2, PtS_2
	6:3	Molybdenum sulphide	MoS_2, WS_2
Chain structures			Sb_2S_3, Bi_2S_3, SiS_2
Molecular structures			All sulphides consisting of finite molecules

* Also the millerite structure (5:5 coordination).

† The coordination numbers here are those of Fe by S and of S_2 groups by Fe (or other metal).

‡ Metacinnabarite—also the hexagonal cinnabar structure.

The Crystal Structures of Simple Sulphides

In Table 22 are set out the structure types of some sulphides, the general form of the table being similar to that of Table 17 (p. 312) for oxides, with which it should be compared. No further discussion is necessary here of the following groups of sulphides, to the structures of which reference has already been made in the section on oxides:

Alkali sulphides, M_2S—anti-fluorite structure.
Group II A sulphides, MS—rock-salt structure.
„ B „ MS—zinc-blende and/or wurtzite structure.

(Hydrosulphides have been dealt with in Chapter X, pp. 345–7.)

In discussing the change in type of structure as we proceed down a Periodic Group towards the more electropositive elements, the dioxides of the elements of Group IV were taken as examples. The structures of

the corresponding disulphides, where known, are set out below, and they may be compared with those of the dioxides shown on p. 313. (For the monosulphides of the Group IV B elements see p. 390.)

CS_2 (finite molecules)
SiS_2 (infinite chains)

TiS_2	(CdI_2 layer structure)	GeS_2	(3-dimensional network of GeS_4 tetrahedra sharing all corners)
ZrS_2	(CdI_2 layer structure)	SnS_2	(CdI_2 structure)
HfS_2	?	(PbS_2)	non-existent.
ThS_2	?		

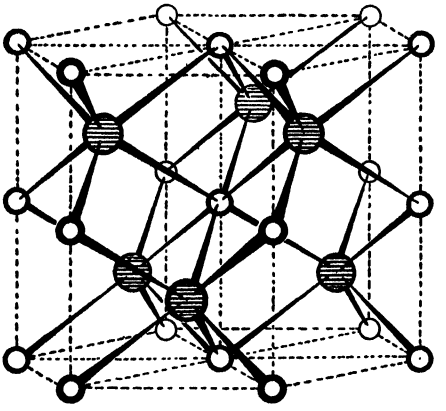


FIG. 111. The structure of NiAs (As atoms shaded). The Ni atom in the centre of the diagram is surrounded octahedrally by six As atoms and has also two near Ni neighbours which are coplanar with four of the As atoms.

We shall now describe some of the more characteristic sulphide structures, viz.

(*a*) the NiAs structure,

(*b*) the structures of disulphides, MS_2,

(*c*) other sulphide structures of special interest,

and then the structures of several complex sulphides to show how some of these compounds are related to simple sulphides.

(*a*) *The Nickel Arsenide Structure*

In this structure, which is illustrated in Fig. 111, each atom has six nearest neighbours of the other sort, but the arrangement of the neighbouring atoms is different for the two kinds of atom. An arsenic atom is surrounded by six Ni atoms at the apices of a trigonal prism. The immediate neighbours of a Ni atom are six As arranged octahedrally, but there are also two Ni atoms sufficiently near to be considered bonded to the

first Ni atom, as may be seen from the interatomic distances in some compounds with this structure:

Compound AB	*Distance from* A *to* 6 B	2 A
NiAs	2·43 A.	2·52 A.
FeS	2·45	2·89
CoTe	2·62	2·68
NiTe	2·64	2·68
CrSb	2·74	2·73
CoSb	2·58	2·60

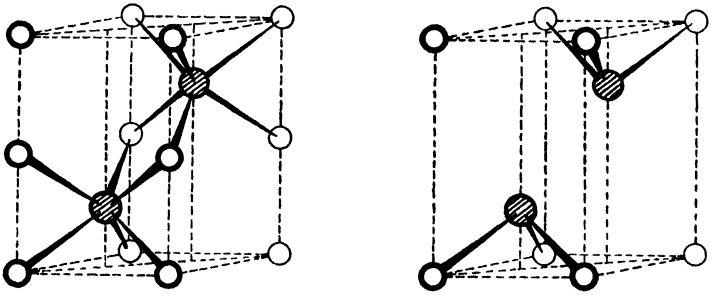
From the above figures it will be seen that in the more metallic systems with this structure these eight neighbours are approximately equidistant from the transition metal atom.

This structure is adopted by many phases AB containing a transition metal (particularly the Group VIII metals) and an element of the later B sub-groups—Sn, As, Sb, Bi, S, Se, Te—which would normally be regarded as alloys. For this reason we used the term phase rather than compound, for we find that these phases have many properties characteristic of intermetallic systems, e.g. their opacity and metallic lustre. From the chemical standpoint the most interesting feature is their variable composition. Ferrous sulphide has the NiAs structure but rarely has the Fe:S ratio precisely unity, so that various formulae ranging from Fe_6S_7 to $Fe_{11}S_{12}$ have been assigned to such non-stoichiometric phases. For this compound the NiAs structure is stable over the range 50–55·5 atomic per cent. S, and it is known from careful density measurements that these apparently sulphur-rich phases are in reality iron-deficient. The lattice of the S atoms remains intact, but some of the iron atoms are missing from the lattice. The alternative possibilities, replacement of some Fe by S or actual additional S in the structure, are definitely disproved.

The sulphides FeS, CoS, and NiS all crystallize with the NiAs structure and NiS also with a peculiar 5:5 coordinated structure as the mineral millerite. Polymorphism is common among sulphides, many having a high-temperature form different from the ordinary form—note, e.g., the zinc-blende-wurtzite transition and the high-temperature forms of Ag_2S and Cu_2S with defect lattices. Manganous sulphide MnS is trimorphous, crystallizing with the rock-salt, zinc-blende, and wurtzite structures. The selenides and tellurides of Fe, Co, and Ni crystallize, like the sulphides, with the NiAs structure, and the Co—Te system is of interest in connexion with the problem of variable composition. In the Fe—S system the range of stability of the phase with the NiAs structure is 50–55·5 per cent. S. In the Co—Te system the phase is homogeneous over the range 50–66·7 atomic per cent. Te (using quenched samples), and at the latter extreme the composition corresponds to the formula $CoTe_2$. Over this whole range the cell dimensions vary continuously, but change only by a very small amount:

	a	*c*
50 per cent. Te	3·882 A.	5·367 A.
66·7 per cent. Te	3·784	5·403

The explanation of this unusual phenomenon, a continuous change from CoTe to $CoTe_2$, is as follows. The compound $CoTe_2$ crystallizes at high temperatures with the CdI_2 structure which is retained in the quenched specimen. (On prolonged annealing it changes over to the marcasite structure.) This CdI_2 structure is very simply related to the NiAs structure



(a) (b)

FIG. 112. Unit cells of the structures of (*a*) CoTe (NiAs structure) and (*b*) $CoTe_2$ (CdI_2 structure). Shaded circles represent Te atoms. Compare with Figures 111 and 20 respectively.

of CoTe, as shown in Fig. 112. In both the extreme structures the Te atoms are arranged in hexagonal close-packing. At the composition CoTe all the octahedral holes are occupied by Co. As the proportion of Co decreases (or that of Te increases) some of these positions become vacant, and finally, at the composition $CoTe_2$, only one-half are occupied, and in a regular manner, forming the CdI_2 type of structure. The same behaviour is found in the Ni—Te system, accounting for the various formulae (Ni_2Te_3, $NiTe_2$) assigned to the mineral melonite. It can clearly have any composition between those corresponding to NiTe and $NiTe_2$.

(*b*) *The Disulphides* MS_2

Disulphides are formed by the elements of Group IV and also by many transition elements. The structures of CS_2, SiS_2, and GeS_2 are mentioned elsewhere. Most of the disulphides of the transition elements have either a layer lattice or the pyrites or marcasite structures. Many of the corresponding dioxides have the essentially ionic rutile structure. The compounds ZrS_2, SnS_2, TiS_2, and PtS_2 all crystallize with the CdI_2 structure, but MoS_2 and WS_2 have a rather different type of layer structure in which each metal atom is surrounded by six S atoms at the apices of a trigonal prism. The plan of a layer of the MoS_2 structure is illustrated in Fig. 34 (p. 145), where it is compared with other AX_2 layers.

The pyrites and marcasite structures, named after the two forms of FeS_2, are of quite a different kind. They contain discrete S_2 groups in which the binding is homopolar, the S—S distance being 2·10 A. Geometrically the pyrites structure is closely related to that of NaCl, the centres of the S_2 groups and of the Fe atoms occupying the positions of

Na^+ and Cl^- in the rock-salt structure. Every Fe atom lies at the centre of an octahedral group of six S atoms, and this is also the case in marcasite, which is a less symmetrical arrangement of the same structural units. The two structures are illustrated in Fig. 113.

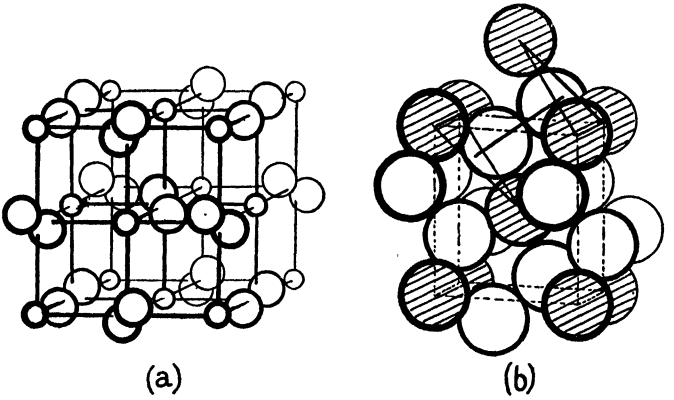


FIG. 113. The structures of the two forms of FeS_2: (*a*) pyrites and (*b*) marcasite. In (*a*) the S—S distance has been reduced to accentuate the resemblance of this structure to that of NaCl. In (*b*) the shaded circles represent Fe atoms, six of which surround each S_2 group, as is also the case in the pyrites structure.

We saw that the NiAs structure is adopted by a number of arsenides and antimonides in addition to sulphides, selenides, and tellurides, and the same is true of the pyrites and marcasite structures. Also, instead of S_2 or As_2 groups we may have mixed groups such as AsS or SbS, and we find a number of compounds structurally related to pyrites and marcasite but with lower symmetry due to the replacement of the symmetrical S_2 or As_2 group by AsS, etc. So FeS_2 and $PtAs_2$ have the pyrites structure but NiSbS a less symmetrical structure related to it—CoAsS, NiAsS, and NiSbS probably have the same structure. Similarly FeS_2 and $FeAs_2$ have the marcasite structure, but FeAsS and FeSbS have related structures of lower symmetry.

(*c*) *Other Sulphide Structures*

The structures of some monosulphides call for brief comment. In their monosulphides the Group II elements are showing their normal group valency and the structures are mostly simple and highly symmetrical:

II A: MgS, CaS, SrS, BaS, rock-salt structure (6:6)
II B: BeS, ZnS, CdS, HgS, wurtzite or blende (4:4).

Many transition metals also form monosulphides, and in many cases the structures are complex and peculiar to one particular sulphide only. For example, CuS (the mineral covelline) has a complicated layer structure. The monosulphides of the Group IV B metals are interesting in this connexion. Whereas PbS crystallizes with the rock-salt structure, both SnS

and GeS are far less symmetrical, though their structures (which are quite different from one another) may both be derived from that structure by sufficient distortion. The environment of the metal atoms in GeS, SnS, and PbS is:

Ge	1 S	2·47 A.	Sn	1 S	2·62 A.	Pb	6 equidistant S atoms at 2·97 A.
	2 S	2·64		2 S	2·68		
	1 S	2·91		2 S	3·27		
	2 S	3·00		1 S	3·39		

The intermediate compound, $PbSnS_2$, apparently has a structure similar to that of SnS. The abnormality of these sulphides is paralleled by the monoxides, as we have seen in the cases of SnO and PbO. The fact that PbS crystallizes with the rock-salt structure does not mean that the Pb—S binding is similar in nature to that of the ionic sulphides and halides, for the latter compounds are colourless and transparent, whereas PbS is opaque and possesses a brilliant metallic lustre. The properties of lead and certain other metals are discussed in Chapter XVI in connexion with the inert pair of electrons, which presumably accounts for many of these abnormal structures.

The chemistry of mercury is also complicated in this way, and although HgS does crystallize (as metacinnabarite) with the zinc-blende structure, it also exists in a second form—cinnabar. The structure of cinnabar may be regarded as a very distorted rock-salt structure in which the number of nearest S neighbours is reduced to two. The tendency of this element to form only two strong bonds is also shown in the halides (p. 513). The neighbours of a Hg atom in the two forms of HgS are:

Cubic form (*metacinnabarite*)	*Hexagonal form* (*cinnabar*)
4 S at 2·53 A.	2 S at 2·52 A.
	2 S 2·91
	2 S 3·25

Cinnabar is notable for its extraordinarily large optical rotatory power which is, of course, a property of the solid only, arising from the spatial arrangement of the atoms.

We have seen that FeS, CoS, and NiS crystallize with the NiAs structure, in which the metal atoms form six (or eight) bonds. Palladium and platinum, however, form four planar bonds in their monosulphides. The structure of PtS is illustrated in Fig. 114. It will be seen that each Pt atom forms four planar bonds and each S atom the usual tetrahedral bonds. In PdS the coordination of the two kinds of atoms is similar to that in PtS, but the structure is not quite so regular.

We have now described the structures of some sulphides in which the metal and S atoms form a covalently linked assembly extending indefinitely in three dimensions, and also others in which these atoms are closely bound into layers with much weaker forces between than within

the layers. The structures of Sb_2S_3 and of SiS_2 are examples of chain structures, containing complexes which are infinite in one dimension only.

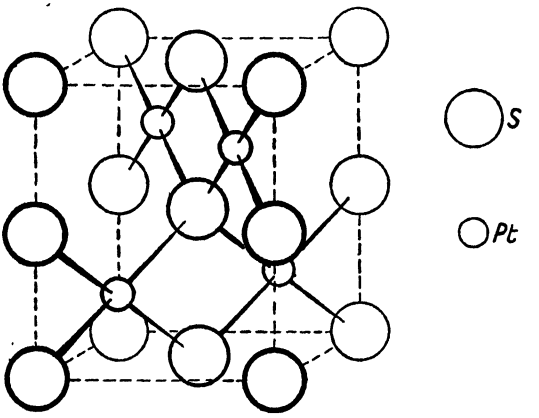
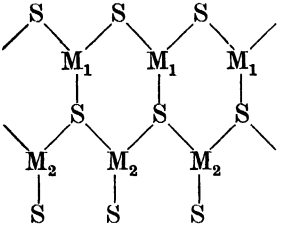


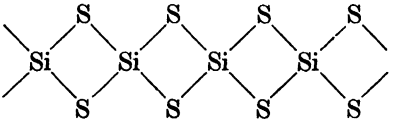
FIG. 114. The structure of PtS, showing the planar coordination of Pt by four S and the tetrahedral coordination of S by four Pt.

A simple chain with the composition M_2S_3 for an element M forming three bonds is



and chains of this type occur in the structure of Sb_2S_3 and of the isomorphous Bi_2S_3. The interatomic distances indicate, however, that these chains are associated in pairs as shown diagrammatically below, for whereas the atoms M_1 (see above) have three S neighbours at 2·50 A. and no others nearer than 3·14 A., the atoms M_2 have S neighbours as follows: one at 2·38, two at 2·67, and two more at 2·83 A. in addition to others at greater distances. This rather unsatisfactory environment of one-half of the Sb atoms necessitates the provisional conclusion that these atoms form two additional weak bonds as shown by the dotted lines in Fig. 115.

The structure of SiS_2 is more straightforward and consists of infinite chains of SiS_4 tetrahedra sharing opposite edges:



the chains being held to one another only by weak van der Waals forces.

Note that in silicates, in which the Si—O bonds have more ionic character than the Si—S bonds, edges are never shared between SiO_4 tetrahedra.

Molecular sulphides to which special interest attaches are described under the appropriate elements.

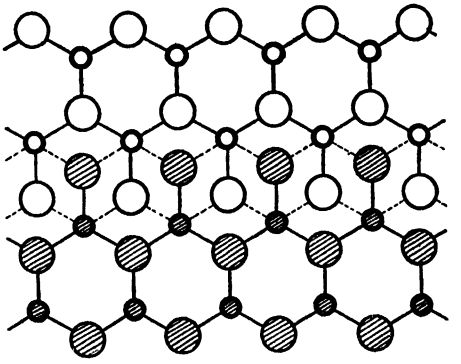


FIG. 115. The double chains in Sb_2S_3 (diagrammatic). The larger circles represent S atoms. All the atoms of one chain are shaded, and the weak secondary Sb—S bonds are shown as broken lines.

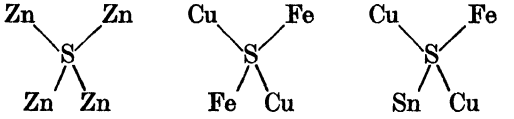
The Crystal Structures of some Complex Sulphides

The fact that simple sulphides exhibit such a variety of different structures, often of considerable complexity, is attributable to the essentially homopolar nature of the M—S bonds. Such bonds tend to be formed at definite angles to one another and they are also limited in number. Further, the semi-metallic properties of many sulphides show that all the bonding electrons are probably not behaving as in simple covalent crystals. All these factors underlie the complexity of the crystal structures of sulphides, and in complex sulphides we have the additional complication that metal atoms of more than one kind are present, each with individual requirements to be satisfied. An extraordinary variety of complex sulphides is found in the mineral world, and since comparatively little systematic examination of these compounds has yet been made, we shall mention here only a few which are structurally related to two simple sulphide structures, those of zinc-blende and wurtzite.

A characteristic of sulphide minerals is that the composition is rarely that of the 'ideal' formula, partial replacement of one kind of atom by another being extremely common. For example, ZnS may contain up to 20 per cent. Fe and in the related mineral colusite Zn is partly replaced by Cu, Fe, Mo, and Sn. Isomorphous replacement is common in oxide structures, but the relation between atoms capable of replacing one another in oxides is quite different from that which holds for sulphide structures, a point which illustrates the difference between the type of binding in the two classes of compounds. In ionic oxides the possibility of isomorphous replacement depends largely on ionic size, since the ions concerned both have to occupy a hole of a certain size (between, say,

four or six O^{2-} ions) in a lattice of oxygen ions which are usually close-packed or approximately so. The particular chemical properties of the ion are of minor importance. So we find the following ions replacing one another in oxide structures: Fe^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+} in octahedral positions, and Na^+ much more often replaces Ca^{2+} (which has about the same ionic size) than K^+ to which it is more closely related chemically. In sulphides, on the other hand, the criterion is the formation of a similar number of bonds, and we find such atoms as Cu, Fe, Mo, Sn, Ag, and Hg replacing Zn in zinc-blende or compounds closely related to it. The elements As and Sb can replace S for the reason given below. In crystals exhibiting isomorphous substitution there is random arrangement of the various metal atoms among the available positions, but in the structures we shall now consider the various kinds of atoms are arranged in a regular manner, the complications arising from substitution being avoided by studying material with a composition approximating to the ideal.

If alternate atoms in the diamond structure are replaced by Zn and S atoms we obtain the structure of zinc-blende, ZnS, in which every Zn atom is surrounded tetrahedrally by four S atoms and every S atom in the same way by four Zn atoms. If now the Zn atoms are replaced by alternate Cu and Fe atoms the structure is that of chalcopyrite, or copper pyrites, $CuFeS_2$. As a result of this substitution the atoms at the corners of the original ZnS unit cell are not all of the same kind so that the repeat unit is doubled in one direction. The unit cell in $CuFeS_2$ is therefore twice as large as that of ZnS. We may proceed a stage farther by replacing one-half of the Fe atoms in $CuFeS_2$ by Sn, and so arrive at the structure of stannite, Cu_2FeSnS_4. The structures of ZnS, $CuFeS_2$, and Cu_2FeSnS_4 are shown in Fig. 116. The nearest neighbours of a S atom in the three structures are:



(ZnS) ($CuFeS_2$) (Cu_2FeSnS_4)

It is worth noting that none of the simple sulphides FeS, CuS, or SnS have the 4-coordinated zinc-blende structure. There are other complex sulphides closely related structurally to zinc-blende, e.g. tetrahedrite, Cu_3SbS_3, and tennantite, Cu_3AsS_3. In these one-quarter of the S positions are unoccupied, since Sb and As form only three strong bonds, but it is not certainly known whether the vacant positions are regularly or randomly distributed. We might expect to find other complex sulphides related to wurtzite, and this is the case with Cu_3AsS_4, the structure of which is derived from that of wurtzite by replacing three-quarters of the Zn atoms by Cu and the remainder by As, the environment of a S atom being therefore three Cu and one As arranged tetrahedrally.

The structural relation of wolfsbergite, $CuSbS_2$, to wurtzite is less simple. This compound has a layer structure in which each Sb atom

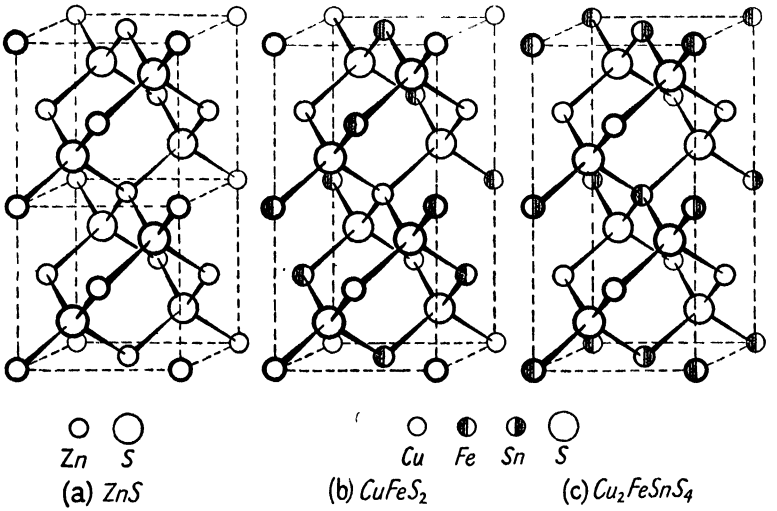


FIG. 116. The crystal structures of (*a*) ZnS, showing two unit cells, (*b*) $CuFeS_2$, and (*c*) Cu_2FeSnS_4.

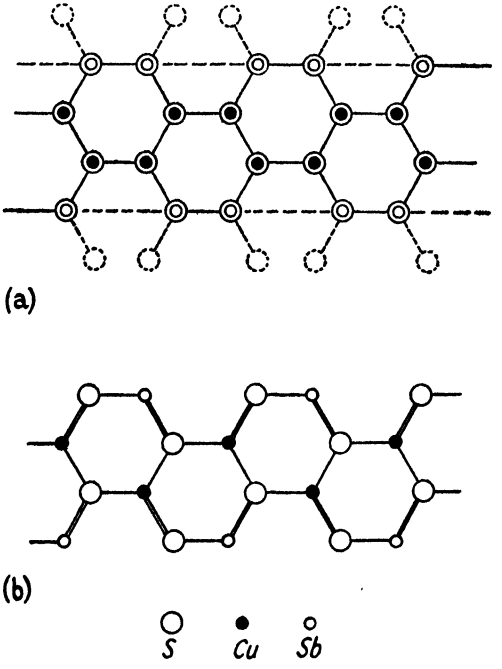


FIG. 117. (*a*) Plan of a portion of the wurtzite structure. The metal atoms, which are all Zn atoms in wurtzite, are shown as small circles of two types to facilitate comparison with Figure 118. (*b*) The same, with certain atoms removed, to show the relation to the layers in $CuSbS_2$.

forms the usual three pyramidal bonds and Cu its four tetrahedral bonds to S atoms. In Fig. 117 (*a*) is shown a plan of part of the wurtzite structure, in which plan Zn and S are superposed since they lie (at different

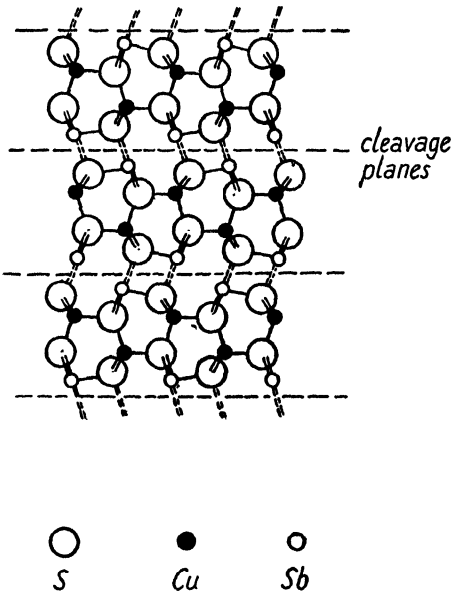


FIG. 118. Elevation of the structure of $CuSbS_2$, viewed parallel to the plane of the layers. The neighbours of an Sb atom in a layer are one S at 2·44 A. and two S at 2·57 A. The broken lines between the layers indicate much weaker Sb—S bonds (Sb—S = 3·11 A.) which account for the very good cleavage parallel to the layers.

heights) on the same lines perpendicular to the plane of the paper. If we take a vertical section through this structure between the dotted lines we see that a metal atom lying on these dotted lines loses one of its S neighbours, shown as a dotted circle, whereas a metal atom lying between the dotted lines retains all its four S neighbours. (It must be remembered that each metal atom is joined to one S atom lying vertically above or below it, so that the number of M—S bonds is one more than the number seen in the plan.) These latter atoms are Cu and the former Sb in the layers of $CuSbS_2$ which are viewed end-on in Fig. 118. Comparison of Figs. 117 and 118 shows the similarity in structure of a $CuSbS_2$ layer and the section of the wurtzite structure between the dotted lines (parallel to the crystallographic $11\bar{2}0$ plane).

CHAPTER XII

NITROGEN AND PHOSPHORUS

As in the case of the elements of Group VI, we shall confine our attention largely to the so-called typical elements, those of the first two short periods. The following notes, by way of introduction to Group V, will give some sort of perspective view of the group as a whole.

Nitrogen stands rather apart from the other elements in Group V. It is the most electronegative element in the group, and from our point of view two of its most important characteristics are the following. Only the four orbitals of the *L* shell are available for bond formation so that nitrogen forms a maximum of four (tetrahedral) bonds, and this maximum is reached only in the NH_4^+ and substituted ammonium ions. In halides and oxy-compounds only three bonds are formed. Also, like the neighbouring members of the first short period, carbon and oxygen, nitrogen has a strong tendency to form multiple bonds. For this reason nitrogen forms a considerable number of compounds which are not paralleled by any other member of this group, and accordingly we shall deal separately with the stereochemistry of nitrogen. Thus, although nitrogen and phosphorus are often grouped together, the only compounds of these elements which are structurally similar are the 3-covalent molecules and the phosphonium and ammonium ions. There are no nitrogen analogues of the pentacovalent phosphorus halides, and there is little resemblance between the oxygen compounds of the two elements, with which we shall deal in more detail below. Monatomic ions of nitrogen and phosphorus are unknown except in the solid state. They occur only in the salt-like nitrides and phosphides of the most electropositive elements. The triatomic ion N_3^-, which has no analogues, is discussed later.

Of the B sub-group elements, arsenic, antimony, and bismuth, the first two show a considerable resemblance to phosphorus. The increasingly metallic (electropositive) character of these elements has become predominant by the time we reach bismuth, which is in many respects a typical metal. Indications of this change are, for example, the decrease in stability and basic properties of the hydrides—from NH_3, which forms many stable salts, to BiH_3, which is no longer basic and has a half-life of only 20 minutes at ordinary temperatures. Again, the hydrolysis of the trichlorides illustrates the progressive change in properties from phosphorus to bismuth. Whereas PCl_3 is hydrolysed to $P(OH)_3$, $AsCl_3$, $SbCl_3$, and $BiCl_3$ dissolve in a small amount of water to form clear solutions, but addition of more water leads to the formation of As_2O_3, SbOCl—which hydrolyses further to Sb_2O_3—and BiOCl. Many properties of bismuth emphasize its metallic character and the closer relation of Sb to As than to Bi. For example, unlike As and Sb, Bi forms no pentahalides,

though not for the same reason as nitrogen, and it forms double nitrates of the type $M_3^{II}[M^{III}(NO_3)_6]_2.24H_2O$, where the divalent metal may be Mg, Zn, Co, or Ni and the trivalent metal Bi or one of a number of rare-earths. Also, each of the elements P, As, and Sb exists in two allotropic forms, a transparent white or yellow form and an opaque, metallic form. Only the latter is known in the case of bismuth. On the other hand, arsenic is best grouped with phosphorus and vanadium when discussing the oxygen chemistry of these elements, since these three are all tetrahedrally coordinated by oxygen, whereas Sb and Bi are octahedrally coordinated.

The A sub-group elements, V, Nb, Ta, and Pa, show very little resemblance to the other elements of Group V, apart from the formal similarity of compounds in which the group valency is exhibited. These elements are typical metals with close-packed structures and high melting-points. The chemistry of protoactinium has been less thoroughly studied than that of V, Nb, and Ta, owing to its rarity. A characteristic of the latter elements is their variable valency, which is most marked in vanadium. Apart from valencies of three and five, exhibited by all elements of Group V, vanadium—being a transition metal—also forms compounds in which it is di- and tetra-valent. The vanadocyanide $K_4V(CN)_6$ is the analogue of the similar iron and chromium compounds, and $VSO_4.7H_2O$ is isomorphous with $FeSO_4.7H_2O$. There are no similar divalent salts of Nb or Ta. The compounds of trivalent vanadium, $[V(NH_3)_6]Cl_3$, $K_3V(CN)_6$, and $V_2(SO_4)_3$ (which forms alums) are also reminiscent of chromium, iron, and cobalt. Finally vanadium, but not Nb or Ta, forms an oxy-radical in such salts as vanadyl sulphate, $(VO)SO_4$, with which may be compared the CrO_2^{2-}, MoO_2^{2-}, WO_2^{2-}, and UO_2^{2-} ions of the elements of Group VI. We shall have something to say of the oxygen chemistry of vanadium in a later section.

THE STRUCTURES OF THE ELEMENTS OF GROUP V

Nitrogen differs from all the other elements in this group in existing at ordinary temperatures as a colourless gas, consisting of diatomic molecules. The strength of the triple bond in the N≡N molecule is remarkably great, the bond energy being 170 k.cals./mole compared with only 23·6 for N—N; contrast the energies of carbon bonds: C—C, 58·6, C=C, 100, and C≡C, 123 k.cals./mole. The simplest alternative way of completing the octet for an atom with five valency electrons is to form three bonds to other atoms. Phosphorus, arsenic, and antimony are all dimorphous. The yellow non-metallic form is in all cases metastable and is prepared by condensing the vapour—at very low temperatures in the cases of arsenic and antimony. The yellow form reverts to the 'metallic' form on heating or on exposure to light, and owing to their instability the structures of these forms of As and Sb have not been studied. The molecular weight in various solvents shows that yellow phosphorus consists of P_4 molecules, the configuration of which has been determined by an electron

diffraction study of the vapour. The same tetrahedral molecules presumably exist in crystalline yellow phosphorus, but a complete study of the crystals has not yet been made. The structures of black phosphorus and of the metallic forms of As, Sb, and Bi are all of the same general type, being layer structures in which each atom forms three strong bonds

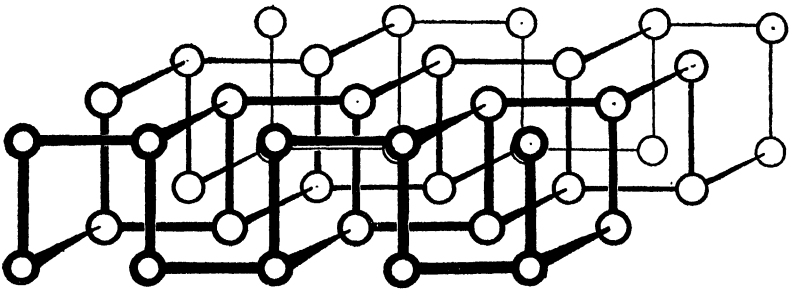


FIG. 119. The crystal structure of black phosphorus—portion of one layer (idealized).

to its three nearest neighbours. A layer of the structure of black phosphorus is shown in idealized form in Fig. 119; in the actual crystal the bond angles are approximately 100° and not 90° as shown.

Arsenic, antimony, and bismuth are isomorphous, with a different kind of layer structure in which each atom has three equidistant nearest neighbours, the next set of neighbours being three more at a greater distance. The distinction between these two sets of neighbours grows less as we go from As to Bi, as is seen from the values of the interatomic distances:

	3 *at*	3 *at*
As . .	2·51	3·15 A.
Sb . .	2·87	3·37
Bi . .	3·10	3·47

The A sub-group metals crystallize with typical metallic structures; see Chapter XVII.

THE STEREOCHEMISTRY OF NITROGEN

The N atom contains five electrons in the outer (*L*) shell. The octet can obviously be completed in two simple ways: by the formation of the N^{3-} ion or by the formation of three electron-pair bonds. The ammonia molecule, NH_3, is the simplest example of the latter, and the same electronic configuration is reached in amines, containing the $—NH_2$ group, in imides (=NH or $>$NH), and in the numerous organic heterocyclic compounds in which there is resonance between the states —N= and =N—. Three single bonds from a N atom are directed towards the apices of a trigonal pyramid, as has been demonstrated by electron diffraction for $N(CH_3)_3$. In this molecule the angle between the N—C bonds is $108\pm4°$. Spectroscopic studies of NH_3 also give a value of 108° for the interbond angle. A pyramidal configuration is to be expected whether we

regard the orbitals used as $3p$ orbitals or three of four sp^3 orbitals, the unshared pair occupying one of the tetrahedral positions in the latter

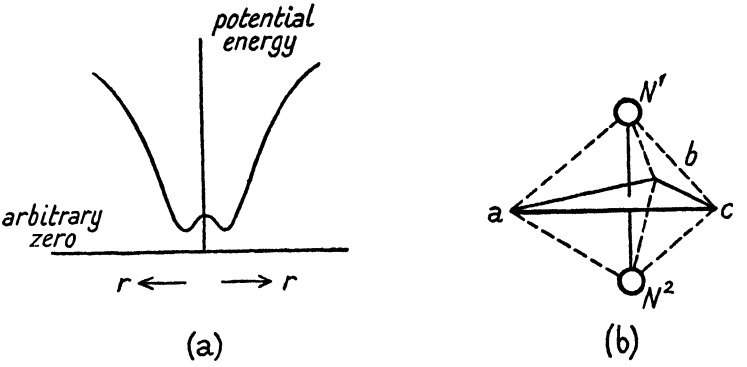


FIG. 120. (*a*) Probable form of the potential energy curve for NH_3. (*b*) The two possible configurations for the molecule NH_3 or Nabc.

case. We should expect a substituted ammonia of the type Nabc containing three different atoms or groups to exhibit optical activity, since the molecule is enantiomorphous. However, no such molecule has been resolved in spite of many attempts, and this at one time cast doubt on the non-planar arrangement of three bonds from a neutral N atom. In the case of NH_3 itself, which has a dipole moment of 1·5 D, it has been suggested that the potential energy curve of the molecule is of the form shown in Fig. 120 (*a*), where the energy is plotted against the distance r of the N atom from the plane of the H atoms. There are two minima corresponding to the two possible positions of the N atom (on each side of the plane of the H atoms), but they are separated by an energy barrier of only about 6 k.cals./mole. For the resolution of *d*- and *l*-modifications of a substance to be detectable at room temperature it has been calculated that the energy of activation for racemization (change of $d \rightleftharpoons l$) must be not less than 20 k.cals./mole. The failure to resolve substituted ammonias may therefore be due to the fact that the molecule can easily turn inside out by movement of the N atom from position N^1 to N^2 (Fig. 120 (*b*)). Apart from electron diffraction studies of molecules like $N(CH_3)_3$, $N(CH_3)_2Cl$, and $N(CH_3)Cl_2$, the X-ray study of crystals of hexamethylene tetramine, $N_4(CH_2)_6$, firmly established the pyramidal arrangement of the bonds from 3-covalent N. The latter molecule has the structure shown in Fig. 121.

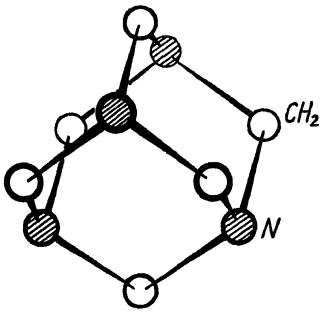
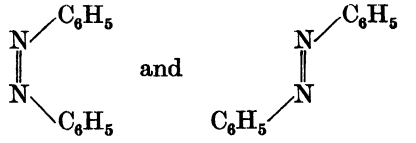


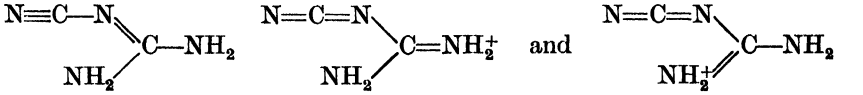
FIG. 121. The structure of the molecule of hexamethylene tetramine, $N_4(CH_2)_6$. N atoms are shaded and H atoms omitted. This molecule, based on a tetrahedral group of N atoms, should be compared with those of $Be_4O(CH_3COO)_6$, P_4O_6, and P_4O_{10}, Figures 81 and 123.

Proof of the non-linear arrangement of one double and one single bond formed by a N atom comes directly from (*a*) X-ray and electron diffraction studies, and indirectly from (*b*) the existence of stereoisomers of compounds containing the systems $\rangle C{=}N\langle$ or —N=N—, and (*c*) the optical activity of an oxime.

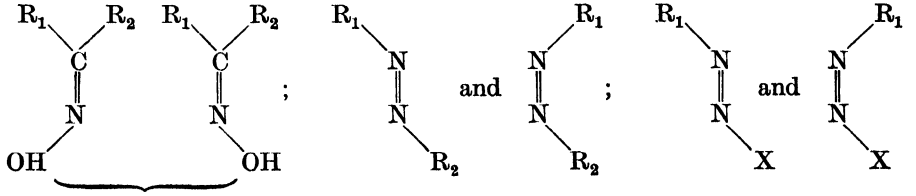
(*a*) As examples of molecules the structures of which have been determined we may quote the cis- and trans- forms of azobenzene



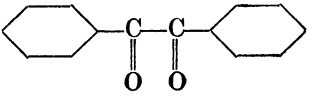
and dicyandiamide, which probably resonates between structures of the following kinds:



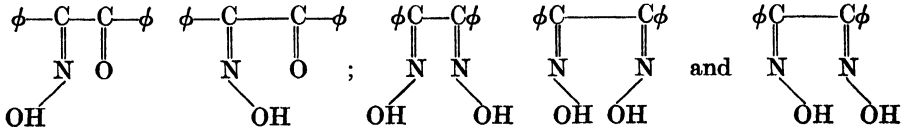
(*b*) Among the compounds containing the atomic groupings $\rangle C{=}N\langle$ or —N=N— we may mention the oximes, many of which are known to exist in two stereoisomeric forms (I),



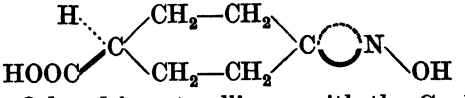
azo-compounds (II), and diazo-compounds (III). The oximes of benzil



are of particular interest in that the two forms of the monoxime and the three forms of the dioxime have all been isolated (ϕ represents the C_6H_5 group).

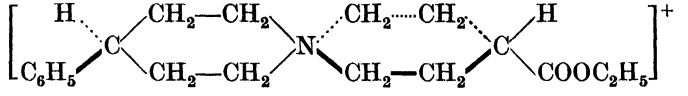


(*c*) The resolution into its optical antimers of the oxime



shows that the N—O bond is not collinear with the C=N bond.

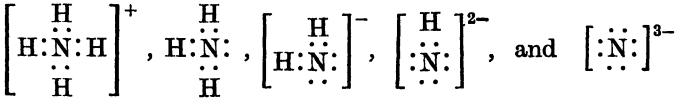
So far we have considered the N atom using only three of the four available L orbitals. When the fourth is used four tetrahedral bonds may be formed, or of course we may have $\rangle N=$, $=N=$, or $-N\equiv$. In all cases the stereochemistry is similar to that of carbon. The N atom in NH_3 and substituted ammonias possesses a pair of unshared electrons which may be used to form the fourth bond. These molecules are able therefore to attach themselves to a great variety of metal atoms, forming the coordination compounds of Werner. These compounds are described in Chapter XVI. The two electrons forming the fourth bond (the co-ordinate link of Sidgwick) are provided by the nitrogen atom. Alternatively the N atom may form four covalent bonds, at the same time giving up one electron to keep the number of valency electrons down to eight. In this way arise the ammonium ion NH_4^+ and the numerous substituted ammonium ions containing organic radicals in place of hydrogen. The tetrahedral configuration of the NH_4^+ ion itself has been proved in very few compounds both because of the difficulty of locating H atoms (owing to their small scattering power for X-rays) and because the ion is rotating in many crystals at ordinary temperatures. In NH_4F, however, the rotation of the ion is prevented by the formation of N—H—F bonds, and the tetrahedral arrangement of the four nearest fluorine neighbours indicates the positions of the hydrogen atoms. The tetrahedral disposition of the four bonds from N is also evident from the crystal structure of aluminium nitride, AlN, which crystallizes with the wurtzite structure (p. 83). The optical activity of substituted ammonium ions of the type $[Nabcd]^+$ and of the ion



provided the earliest proofs of the tetrahedral arrangement of four bonds from a nitrogen atom.

Amides

We have mentioned that the N atom can complete its octet by forming the NH_4^+ ion, the NH_3 molecule, and the N^{3-} ion. The other two intermediate ions, NH_2^- and NH^{2-}, are also formed, so that we have the complete series:



The latter three ions are known to exist in the salt-like amides, imides, and nitrides of the most electropositive metals. The alkali, alkaline-earth, and zinc amides are colourless crystalline compounds formed directly by the action of ammonia on the metal, using either ammonia gas and the molten metal or a solution of the metal in liquid ammonia. The NH_2^- ion

is isoelectronic with the hydroxyl and fluorine ions and we have the corresponding reactions:

$$\begin{array}{rcl} & & HF \rightarrow NaF \\ Na & + & H_2O \rightarrow NaOH \\ & & H_3N \rightarrow NaNH_2 \end{array}$$

A solution of $NaNH_2$ in liquid ammonia is a good conductor of electricity, indicating that the salt is ionized in this solvent. This salt is used in organic technology as a dehydrating agent, for the NH_2^- ion has a great affinity for H^+ ions:

$$NH_2^- + H^+ \rightarrow NH_3$$

or alternatively $(Na)NH_2 + H_2O \rightarrow (Na)OH + NH_3$.

The crystal structures of the metallic amides have not yet been determined. The alkaline-earth imides, however, have been shown to crystallize with the rock-salt structure like the corresponding oxides, the rotating NH^{2-} ion possessing spherical symmetry.

The Halides of Nitrogen

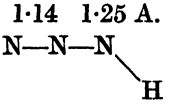
The halides of nitrogen present no points of particular interest from the stereochemical standpoint. Only trihalides are known, and of these the tribromide does not appear to have been prepared, though there is some evidence for the existence of an ammine ($NBr_3.6NH_3$) stable at temperatures below $-70°$ C. The so-called tri-iodide made from iodine and ammonia is $NI_3.NH_3$ and not the simple halide. The latter is apparently formed by the action of dry NH_3 on $KIBr_2$. The trifluoride has been prepared by electrolysis of fused NH_4HF_2 and is quite stable when pure.

Azides

Reference has already been made to the S_3^{2-} and the I_3^- ions which may be formulated with single bonds, giving the central iodine atom in the latter ion a group of ten valency electrons. The azide ion (and radical) is of quite a different type, involving multiple bonds, and apparently resonating between a number of structures. No other element forms an ion of this kind. Hydrazoic acid N_3H can be prepared by the action of hydrazine (N_2H_4) on NCl_3 or HNO_2, but it is best obtained from its sodium salt, which results from a very interesting reaction. When nitrous oxide is passed into molten sodamide the following reaction takes place:

$$NH_2^- + N_2O \rightarrow N_3^- + H_2O.$$

Hydrazoic acid has been studied by the electron diffraction method. The results are consistent with a linear arrangement of N atoms; compare the structure of the isoelectronic N_2O molecule (described later).



The azides of the alkali and alkaline-earth metals are colourless crystalline

salts which can almost be melted without decomposition taking place, but those of the univalent heavy metals (e.g. Ag) are highly explosive, and others (e.g. Pb) explode on detonation. X-ray studies show that the alkali azides contain the N_3^- ion which is linear and symmetrical, with the structure:

$$\underset{[N—N—N]^-}{1{\cdot}15 \quad 1{\cdot}15\,A.}$$

An interesting example of isomorphism is that of NH_4N_3 and $NH_4(F—H—F)$.

The explosive heavy metal azides are probably essentially covalent compounds. Other covalent azides include the halogen azides, N_3Cl, N_3Br,

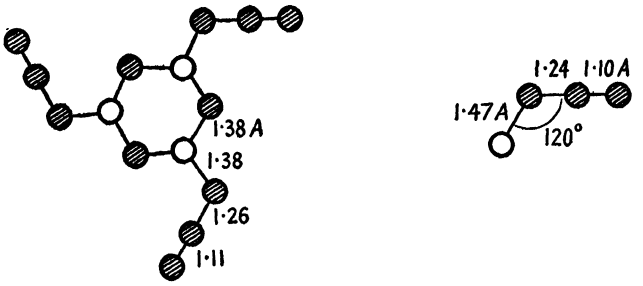
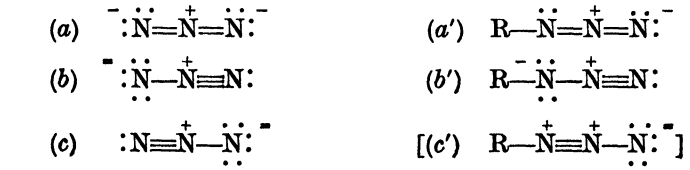


FIG. 122. The molecular structures of (*a*) cyanuric triazide and (*b*) methyl azide. N atoms are shaded and H atoms omitted.

and N_3I (made by the action of iodine on AgN_3), and the organic azides. Of the latter, two have been studied; cyanuric triazide in the crystalline state by X-rays and methyl azide in the vapour state by electron diffraction. The structures of these molecules are shown above. In each the azide group is unsymmetrical, in contrast to the azide ion. The difference in structure between the N_3^- ion and the N_3 group in the covalent azides, and also the much greater stability of the ionic azides, has been explained in the following way. The ion resonates between the three configurations (*a*), (*b*), and (*c*), each of which is equally important, so that the two bonds are of the same length and the ion is stabilized by a considerable resonance energy. Of the three corresponding structures for a covalent azide, however, the last is unstable, for it involves positive charges on adjacent



atoms (the 'Adjacent Charge' rule). There is, therefore, resonance between (*a'*) and (*b'*) only, resulting in an unsymmetrical N_3 group and a smaller resonance energy and stability. For comparison with the interatomic

distances in azides we give the following bond lengths calculated from the covalent radii of Table 6:

N—N	1·48 A.	C—N	1·46 A.
N=N	1·28	C=N	1·27
N≡N	1·15	C≡N	1·14

Cyanogen and Hydrazine

In the cyanogen molecule, which is linear, the normal state N≡C—C≡N is most important, but there is resonance to some extent with the structures $\{\bar{N}=C=C=\overset{+}{N},\ \overset{+}{N}=C=C=\bar{N}\}$, just as in the case of diacetylene, HC≡C—C≡CH.

Hydrazine, N_2H_4, has been examined by the electron diffraction method and one-half the N—N bond length taken as the covalent radius of nitrogen (see Table 6). For the structure of hydrazinium difluoride see p. 259.

THE OXYGEN COMPOUNDS OF NITROGEN

Oxides

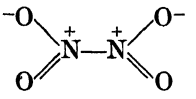
Five oxides of nitrogen have been known for a long time: N_2O, NO, N_2O_3, N_2O_4, and N_2O_5. A sixth, NO_3, is said to be formed in discharge tubes containing N_2O_4 and O_2 at low pressures. It has at most a short life, like others of this kind which have been described (PO_3, SO, SO_4) and radicals like OH, NH, and CH_3, for the separate existence of which there is spectroscopic evidence. We shall confine our attention to the more stable compounds of ordinary chemical experience. In connexion with the oxides of nitrogen the following points of interest may be noted. No compounds analogous to N_2O and NO are formed by the other elements of Group V. These form tri-, tetr-, and pent-oxides, but, although the structures of these nitrogen oxides are not known, it is unlikely that these are structurally similar to the molecular nitrogen compounds.

The trioxide and the pentoxide are the anhydrides of nitrous and nitric acids respectively, but N_2O is not related in this way to hyponitrous acid, $H_2N_2O_2$. Although N_2O is quite soluble in water it does not form the latter acid. Nitrous oxide cannot be directly oxidized to the other oxides although it is easily obtained by the reduction of HNO_3, HNO_2, or moist NO. The oxides NO, N_2O_3, and N_2O_4, on the other hand, are easily interconvertible and are all obtained by reducing nitric acid with As_2O_3, the product depending on the concentration of the acid. The trioxide, N_2O_3, probably exists only in the liquid and solid phases, which are blue in colour, for the vapour is almost completely dissociated into NO and NO_2, as may be seen from its brown colour. The tetroxide, N_2O_4, forms colourless crystals (at −10° C.), but its vapour at ordinary temperatures consists of a mixture of N_2O_4 and NO_2, and at about 150° C. the gas is entirely dissociated into NO_2. On further heating decomposition into NO and oxygen takes place, and this is complete at about 600° C. Since the

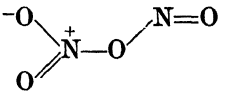
pentoxide is easily decomposed to N_2O_4 we have the following relationship between these oxides:

$$N_2O_5 \rightarrow N_2O_4 \rightleftharpoons \underbrace{NO_2 \rightleftharpoons NO}_{N_2O_3} + O$$

The configuration of the NO_2 molecule is not known, and the structure of N_2O_4 is not known with certainty. The available X-ray data and entropy measurements suggest the symmetrical form (*a*), but since this places formal charges of similar sign on adjacent atoms Pauling has suggested that the unsymmetrical structure (*b*) should be more stable.



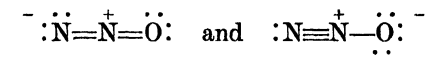
(*a*)



(*b*)

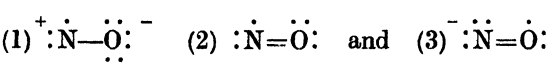
In discussing the structure of the $N_2H_6^{2+}$ ion (p. 260), however, we suggested resonance involving the structure with adjacent N^+ atoms. In this case the comparatively large contribution from the structure with adjacent + charges has been attributed to the fact that this is the only completely covalent structure for the molecule. The other (ionic) structures also lose in stability because they contain fewer covalent bonds. A compromise is therefore reached between the form contravening the 'adjacent charge rule' and the ionic structures. In the case of N_2O_4 the marked instability in the gaseous phase might well be interpreted as evidence for structure (*a*).

The molecule of nitrous oxide, N_2O, is linear. On account of the similar scattering powers of N and O it is impossible to distinguish by electron diffraction between the alternatives NNO and NON, but the former is supported by spectroscopic data, and the assumption that the molecule resonates between the structures



accounts satisfactorily for the length of the molecule (2·31 A.) and for the electric dipole moment, which is approximately zero. The probable bond lengths are N—N = 1·12 and N—O = 1·19 A.

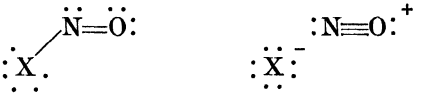
Nitric oxide, NO, is one of the few compounds the molecules of which contain an odd number of electrons, and its structure should explain why it does not exist in a stable dimeric form. The interatomic distance N—O is found to be 1·14 A., intermediate between the values (Pauling-Huggins) for N=O (1·18 A.) and N≡O (1·06 A.). The molecule is represented by :N≝O: with a double and a 3-electron bond, the latter being half as strong as an electron-pair bond. The very small dipole moment is explained as follows. The molecule resonates between the structures:



The first structure is included because it is known (from the observed dipole moments of aldehydes and ketones, nearly 3 e.s.u., containing C=O) that a double bond between atoms of different electronegativities has at least twice as much ionic character as a single bond between the same atoms. Alternatively, we may say that the molecule resonates between (2) and (3) if we remember that the structure (2) has some ionic character and therefore involves structure (1). The failure of NO to polymerize is to be attributed to the increased stability due to resonance.

Nitrosyl Compounds

The loss of an electron by NO should lead to a stable ion $[:N{\equiv}O:]^+$ since this contains a triple bond compared with a $2\frac{1}{2}$-bond (double+3-electron bonds) in NO. It has been shown that certain nitrosyl compounds, $NO.ClO_4$, $NO.BF_4$, and $(NO)_2SnCl_6$ (usually written $SnCl_4.2NOCl$), are structurally similar to the corresponding ammonium salts, NH_4ClO_4, etc., and presumably contain such NO^+ ions. The precise electronic structures of the molecular nitrosyl halides are not certain. Electron diffraction studies show that NOCl and NOBr form non-linear molecules (interbond angle about 125°) in which the N—O distance is about 1·12 A., the same as in NO. This distance and the fact that the N—X distances are considerably greater than the sums of the appropriate covalent radii suggest that these molecules are not adequately represented by the simple structure (1) but that there may be resonance with the ionic structure (2):

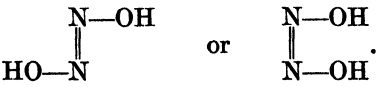


(1) (2)

Acids and Oxy-ions

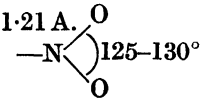
The existence of three oxy-acids of nitrogen is well established, nitrous acid, HNO_2, nitric, HNO_3, and hyponitrous, $H_2N_2O_2$. The preparation of salts of other acids, hydronitrous, H_2NO_2, and pernitric, HNO_5, has been described, but nothing is known of their structures and the corresponding acids have not been isolated. Only dilute solutions of nitrous acid have been prepared and these rapidly decompose, evolving oxides of nitrogen. Pure nitric acid can be made by freezing dilute solutions (since the freezing-point of HNO_3 is about −40° C.), but it is not stable. Dissociation into N_2O_5 and H_2O takes place, the former decomposes, and the acid becomes more dilute. If strong solutions of the acid are kept in the dark, however, decomposition of the N_2O_5 is retarded and the concentration of nitric acid remains constant. In contrast to nitrous and nitric acids, hyponitrous acid crystallizes from ether as colourless crystals which easily decompose, explosively if heated. The structure of this acid has not been determined, but it is known that the molecular weights of the free acid and also of its esters correspond to the double formula,

$H_2N_2O_2$, that it is decomposed by sulphuric acid to N_2O, and that it can be reduced to hydrazine, $H_2N—NH_2$. It is therefore represented

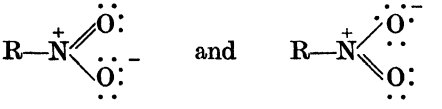


It has been suggested that nitramide (usually written $NH_2.NO_2$) may be the cis- and hyponitrous acid the trans- isomer. Nitramide decomposes in alkaline solution to N_2O and like $H_2N_2O_2$ may also be reduced to hydrazine.

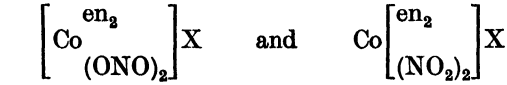
Stable metallic nitrites are comparatively few in number, being limited to those of the alkalis, alkaline-earths, Zn and Cd, Ag^I and Hg^I. The alkali nitrites decompose at red heat, the others at progressively lower temperatures. The insoluble, more deeply coloured nitrites of heavy metals such as Hg are probably essentially covalent compounds in contrast to the simple ionic nitrites of the alkali metals. Potassium nitrite has been shown to contain non-linear $O\diagup^{N}\diagdown O$ ions with interbond angle of about 130°, but the N—O distance of 1·13 A. appears remarkably short. By the interaction of metallic nitrites with alkyl halides two series of compounds are obtained, the nitrites—in which the NO_2 group is attached to carbon through oxygen—and the nitro-compounds in which nitrogen is directly linked to carbon. The aromatic nitro-compounds (e.g. $C_6H_5NO_2$) are prepared by the action of nitric acid, under suitable conditions, on the hydrocarbon itself. The NO_2 group in organic nitro-compounds is known to be symmetrical from an electron diffraction study of nitromethane, $CH_3.NO_2$, and to have the configuration shown. The observed



dipole moments, about $3{\cdot}0 \times 10^{-18}$ e.s.u., of the aliphatic nitro-compounds are consistent with this configuration, which results from resonance between



Isomerism of the same type as in the organic nitrites and nitro-compounds is found in cobaltammines, e.g.

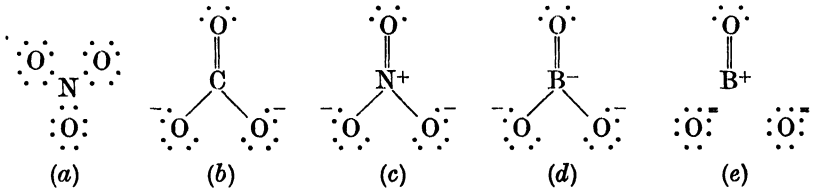


Nitrates, $A_m(NO_3)_n$, are quite different structurally from other salts of the type $A_m(MO_3)_n$ formed by other Group V elements. The planar NO_3^- ion (containing pentavalent nitrogen) in these salts is geometrically similar to the planar BO_3^{3-} and CO_3^{2-} ions and is not related to the pyramidal

PO_3^{3-}, SO_3^{2-}, or ClO_3^- ions of the elements of the second short period or to the complex $(MO_3)_n$ ions in meta-phosphates and vanadates (see below). Although it might appear that these planar ions could be represented by simple single-bond structures of the type (*a*), it is clear from the interatomic distances that their structures are not so simple. The observed distances are given below:

	B—O	C—O	N—O
Observed in ions MO_3 . .	1·35	1·31	1·21 A.

If we calculate the distances B—O, C—O, and N—O (from the covalent radii of Table 6) assuming resonance of the graphite type, one double-bond resonating between the three positions, we obtain a value of about 1·31 A. for each of these distances. This agrees well with that observed in the CO_3^{2-} ion. The B—O distance is not worth discussing further because of the uncertainty in the radius of B (see p. 84), but there is a considerable discrepancy in the case of the NO_3^- ion. Pauling calculated the N—O distance in this ion to be 1·23 A. using the radii of Table 7 and making an allowance (of −0·04 A.) on account of the positive formal charge on the N atom. Clearly, any detailed discussion of such bond lengths is not justified in the present state of our knowledge. For the present we shall assume that the structures of the carbonate and nitrate ions are reasonably accounted for in terms of resonance between the three equivalent structures of type (*b*) or (*c*). For the BO_3^{3-} ion, however, this



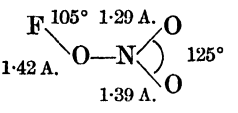
(*a*) (*b*) (*c*) (*d*) (*e*)

type of resonance (*d*) would involve a negative formal charge on the boron atom (which is electropositive with respect to oxygen), and it has been suggested that resonance with ionic structures of the type (*e*) is more likely.

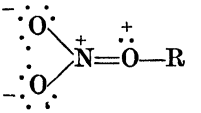
Condensation of CO_3^{2-} or NO_3^- to form complex anions does not occur, whereas we do find $B_3O_9^{3-}$ and infinite $(BO_2)_n^{n-}$ ions. The isoelectronic analogues of $B_3O_9^{3-}$ would be the neutral C_3O_9 and the $N_3O_9^{3+}$ cation, but it is possible to formulate a non-planar ion $N_3O_9^{3-}$ with a pair of unshared electrons on each N atom. In such an ion, however, resonance of the type indicated above, which stabilizes the NO_3^- ion, would not be possible. It is not yet possible to say why certain elements form these extended oxy-anions, and this subject has already been discussed in Chapter IX, where we saw that any 'explanation' in terms of an extreme electrostatic picture is unsatisfactory as the bonds are certainly not 100 per cent. ionic in character. The problem is much more complex, for although it is true that the elements with the most marked tendency to form condensed oxy-ions are those with oxygen coordination number equal to their normal valency (B, Si, Mo, W) so that the electrostatic strength of the

bond M—O is unity, other elements—notably P and V—also form such ions and to these the same argument cannot be applied. It is noteworthy that the elements forming numerous condensed oxy-anions are atoms of moderate electronegativity, around 2 on Pauling's electronegativity scale.

Covalent nitrates are in general far less stable than the ionic metallic nitrates. The structure of the explosive gas $F.NO_3$ has been studied by the electron diffraction method, the approximate dimensions being those shown below (1). It will be noticed that the distance from N to the O atom bound to F is greater than the other two N—O distances. In ionic



(1)

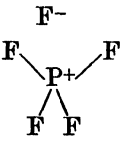


(2)

nitrates there is resonance between the three equivalent structures of type (*c*), p. 409, but in covalent nitrates there is likely to be resonance only between two forms. The third, shown above (2), would involve positive charges on the adjacent N and O atoms. As in the case of the azides, already referred to, the greater stability of the ionic as compared with the covalent nitrates may be due to the smaller resonance energy in the latter.

THE STEREOCHEMISTRY OF PHOSPHORUS AND THE SUB-GROUP ELEMENTS

Phosphorus, like nitrogen, has five valency electrons. These are in the third quantum shell, in which there are *d* orbitals in addition to the *s* and *p* orbitals. In most of its compounds phosphorus forms only four bonds, this number being exceeded only with the halogens, and the most stable compounds in which more than four bonds are formed are those with fluorine, the most electronegative of the halogens. The stability of the pentahalides decreases rapidly with increasing atomic weight of the halogen. The pentafluoride is stable up to high temperatures, PCl_5 is about half dissociated at 200° C., PBr_5 is less stable, and PI_5 is not known. Although, therefore, one 3*d* orbital may be used in the pentahalides (and two in the PF_6^- ion) it is possible that the molecule PF_5 may resonate chiefly among structures of the type shown in the accompanying diagram,



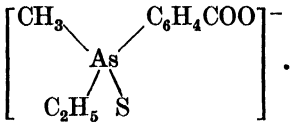
so that only four orbitals are used. The existence of PBr_5 is difficult to account for on this view because of the very small difference between the electronegativities of P and Br, but, on the other hand, the stability of

the PBr_5 molecule in the vapour state is small and in the solid state it apparently exists as $[PBr_4]^+Br^-$. Six bonds are formed only with fluorine, in the PF_6^- ion, and hexafluorophosphates only of large cations like K, NH_4, Ba, and $[Co(NH_3)_6]^{3+}$ are known in the crystalline state.

The elements of the A and B sub-groups form far more numerous complex halogen ions. In some cases the free acid may be isolated in the crystalline state, e.g. $HSbCl_6.4\frac{1}{2}(?)H_2O$, $HSbBr_6.3H_2O$, and H_3BiF_6. The salts of the type $(NH_4)_2SbBr_6$ apparently containing tetravalent antimony have already been mentioned (p. 232). The elements Nb and Ta of the A sub-group are, like Zr and Hf, notable for the high coordination numbers exhibited in their complex fluorides and oxyfluorides, e.g. K_2NbF_7, K_3NbOF_6 (isomorphous with K_3ZrF_7), and Na_3TaF_8.

The pyramidal configuration of three bonds formed by phosphorus has been demonstrated by electron diffraction studies of $P(CH_3)_3$, of all four trihalides, and $PFCl_2$. All have a pyramidal configuration and bond angles of about 100°. In the tetrahedral P_4 molecule the bonds are also pyramidal but the interbond angle is here only 60°, and the same is true in the As_4 molecule. The stereochemistry of 3-covalent As and Sb is exactly similar to that of P. In all the following molecules the bonds are arranged pyramidally with interbond angles of approximately 100°: $As(CH_3)_3$, $AsCl_3$, $AsBr_3$, AsI_3, and $SbCl_3$, $SbBr_3$, and SbI_3, all of which have been studied in the vapour state.

The tetrahedral arrangement of four bonds from P has been verified in a number of oxyhalide molecules—POF_3, POF_2Cl, $POFCl_2$, and $POCl_3$—in all of which the P—O distance has the same value (1·55 A.) as in the tetrahedral PO_4^{3-} ion. The P—Cl distance is 2·00 A. as in PCl_3, and P—F 1·51 A. as in PF_5 (see below). The stereochemistry of P, both 3- and 4-covalent, in its oxides and oxy-ions is described in the next section. In the case of As the tetrahedral bond arrangement has been proved by the resolution of the asymmetrical ion

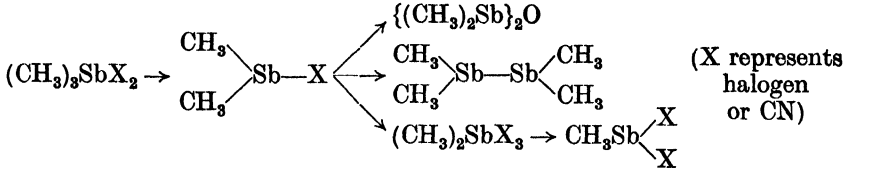


Intermediate between the neutral molecule POF_3 and the ion PO_4^{3-} are the ions $PO_2F_2^-$ and PO_3F^{2-}. Salts of both mono- and di-fluorophosphoric acid have been prepared, e.g. the K and NH_4 salts and several others, but so far their structures have not been investigated.

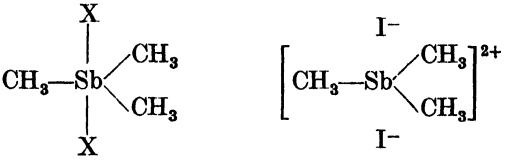
The compounds in which the Group V elements are pentacovalent are of particular interest from the stereochemical standpoint. Electron diffraction studies of three pentahalides of phosphorus, PF_5, PF_3Cl_2, and PCl_5, show that in the vapour state these compounds exist as trigonal bipyramidal molecules. A study of crystalline PCl_5 shows that these molecules do not persist in the solid state. This had been suggested by a comparison of the Raman spectrum of the compound in the different states of aggregation, and the appreciable electrical conductivity of PCl_5

in indifferent solvents (e.g. nitrobenzene) appeared to indicate that the compound could exist in an ionized form. The crystal is built up of tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$ ions which are packed in much the same way as the Cs^+ and Cl^- ions in CsCl. The crystal structures of compounds AX_5 are of unusual interest, for there are a number of possible structure types, of which the simplest are: (1) AX_5 molecules, (2) $[AX_4][AX_6]$, (3) rings or infinite chains consisting of octahedra AX_6 sharing two opposite corners, and (4) $[AX_4]X$. The second of these is realized in phosphorus pentachloride, and a preliminary study of the pentabromide suggests that in the solid state this compound exists in the form $[PBr_4]Br$.

Arsenic and antimony form a number of organometallic compounds of the following types:



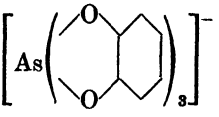
The compounds $(CH_3)_3SbX_2$ are interesting since they involve 5-covalent metal atoms. The crystal structure of these antimony compounds has been studied, and it is found that the three methyl groups are arranged in the plane of the metal atom and the two halogen atoms lie at the remaining apices of the trigonal bipyramid. It is not certain that the halogen atoms are covalently bound to the antimony atom, and it is possible that the compounds are intermediate between the molecule (1) and the ionic form (2). Hydrolysis of these compounds takes place in



(1) (2)

two stages, the first product $(CH_3)_3SbX(OH)$ being converted later into $(CH_3)_3Sb(OH)_2$. The fact that the intermediate compound $(CH_3)_3SbX(OH)$ is a strong electrolyte, whereas $(CH_3)_3Sb(OH)_2$ is a very weak base, suggests that it may be a substituted stibonium hydroxide, $[(CH_3)_3SbX]OH$, the symmetrical dihydroxide being similar in structure to the dihalides.

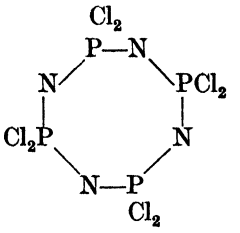
In their oxides, acids, and oxy-salts, P, As, and V exhibit a maximum oxygen coordination number of 4, but arsenic shows a covalency of 6 towards oxygen in ions like that of the catechol derivative. The resolu-



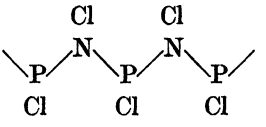
tion of this ion into its optical antimers confirms the octahedral configuration of the six arsenic bonds.

Cyclic Phosphorus-Nitrogen Compounds

There are a number of interesting compounds containing chains or rings of alternate P and N atoms. When PCl_5 and NH_4Cl are heated together compounds called phospho-chloronitrides (or phosphonitrile-chlorides) are produced, with empirical formula $(PNCl_2)_n$. According to the temperature and duration of heating various products are obtained, separable by fractional distillation, with $n = 3, 4, 5, 6$, and 7, and they have definite melting- and boiling-points. The first two crystallize as beautiful lustrous colourless crystals from organic solvents such as benzene and ligroin. The final product of the above reaction is a highly polymerized substance $(PNCl_2)_x$ with remarkable physical properties. It forms a colourless elastic mass like rubber (compare plastic sulphur), which may be depolymerized into the less complex chloronitrides if heated to a sufficiently high temperature. X-ray studies of the tri- and tetra-compounds show that they consist of cyclic molecules, and a complete study has been made of the latter. The molecule forms a puckered 8-membered ring (see (1) below) of alternate P and N atoms, with two Cl atoms attached to each P atom. The phosphorus interbond angles are approximately tetrahedral, the N—P—N angles in the ring being about 120°. The P—N distance is 1·67 A., comparison of which with the values expected for P—N (1·76 A.) and P=N (1·57 A.) suggesting resonance between single and double bonds as in aromatic carbon nuclei. An electron diffraction study of $(PNCl_2)_3$ vapour confirms the ring structure of this molecule and gives P—N = 1·65±0·03 A., P—Cl = 1·97±0·03 A., and the Cl—P—Cl bond angle as 107–110°. The properties of the rubber-like polymer indicate that

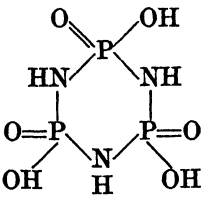


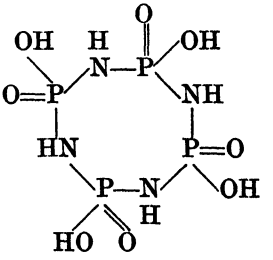
(1)



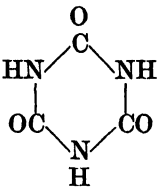
(2)

it almost certainly contains chains, probably with the structure (2). Hydrolysis of these chloronitrides yields metaphosphimic acids, $[PO(OH)NH]_n$, which also exist in various polymeric forms. Only the tri- and tetra-acids, presumably with the structures

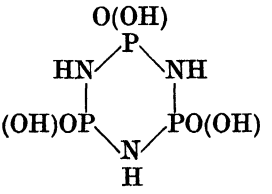




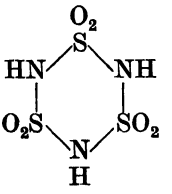
give crystalline salts. The higher members give syrupy or highly polymerized metallic derivatives. These rings may be broken open by boiling with acids, when open-chain compounds such as $PO(OH)_2.NH.PO(OH).NH.PO(OH)_2$ are formed. The carbon and sulphur analogues of these phosphimic acids are the polymerized forms of cyanic acid and sulphimide. We may write the formulae of these compounds CO(NH), PO(OH)NH, and $SO_2(NH)$ to show their relation to one another. Cyanuric acid and the gelatinous cyamelide correspond to trisulphimide and gelatinous sulphomelide; compare:



Cyanuric acid



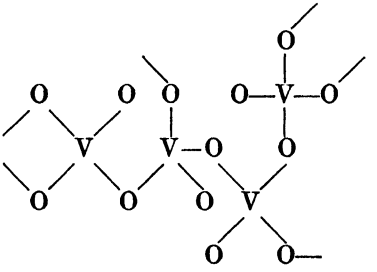
Trimetaphosphimic acid



Trisulphimide

Oxides

The oxides of nitrogen have already been discussed. We shall have little to say about the oxides of the A sub-group elements. They all form pentoxides and a number of lower oxides (e.g. VO, V_2O_3, VO_2), these being basic and giving rise to salts as in the case of other transition metals. Of the structures of the A sub-group oxides only those of V_2O_3 and V_2O_5 are known. The former crystallizes with the corundum structure (α-Al_2O_3, p. 313). In crystalline V_2O_5, VO_4 tetrahedra are joined together into an infinite 3-dimensional network by sharing three corners with other tetrahedra, as shown (purely diagrammatically) in the accompanying sketch. In this way the V:O ratio of 2:5 is attained. It is unlikely that the



other A sub-group oxides are related at all closely, as regards structure, to those of P and the B sub-group elements, of which more is known.

Phosphorus, arsenic, antimony, and bismuth all form pentoxides. Of these, only P_2O_5 can be prepared by direct oxidation of the element, for the other pentoxides decompose at high temperatures into the trioxides and oxygen. Bismuth pentoxide is a rather ill-defined compound of which little is known, and the structures of As_2O_5 and Sb_2O_5 are unknown. The structure of the P_4O_{10} molecule in phosphorus pentoxide vapour has been

studied by the electron diffraction method. The molecule consists of the P_4O_6 nucleus with an additional oxygen atom attached to each P, completing the tetrahedron of oxygen atoms around it; see Fig. 123. Phosphorus pentoxide is remarkable for the number of forms in which it can exist. In addition to forming a glass it has three polymorphic crystalline modifications. The structure of the tetragonal form is not known. The low-temperature rhombohedral form is built up of discrete P_4O_{10} molecules of the same type as those which have been studied in the vapour.

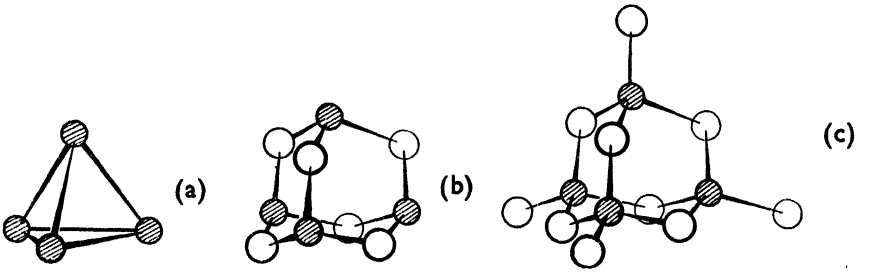


FIG. 123. The structures of the molecules (*a*) P_4, (*b*) P_4O_6, and (*c*) P_4O_{10} in the vapour state (diagrammatic). Shaded circles represent P atoms.

The high-temperature orthorhombic form consists of an infinite array of PO_4 tetrahedra, each of which shares three of its oxygen atoms with three other tetrahedra (compare V_2O_5 above). The structure consists of rings of ten PO_4 tetrahedra linked up to form a 3-dimensional network in which the oxygen atoms are approximately close-packed. Dioxides of all these elements have been described, all of which behave chemically like mixtures of the trioxides and pentoxides. The oxide P_2O_4 is described as a well-crystallized compound with a vapour density corresponding to the formula P_8O_{16}, which is hydrolysed by water to a mixture of phosphorous and phosphoric acids. The structures of these dioxides are not known (see, however, Sb_2O_4 below).

Phosphorus and arsenic trioxides have been studied in the vapour state by the electron diffraction method. They form dimeric molecules P_4O_6 and As_4O_6 as shown in Fig. 123. The P atoms in P_4O_6 lie at the apices of a tetrahedron as in the P_4 molecule, from which the idealized form of the P_4O_6 molecule may be derived by placing an O atom on each edge of the tetrahedron. It appears that the bonds in these molecules have a considerable amount of double-bond character. For single bonds we should expect the angles between the O bonds to be 109° 28′ and for one double and one single bond 125° 16′. The observed value is about 126°. The P—O and As—O distances, 1·64 and 1·80 A. respectively, also support this view. The structure of solid P_4O_6 is unfortunately not known, but those of As_2O_3, Sb_2O_3, and Bi_2O_3 (which exist in two forms) have all been determined, and they form an interesting series. In As_4O_6 and the cubic form of Sb_4O_6 there exist molecules with tetrahedral configuration very similar to those in the vapour of P_4O_6 and As_4O_6 but with interesting

differences in O bond angles and interatomic distances. In the As_4O_6 molecule in the crystal the O bond angles have the tetrahedral value ($\sim 109°$) and the As—O distance is 2·00 A., indicating that the bonds are single covalent bonds. Pauling suggests that each O atom may be forming

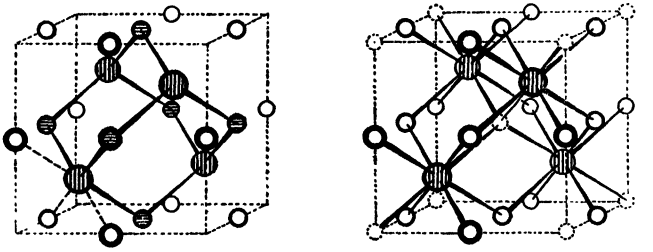
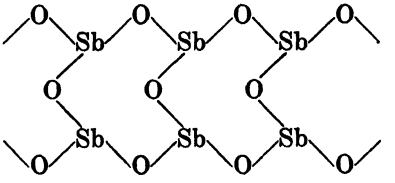


FIG. 124. The structures of (*a*) Bi_2O_3 and (*b*) CaF_2. Metal atoms are shaded vertically.

additional weak bonds with the two nearest As atoms of adjacent molecules, so preventing the use of its pairs of unshared electrons in the intramolecular bonds. The same argument would apply to the cubic form of antimony trioxide (senarmontite), with O bond angles of about 109° and Sb—O distances of $2·2 \pm 0·1$ A. The second form of Sb_2O_3 (valentinite) is described below.

Bismuth trioxide also is dimorphous, crystallizing in a monoclinic and a tetragonal, pseudo-cubic, form. The latter is similar in structure to cubic As_4O_6 and Sb_4O_6, but no molecules can be distinguished in the structure, which is similar to that of Zn_3P_2 (p. 426) and Mn_2O_3 (p. 314). Each Bi atom has six O neighbours (at 2·40 A.) arranged at six of the eight corners of a cube, those at two diagonally opposite corners being missing (see Fig. 124 (*a*)). This structure is simply related geometrically to the fluorite structure which is shown in the same orientation in Fig. 124 (*b*). Removal of one-quarter of the anions (those shown as dotted circles) from the unit cell of the latter leaves the arrangement shown in (*a*). (In (*b*) there are eight F per unit cell, i.e. four CaF_2, and in (*a*) six O, i.e. two Bi_2O_3.) If the metal atoms and the shaded O atoms are drawn in a little towards the body-centre of the cube the structure becomes that of As_4O_6 and Sb_4O_6, containing discrete molecules. The remaining O atoms then form parts of neighbouring molecules. The second form of antimony trioxide (valentinite) has a different type of structure. Instead of finite molecules Sb_4O_6 there are infinite double chains of the type shown below, with Sb—O = 2·00 A., O bond angles of 116° and 132°, and Sb bond angles of 81°, 93°, and 99°.



The Oxy-acids of Phosphorus and their Salts

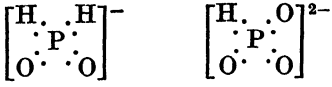
The number and stability of the oxy-acids of phosphorus are in marked contrast to those of nitrogen. The formulae and basicities of the acids are set out in the accompanying table. The so-called 'per-acids', H_3PO_5 and $H_4P_2O_8$, are omitted as nothing is known of their structures. The latter is presumably analogous to $H_2S_2O_8$. Little appears to be known about metaphosphorous acid and we shall not discuss it further. Apart from metaphosphoric acid, which is usually obtained as a glass, all the acids in Table 23 can be obtained crystalline at ordinary temperatures. Nevertheless there have been no studies of the atomic arrangement in these acids, but the following points have a direct bearing on their structures. We shall deal first with the first set of four acids.

TABLE 23

The Oxy-acids of Phosphorus

	Empirical formula	*Basicity*	*Structural formula*
Orthophosphorous	H_3PO_3	2	$H_2[HPO_3]$
Hypophosphorous	H_3PO_2	1	$H[H_2PO_2]$
(Metaphosphorous	HPO_2)	..	..
Pyrophosphorous	$H_4P_2O_5$	2	$H_2[H_2P_2O_5]$
Hypophosphoric	H_2PO_3	4	$H_4[P_2O_6]$
Orthophosphoric	H_3PO_4	3	H_3PO_4
Metaphosphoric	HPO_3	See text	
Pyrophosphoric	$H_4P_2O_7$	4	$H_4P_2O_7$

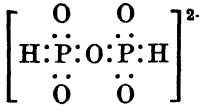
A striking feature of these acids is their abnormal basicities. We might expect H_3PO_3 to contain pyramidal PO_3^{3-} ions exactly analogous to the pyramidal SO_3^{2-} and ClO_3^- ions and containing trivalent P. No phosphites have yet been studied by X-ray methods, but the basicity suggests that the acid is really $H_2[HPO_3]$. The structure of the crystalline ammonium salt of hypophosphorous acid, $NH_4H_2PO_2$, has been studied. This is not an acid salt, in which there would be PO_2^{3-} ions joined together by hydrogen bonds and NH_4^+ ions, for the closest approach of O atoms attached to different P atoms is 3·45 A. (see p. 252). Instead, the salt contains tetrahedral $[H_2PO_2]^-$ ions. The hypothetical HPO_3^{2-} ion would then be a member of the series:



with which may be compared the series:

$$POF_3 \quad PO_2F_2^- \quad PO_3F^{2-} \text{ and } PO_4^{3-}.$$

Pyrophosphorous acid is described as dibasic, and the ion $H_2P_2O_5^{2-}$ may be formulated



The constitution of hypophosphoric acid, with empirical formula H_2PO_3, has been a matter of controversy for a long time. The early work on the molecular weights of its esters indicated the simple formula H_2PO_3, but it is now known that this work was unreliable. Cryoscopic measurements show that the molecular weights of the ethyl ester and of the free acid correspond to the formulae $(C_2H_5)_4P_2O_6$ and $H_4P_2O_6$ respectively. The magnetic evidence is conclusive on this point. The molecule H_2PO_3 would be paramagnetic since there would be an odd unpaired electron, but the salts $Na_2H_2P_2O_6$ and $Ag_4P_2O_6$ are in fact diamagnetic.

We now come to the extensive oxygen chemistry of pentavalent phosphorus, which is based on PO_4 tetrahedra. This field has so far received comparatively little study, but it will be apparent from the following remarks that the structural chemistry of phosphates has much in common with that of silicates (which are based on SiO_4 tetrahedra), a subject dealt with in Chapter XIV. Just as SiO_4 tetrahedra link together in various ways to form Si_2O_7 ions, ring and chain ions of composition $(SiO_3)_n$ in the metasilicates, layers, and infinite 3-dimensional complexes, so there are indications that PO_4 tetrahedra join up to form highly complex ions.

Discrete PO_4^{3-} ions exist in normal orthophosphates, in acid phosphates —where they are held together by hydrogen bonds as well as by the positive ions (see the structure of KH_2PO_4 described on p. 260)—and in orthophosphoric acid itself. In this acid the PO_4^{3-} ions must be linked by hydrogen bonds as in H_2SO_4 or $HClO_4$, but the structures of these acids await study. The structures of a number of orthophosphates, particularly those of Group III elements, illustrate the similarity of the oxygen chemistry of P to that of Si.

Phosphates, etc.	*Silicates with similar or closely related structures*
BPO_4, $BAsO_4$	β-cristobalite, SiO_2
$AlPO_4$, $AlAsO_4$	quartz, SiO_2
YPO_4, $YAsO_4$, YVO_4	$ZrSiO_4$ (zircon)
Li_3PO_4, $LiMnPO_4$	Mg_2SiO_4*
$Cu_2(OH)PO_4$, $Zn_2(OH)AsO_4$	Al_2OSiO_4

* In the olivine structure the O atoms are approximately in hexagonal close-packing. In this arrangement the number of octahedral holes is equal to the number of O atoms so that there is room for the additional Li^+ ions.

Linking of two PO_4 tetrahedra to form the $P_2O_7^{4-}$ ion ($O_3P—O—PO_3$) occurs in pyrophosphoric acid, $H_4P_2O_7$, and the pyrophosphates. Only normal (i.e. $M^I_4P_2O_7$, $M^{II}_2P_2O_7$, $M^{IV}P_2O_7$) and dihydrogen salts (e.g. $M^I_2H_2P_2O_7$) appear to be known. The non-existence of salts of the types

$M_3HP_2O_7$ and $MH_3P_2O_7$ is presumably due to the fact that stable frameworks of P_2O_7 groups linked by hydrogen bonds are not possible for these particular H:O ratios (see the structure of $(NH_4)_2H_3IO_6$, p. 260). The crystal structures of the pyrophosphates MP_2O_7 of a number of tetravalent elements (Si, Ti, Zr, Hf, Sn, U) have been determined and the P_2O_7 ion found to consist of two PO_4 tetrahedra joined by sharing one O atom. The P—O distance is 1·55 A. as in PO_4^{3-}.

In comparison with the chemistry of the ortho- and pyro-phosphates that of the metaphosphates is very complex. In these the condensation of PO_4 tetrahedra has proceeded further to the formation of rings or chains, of empirical composition $(PO_3)_n$, exactly analogous to the metasilicates. The ring ions may be composed of various numbers of PO_4 tetrahedra; compare the Si_3O_9 and Si_6O_{18} ions, p. 473. Metaphosphoric acid itself has not been obtained crystalline; it is obtained as a glass or syrup. We have already seen (p. 124) that the glassy state is characteristic of substances containing chains (selenium, plastic sulphur, borates, and silicates). In solution the acid is obviously highly polymerized and like certain other compounds containing very complex ions it has the property of coagulating albumen. Some metaphosphates are obtained as rubbery or horn-like masses and in some cases are obviously mixtures of various metaphosphates. Thus the solid obtained by heating $NaNH_4HPO_4$, of empirical composition $NaPO_3$, is not homogeneous, part being soluble and the remainder insoluble in water. Up to the present the crystal structure of only one metaphosphate has been determined. Aluminium metaphosphate, usually written $Al(PO_3)_3$, actually contains ions of the composition $[P_4O_{12}]^{4-}$ consisting of rings of the type shown in Fig. 125. The salt should therefore be formulated $Al_4(P_4O_{12})_3$. Infinite chain ions $(PO_3)_n^{n-}$ have not yet been found in metaphosphates; they may exist in salts like $Ca(PO_3)_2$ (compare the $(SiO_3)_n^{2n-}$ ions in $CaSiO_3$).

The other two main types of complex which we might expect to be formed by the linking together of PO_4 tetrahedra are layers (infinite 2-dimensional) and infinite 3-dimensional networks. We have already seen that one form of crystalline P_2O_5 consists of a network of the latter type.

Layer phosphate structures are so far represented by only one substance. The mineral autunite, $Ca(UO_2)_2(PO_4)_2.nH_2O$, exhibits base exchange and reversible hydration like the zeolites (p. 482). It may be prepared in various ways from solutions containing the component ions. By treating the crystals with concentrated NaCl solution all the Ca^{2+} ions may be replaced by Na^+, and replacement by K^+, Ba^{2+}, Cu^{2+}, and H^+ is also possible. The naturally occurring crystals contain about ten H_2O per Ca atom, and dehydration experiments on artificial material indicate that two fairly well-defined hydrates exist, with about $10\frac{1}{2}$ and $6\frac{1}{2}$ molecules of water respectively. The latter hydrate is called meta-autunite I. These two hydrates may be reversibly interconverted, but at temperatures above 75° C. meta-autunite I changes, apparently

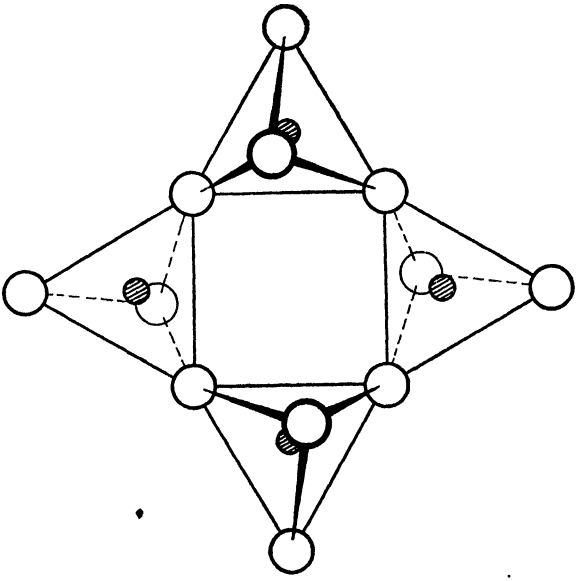


FIG. 125. The $[P_4O_{12}]^{4-}$ ion in aluminium metaphosphate (diagrammatic) composed of PO_4 tetrahedra sharing corners. These ions are held together by the Al^{3+} ions so that the unshared O atoms of different $P_4O_{12}^{4-}$ ions form octahedral coordination groups around the metal ions.

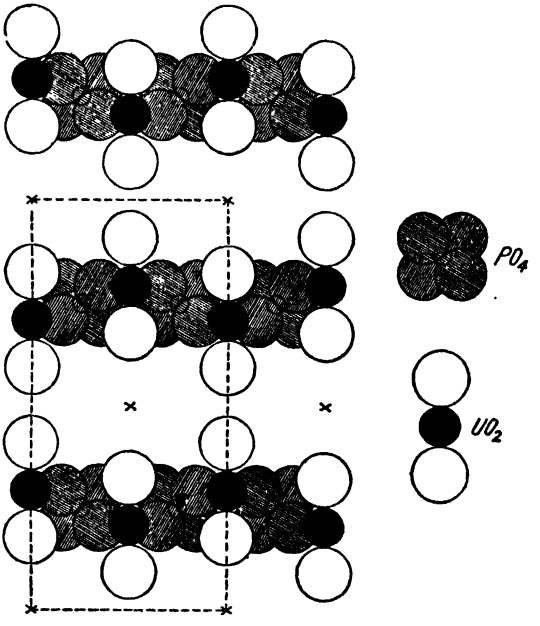


FIG. 126. Elevation of the structure of autunite, $Ca(UO_2)_2(PO_4)_2\,nH_2O$ (after Beintema).

irreversibly, into a still less hydrated form, meta-autunite II. In all three compounds the water content is not quite constant but varies, between

certain limits, with the temperature and the vapour pressure of water above the crystals. Autunite exhibits a pronounced cleavage like micas and is built up of layers which are reminiscent of the Si_3AlO_{10} layers in those minerals. In a layer there are PO_4 tetrahedra and UO_6 octahedra (probably deformed to give the U atoms two nearest neighbours as in uranyl compounds) which are linked together by sharing corners. These layers are seen end-on in Fig. 126. The positive ions and water molecules occupy the large cavities, the centres of which are marked by crosses, between the layers. The fact that autunite can be converted reversibly into meta-autunite I suggests that the latter is built up from similar layers, and the structure proposed for meta-autunite I is derived from that of Fig. 126 merely by movement of the layers relative to one another. The layers are now more closely packed and the large cavities have disappeared. The positions of the Ca^{2+} ions in the autunite structure are not known with certainty, but the fact that they are replaceable by twice their number of univalent ions suggests that they occupy statistically, in association with the water molecules, one-half of the positions indicated by crosses in Fig. 126.

THE OXYGEN CHEMISTRY OF THE ELEMENTS OF THE GROUP V SUB-GROUPS

The maximum oxygen coordination numbers of the elements of Group V are:

		V	Nb	Ta	(A sub-group)
N	P				
		As	Sb	Bi	(B sub-group)
3	4		6		

We have outlined the oxygen chemistry of N and P, and we have now to consider the elements of the A and B sub-groups. The oxygen chemistry of vanadium, the least electropositive of the A sub-group elements, resembles that of phosphorus in many ways. Since the two elements have the same oxygen coordination number, their oxy-compounds of similar formula type are structurally similar and often isomorphous, and also isomorphous with the corresponding arsenates. Thus the dodecahydrates of Na_3PO_4, Na_3AsO_4, and Na_3VO_4 are isomorphous, as also are the complex salts $Pb_5(PO_4)Cl$, $Pb_5(AsO_4)Cl$, and $Pb_5(VO_4)Cl$. Vanadium is widely distributed in nature, occurring usually with phosphorus as vanadates (though the large deposit of the rare mineral patronite, V_2S_5, is a very important source of the element), whereas Nb and Ta are generally associated with other transition metals and rare-earths. Ortho-, meta-, and pyro-vanadates are known, but the order of stability of these salts in aqueous solution is the reverse of that of the corresponding phosphates. Whereas meta- and pyro-phosphates are converted into orthophosphates on boiling in solution, i.e. the complex ions break down into simple PO_4^{3-} ions, the orthovanadate ion VO_4^{3-} is rapidly converted into the pyro-ion, $V_2O_7^{4-}$, in the cold, and on boiling, further condensation

into metavanadate ions $(VO_3)_n^{n-}$ takes place. The particular type of vanadate which is obtained from a solution depends on the temperature and also on the acidity of the solution. Acidification of a vanadate solution with acetic acid leads to condensation of VO_4 groups to form deeply coloured polyvanadates, which may contain ions of the type $[V_6O_{18}]^{6-}$.

In the case of arsenic the condensed ions are much less stable. Only orthoarsenates exist in solution, and orthoarsenic acid is known both in the anhydrous state and as the hemihydrate, $H_3AsO_4.\frac{1}{2}H_2O$. The pyro- and meta-acids are not known, and the corresponding salts—which are stable only in the solid state—are prepared by heating the mono- and di-hydrogen orthoarsenates, just as the corresponding phosphates are prepared: $2M_2HPO_4 \rightarrow M_4P_2O_7$ and $MH_2PO_4 \rightarrow MPO_3$.

The oxygen chemistry of antimony is entirely different from that of phosphorus, arsenic, and vanadium on account of the different oxygen coordination number (see above). This has, however, only been realized in recent years as a result of the study of the structures of crystalline antimonates, and the old formulae assigned to these compounds were similar to those of phosphates, etc. As we shall see, these formulae require revision. The free oxy-acids of antimony are still less stable than those of arsenic. Various hydrated forms of the trioxide and pentoxide have been described as antimonious and antimonic acids, but their structures are unknown.

Of the antimonates, ortho-salts containing SbO_4^{3-} do not exist because antimony does not form such an ion. Meta- and pyro-salts are known to which have been assigned formulae analogous to those of the meta- and pyro-phosphates, e.g. $NaSbO_3$, $LiSbO_3.3H_2O$, and $Na_2H_2Sb_2O_7.5H_2O$. In no case is there any structural similarity between the phosphorus and antimony compounds, and no pyroantimonate ion exists in the so-called pyroantimonates. A study of the crystal structure of sodium 'pyroantimonate', $Na_2H_2Sb_2O_7.5H_2O$, shows that its correct structural formula is $NaSb(OH)_6$ and the isomorphous silver salt is $AgSb(OH)_6$. In the pseudo-cubic sodium salt the Na and Sb atoms are arranged in the same way as the Na^+ and Cl^- ions in NaCl, and each Sb atom is the centre of an $Sb(OH)_6^-$ ion. By the action of 40 per cent. HF, $Na[Sb(OH)_6]$ is converted into $Na[SbF_6]$ which has a quite similar structure. If a solution of sodium 'pyroantimonate' is added to one of a magnesium salt the precipitate has the empirical composition $Mg(SbO_3)_2.12H_2O$ and this was considered to be a hydrated meta-antimonate. Its formulation as $[Mg(H_2O)_6][Sb(OH)_6]$, resulting from an X-ray study of the crystals, shows that it is a hydrated antimonate of exactly the same type as sodium pyroantimonate. The old and new formulae of such antimonates are summarized below.

Old formula	*Correct structural formula*
$Na_2H_2Sb_2O_7.5H_2O$	$Na[Sb(OH)_6]$
$Mg(SbO_3)_2.12H_2O$	$MgSb(OH)_6.6H_2O$ or $[Mg(H_2O)_6][Sb(OH)_6]$
(Co and Ni salts similar)	
$Cu(NH_3)_3(SbO_3)_2.9H_2O$	$[Cu(NH_3)_3(H_2O)_3][Sb(OH)_6]_2$
$LiSbO_3.3H_2O$	$Li[Sb(OH)_6]$

The partial hydrolysis of $NaSbF_6$ leads to the formation of a salt originally formulated $NaF.SbOF_3.H_2O$. Its correct formula is $Na[SbF_4(OH)_2]$, showing that it is of the same type as $NaSbF_6$ and $NaSb(OH)_6$.

The structures of a few anhydrous meta-antimonates have also been studied. The salt $NaSbO_3$ may be prepared by heating $NaSb(OH)_6$ in air or by fusing Sb_2O_3 with sodium carbonate—there are similar silver and lithium salts. The sodium salt is dimorphous, one form being isomorphous with ilmenite, $FeTiO_3$ (see p. 331), and the other being closely related to a number of other complex antimony, niobium, and bismuth oxy-compounds. All the following compounds have very similar structures: the minerals pyrochlorite, $CaNaNb_2O_6F$, and romeite, $CaNaSb_2O_6(OH)$, $Sb_3O_6(OH)$, $BiTa_2O_6F$, and the simple antimonates $NaSbO_3$ and $AgSbO_3$. The third of these, $Sb_3O_6(OH)$, is of interest in connexion with the structure of Sb_2O_4. When hydrated Sb_2O_5 is heated (at about 800° C.) it is not directly converted into Sb_2O_4, as was at one time supposed, but into $Sb_3O_6(OH)$. This latter compound is converted into the tetroxide only after prolonged heating at 900° C., and $Sb_3O_6(OH)$ had been confused with the tetroxide which is also formed by the oxidation of Sb_2O_3 in air. The tetroxide is apparently isomorphous with $SbTaO_4$, in which both the Sb and Ta atoms are octahedrally coordinated by oxygen, and may be regarded as $Sb^{III}Sb^{V}O_4$. The compound $BiTa_2O_6F$ is prepared by heating BiOF with Ta_2O_5. The structures of the above-mentioned compounds are related in the following way. In the unit cell of the pyrochlorite structure there are eight formula weights, i.e. $8[CaNaNb_2O_6F]$. The $8Ca^{II}+8Na^{I}$ may be replaced by $8Sb^{III}$, the Nb^{V} by Sb^{V}, and the F by OH, giving $Sb^{III}Sb^{V}_2O_6(OH)$, which we mentioned above as an intermediate product in the heating of $Sb_2O_5.nH_2O$. Alternatively the $8Ca^{II}+8Na^{I}$ may be replaced by $16Na^{I}$ (or Ag^{I}) and the 8OH omitted, giving $Na_{16}Sb_{16}O_{48}$, or $NaSbO_3$. These relationships may be summarized as follows:

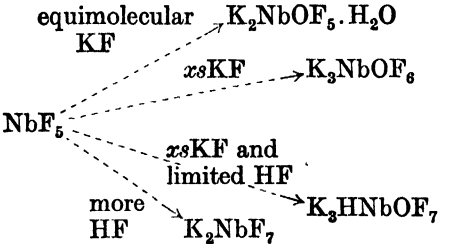
Pyrochlorite	$NaSbO_3$	$Sb_3O_6(OH)$	$BiTa_2O_6F$
$8\ Ca^{II}+8\ Na^{I}$	$16\ Na^{I}$	$8\ Sb^{III}$	$8\ Bi^{III}$
$16\ Nb^{V}$	$16\ Sb^{V}$	$16\ Sb^{V}$	$16\ Ta^{V}$
48 O	48 O	48 O	48 O
8 F	..	8 OH	8 F

Complex Fluorides of Group V A Metals

The metals of the third, fourth, and fifth A sub-groups are notable for the formation of extended series of complex fluorides. Some of the aluminofluorides are described in Chapter VIII. In Group V A there is an interesting gradation in properties from V to Ta. In complex salts vanadium prefers bonds to oxygen rather than fluorine—note the extensive oxygen chemistry of vanadium and the formation of VOF_2 and VOF_3 (no oxyfluorides of Nb or Ta are known in the free state). The most stable salts obtained by the addition of metallic fluorides to a solution of Nb_2O_5 in HF are those containing the ion $[NbOF_5]^{2-}$. This ion is much more stable than simple NbF_n ions. For example, K_2NbF_7 is prepared

from a solution of $K_2NbOF_5.H_2O$ in HF but is easily hydrolysed back to that salt, while Rb_2NbF_6 is made by repeated crystallization of Rb_2NbOF_5 from HF. Finally, tantalum prefers to form complex fluorides of the type $R_mTaF_n.xH_2O$ rather than oxyfluorides, and in these n rises to 8. The V and Nb analogues of salts like Na_3TaF_8 are not known.

The following scheme illustrates, for the potassium-niobium fluorides, how the composition of the product varies with the relative concentrations of the component halides and of HF:



These complex fluorides provide many interesting examples of isomorphism. In the following table compounds in the same horizontal row are isomorphous.

IV	V	VI
$K_2TiF_6.H_2O$	$K_2NbOF_5.H_2O$	$K_2WO_2F_4.H_2O$
$(NH_4)_3TiF_7$	$(NH_4)_3NbOF_6$, $(NH_4)_3TaOF_6$	
K_3ZrF_7	K_3NbOF_6	
K_3HSnF_8, K_3HPbF_8	K_3HNbOF_7	

The structures of these salts are of considerable interest on account of the shape of the coordination group around the metal atom in the complex ion. An early X-ray study of $(NH_4)_3ZrF_7$ suggested that the crystal was composed of NH_4^+, ZrF_6^{2-}, and F^- ions. Later work has, however, shown the presence of ZrF_7^{3-} groups with the configuration illustrated in Fig. 28 (*a*), p. 113, derived from an octahedron by adding one F^- ion beyond the centre of one face and subsequently rearranging the other F^- ions slightly. The salt $(NH_4)_3SiF_7$, on the other hand, contains SiF_6^{2-} and discrete F^- ions. The $NbOF_6^{3-}$ ion, which occurs in K_3NbOF_6, has the same configuration

Empirical formula	*Type of complex ion*	*Shape*	*Structural formula (if different from empirical)*
$(NH_4)_3SiF_7$	$[SiF_6]^{2-}$	Octahedral	$(NH_4)_3[SiF_6]F$
$(NH_4)_3ZrF_7$	$[ZrF_7]^{3-}$	Fig. 28 (*a*)	..
K_2NbF_7, K_2TaF_7	$[NbF_7]^{2-}$, $[TaF_7]^{2-}$	Fig. 28 (*b*)	..
K_3NbOF_6	$[NbOF_6]^{3-}$	Fig. 28 (*a*)	..
$K_2NbOF_5.H_2O$	$[NbOF_5]^{2-}$	Octahedral	..
K_3HNbOF_7	$[HF_2]^-$	Linear	$K_3[HF_2][NbOF_5]$
	$[NbOF_5]^{2-}$	Octahedral	

as the ZrF_7^{3-} ion. The corresponding NbF_7^{2-} and TaF_7^{2-} ions have a different shape, shown in Fig. 28 (*b*). Finally, octahedral $NbOF_5^{2-}$ ions occur in $K_2NbOF_5.H_2O$ and also in the salt with the empirical formula K_3HNbOF_7. The latter is composed of K^+, octahedral $[NbOF_5]^{2-}$, and linear $[HF_2]^-$ ions. These results of structural studies are summarized above.

NITRIDES AND PHOSPHIDES

We shall confine our attention chiefly to the nitrides, but shall indicate the structures of the corresponding phosphides, arsenides, and stibides where these are known. Most elements combine with nitrogen, and the nitrides include some of the most stable compounds known. The compounds of metals with the heavier V B sub-group elements resemble alloys rather than salts or covalent compounds, and only in the case of some of the more electropositive metals are the bismuthides formally similar to the nitrides and phosphides. The nitrides fall naturally into a number of groups, with which we shall deal in turn.

Ionic Nitrides

This group includes the nitrides of

Li—the other alkali nitrides are apparently not known, at any rate in a pure state.

Be, Mg, and the metals of II A and II B. (The chocolate-coloured explosive nitride of mercury, Hg_3N_2, made from HgI_2 and KNH_2 in liquid ammonia may be different in structure from the other Group II nitrides.)

Ge (Ge_3N_4), Th (Th_3N_4), but not those of the IV A metals of the type TiN.

These nitrides, with formulae corresponding to the normal valency of the metal in combination with N^{III} (i.e. Li_3N, Be_3N_2, Ge_3N_4), form colourless transparent crystals and are the analogues of the oxides. They are formed by direct union of the metal with nitrogen, or in some cases by heating the amide. Compare, for example,

$$3Ba(NH_2)_2 \rightarrow Ba_3N_2 + 4NH_3$$

with

$$Ba(OH)_2 \rightarrow BaO + H_2O.$$

They have high melting-points, ranging from 2,200° (Be_3N_2) to 900° (Ca_3N_2), and are hydrolysed by water to the hydroxides, with liberation of ammonia. Many of these nitrides, phosphides, etc., are anti-isomorphous with oxides M_2O_3, i.e. the metal atoms occupy the positions of the oxygen atoms and the nitrogen (or phosphorus) those of the metal atoms in the M_2O_3 structures. Before recording the structures of the nitrides M_3N_2 we should mention that Li_3N has a simple hexagonal structure in which one-third of the Li atoms have two nearest N neighbours (at 1·94 A.) and the remainder three (at 2·11 A.). The N atoms are surrounded by two Li at 1·94 A. and six more at 2·11 A.

The structures of the compounds of the type M_3N_2 are summarized below, where A represents the anti-Mn_2O_3, B the Zn_3P_2, and C the anti-La_2O_3 structure.

	Be	Mg	Zn	Cd	Ca
N . .	A	A	..	..	A
P . .	A	A	B	B	..
As . .	..	A	B	B	..
Sb . .	..	C	..	..	..
Bi . .	..	C	..	..	..

The Mn_2O_3 and La_2O_3 structures have been described on pp. 313 and 314. The former may be regarded as derived from the fluorite structure by removal in a regular way of one-quarter of the anions followed by slight adjustments in the positions of the remaining atoms. The structure is notable for the peculiar environments of the two crystallographically different types of Mn atoms. The pseudo-cubic Zn_3P_2 structure is closely related to the anti-Mn_2O_3 structure. Zinc atoms are surrounded tetrahedrally by four P and P by six Zn at six of the corners of a distorted cube. The idealized (cubic) Zn_3P_2 structure is similar to that of Bi_2O_3 which has already been illustrated in Fig. 124, p. 416. These nitrides and phosphides are regarded as ionic crystals containing N^{3-} and P^{3-} ions, with radii about 1·4 and 1·85 A. respectively, slightly larger than O^{2-} and S^{2-} respectively. The environment of the metal atoms should be compared with that in the interstitial nitrides. In the latter a metal atom is, as in the pure metal, equidistant from and in contact with a large number (often 12) of other metal atoms. In the ionic compounds, however, the next nearest neighbours of a metal atom are a small number of metal atoms, three in Zn_3P_2 and six in Mg_3P_2, and the metal–metal distances are greater than in the pure metal. For example, in Zn_3P_2 the Zn–Zn distances range from 3·00–3·07 A. compared with 2·66 and 2·91 A. for the two sets of six neighbours in metallic zinc. In Cu_3P_2, on the other hand, the Cu–Cu distance is 2·56 A. throughout the structure, the same as in copper itself.

Of the nitrides of Group IV metals, Ge_3N_4 has a structure similar to that of phenacite (Be_2SiO_4, p. 470), every Ge atom having four N neighbours.

Covalent Nitrides

These comprise the nitrides of some of the elements of Group III and also certain compounds like Si_3N_4 and P_3N_5. The structures of the latter are not known. These compounds are, like BN, white powders with very high melting-points and great chemical stability. The structures of the Group III nitrides, phosphides, etc., are interesting because these compounds consist of equal numbers of atoms of elements of Groups III and V and their structures are geometrically the same as those of the two forms of carbon. Thus BN crystallizes with the graphite structure (see Fig. 129,

p. 436) with alternate B and N atoms arranged in layers, while the compounds set out below all crystallize with either the zinc-blende structure (Z), Fig. 11, p. 83, which arises by replacing the C atoms in diamond alternately by tri- and penta-valent atoms, or the closely related wurtzite structure (W), also illustrated in Fig. 11.

	Al	Ga	In
N . .	W	W	W
P . .	Z	Z	..
As . .	Z	Z	..
Sb . .	Z	Z	Z

Nitrides, etc., of the Transition Metals

These compounds are very numerous, more than one phosphide, for example, being formed by many transition metals. Of the great variety of structures adopted by these compounds few warrant description in this book, and we shall merely indicate some of the simpler types of structures. It is convenient to subdivide these nitrides into two groups:

(1) *The Interstitial Nitrides.* These will be considered in more detail in Chapter XVII. The characteristic feature of these compounds is that the small non-metal atoms occupy some or all of the interstices in the (usually close-packed) metal structure. The arrangement of the metal atoms is therefore the same, or very nearly the same, as in the pure metal. According to the number and nature (i.e. whether tetrahedral or octahedral) of the interstices occupied by the non-metal atoms, the relative positions of the metal and non-metal atoms may be the same as in certain simple structures such as the NaCl and CaF_2 structures. Thus we find all the following compounds crystallizing with the rock-salt structure: ScN, CeN, LaN, TiN, ZrN, VN, NbN, PrN, LaP, PrP, GeP; and Ir_2P, Rh_2P with the anti-fluorite structure.

(2) *Phosphides, arsenides, etc., with other structures.* For the larger Group V B atoms interstitial structures are not possible (see p. 565) and other structure types are found. These are in some cases similar to those of certain sulphides (e.g. $PtAs_2$ with the pyrites structure and FeP_2 with the marcasite structure), selenides and tellurides (e.g. FeP, CoP, MnAs, FeAs, and CoAs with the NiAs structure, which is adopted by the selenides and tellurides of a number of transition metals). These latter compounds are in many ways intermediate between covalent compounds and true metallic alloys. The structures of these and of the pure elements form the subject of Chapter XVII.

CHAPTER XIII

CARBON

THE carbon atom possesses four valency electrons ($2s^22p^2$) and therefore by forming four electron-pair bonds it acquires the stable neon structure with the completed second quantum group of eight electrons. As we have already seen, these four bonds are disposed tetrahedrally and the orbitals used are termed sp^3 hybrids. The other simple ways in which the octet can be completed are by the formation of one double and two single, of two double, or of one triple and one single bond:

(*a*)  (*b*)  (*c*) =C= and (*d*) ≡C—

We shall therefore consider the stereochemistry of carbon under the following heads:

(i) The tetrahedral carbon atom—in molecules and in diamond.

(ii) 3-covalent carbon. In addition to the simple bond arrangement shown in (*b*) above we also find carbon forming three equivalent bonds, so that here we have also to discuss
   (1) the carbonate ion;
   (2) benzene, graphite, and compounds related to it;
   (3) cyclic carbon-nitrogen compounds;
   in all of which resonance occurs. We shall also mention the unstable 'free radicals' of the type R_3C which are also stabilized by resonance.

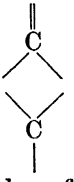
(iii) In a simple molecule like that of acetylene, C_2H_2, we have an example of ≡C—, there being no possibility of resonance with a structure involving =C=. However, in many molecules which can be represented with carbon forming two double bonds, =C=, it is probable that resonance with forms involving ≡C— does occur, and we shall therefore consider (*c*) and (*d*) together. Resonance of this kind occurs in diacetylene, HC≡C—C≡CH, leading to a length of 1·36 A. for the central C—C bond (as in cyanogen, NC.CN), the length of the normal double bond between these atoms. The compounds to be dealt with include the oxides (CO is conveniently included here although the carbon atom in this molecule is linked to only one atom), oxysulphide and disulphide, cyanides and carbonyls. We have already seen that the molecules N_2 and O_2 contain multiple bonds

:N:::N: and :O⋮⋮O:

The isoelectronic carbon analogue of the N_2 molecule is a doubly charged ion $[:C:::C:]^{2-}$ found in a number of carbides, and a short account of these compounds will be included in this section. The intermediate atomic group is the cyanide ion $[C{\equiv}N]^-$.

Carbon is unique for the number and variety of its compounds based

on skeletons of carbon atoms directly linked together. There are also compounds based on mixed C—N, C—O, and C—N—O skeletons, particularly cyclic systems, to some of which we shall refer later. In finite molecules the only possible types of extended carbon skeleton are chains (simple or branched), rings, baskets (which may be regarded as ring systems joined up to form a closed hollow basket just as the ends of a chain may be joined up to form a ring), or combinations of these. It is usual to divide these compounds into two classes. Those of the first class, the aliphatic compounds, are based on the normal tetrahedral carbon atom. The aromatic compounds are based on the hexagonal C_6 ring, in which some of the C atoms may be replaced by N, etc. Corresponding to these two types of carbon skeleton in finite molecules are the two allotropic forms of crystalline carbon, diamond—in which each C atom is linked by tetrahedral sp^3 bonds to its four neighbours, and graphite—in which each atom forms three coplanar bonds leading to the arrangement of the atoms in sheets.

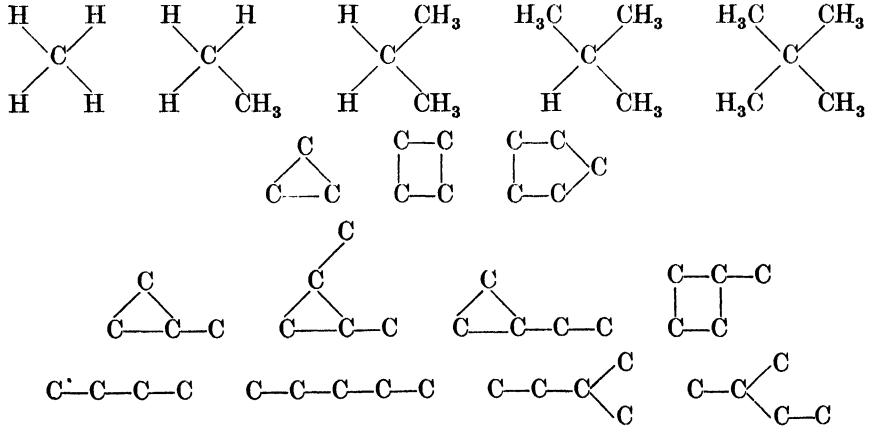


(diamond)—aliphatic carbon compounds { chains / rings

(graphite)—aromatic carbon compounds

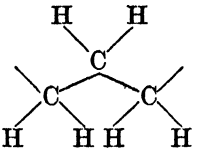
(There are also, of course, 'mixed' compounds containing C_6 rings and, for example, aliphatic side-chains or rings.)

The structural formulae of some of the simplest saturated hydrocarbons set out below show how a carbon atom forms with equal facility a bond to a second carbon as to a hydrogen atom, so that on the one hand a comparatively simple molecule such as C_5H_{12} exists in a number of stereoisomeric forms and on the other hand there is no limit to the number of carbon atoms which join up to form long-chain hydrocarbons. Saturated hydrocarbons containing simple carbon chains ranging from C_2H_6 to $C_{1000}H_{2002}$ have been prepared and studied.

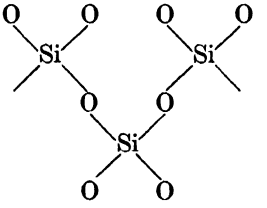


Carbon skeletons in simple hydrocarbons CH_4 to C_5H_{12}.

In contrast to the very extensive carbon-hydrogen chemistry is the small number of silicon-hydrogen compounds. Silicon hydrides containing more than six silicon atoms, with silicon skeletons analogous to the carbon skeletons of the hydrocarbons, are not known. Moreover, whereas saturated hydrocarbons are not attacked by water, the silicon hydrides are readily hydrolysed, the Si—Si bonds being broken and the system Si—O—Si being formed. Silicon prefers bonds to oxygen, and the complexity of silicate chemistry rivals that of carbon-hydrogen compounds. Instead of



we have

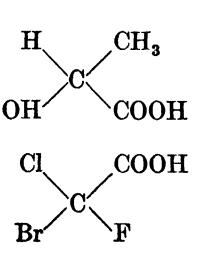


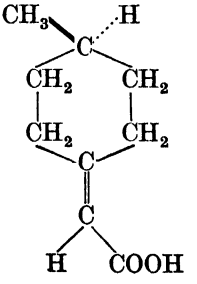
as the basis for complex silicon compounds.

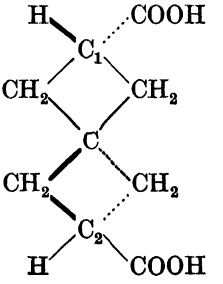
Further investigation may show that there is also an extensive carbon-fluorine chemistry. Direct fluorination of carbon, using mercury as a catalyst, yields chiefly CF_4 and C_2F_6, but the following products have also been isolated: C_3F_8, C_4F_{10} (two isomers), C_5F_{10}, C_6F_{12}, and C_7F_{12}. They are all colourless compounds, very stable towards chemical reagents.

THE TETRAHEDRAL CARBON ATOM

We shall not be concerned here with the early work in organic chemistry which led to the idea of the tetrahedral disposition of four bonds from a carbon atom. This arrangement of bonds accounts for the observed numbers of isomers of compounds and was confirmed by the resolution of a variety of compounds into their optical antimers. The criteria for the appearance of optical activity have already been discussed in Chapter VI, where further examples of enantiomorphous molecules will be found. A molecule Ca_2b_2 would exist in two stereoisomeric forms if the carbon bonds were planar or directed towards the corners of the base of a tetragonal pyramid, but in only one form if the arrangement of the bonds is tetrahedral. Only one form of such molecules is known. The following are examples of optically active molecules:







In the fourth of these molecules the two rings are in mutually perpendicular planes, as are also the terminal C_1—H and C_2—H and the C_1—COOH and C_2—COOH bonds respectively.

We have observed (Chapter III) that the optical activity of a molecule such as C*abcd* does not prove that the interbond angles are 109° 28′ but only that the general arrangement of the carbon bonds approximates to

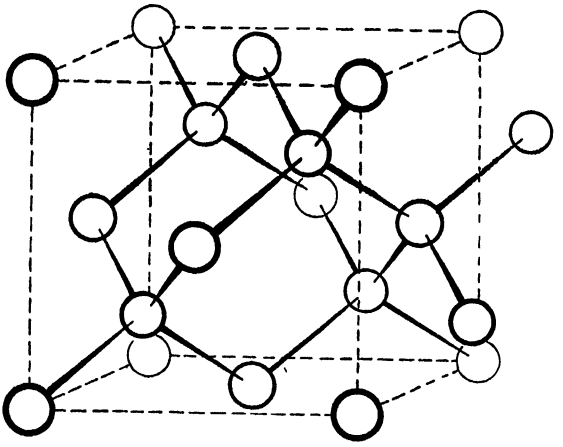


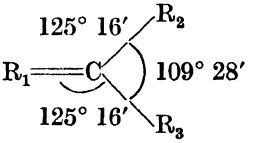
FIG. 127. The crystal structure of diamond.

the tetrahedral, and that they do not, for example, lie in one plane. The wave-mechanical calculations require that the bond angles are in fact very close to 109° 28′ since any large alteration in the bond angles would appreciably weaken the sp^3 bonds. It is therefore interesting to see whether this is the case. The early data on methylene chloride CH_2Cl_2 (from dipole moment and X-ray diffraction by the gas) suggested that the Cl—C—Cl bond angle was about 125°, but a later study of this compound by electron diffraction shows that the angle is within a degree or two of the true tetrahedral angle. A considerable number of simple compounds have now been studied in this way, including CCl_4, $C(CH_3)_4$, $C(CH_3)_3Cl$, CH_2Cl_2, CH_2F_2, and $CHCl_3$, and in every case the angles between the C—C and/or C—X bonds are 109° 28′ to within the experimental error.

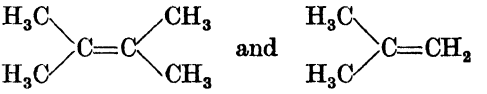
The earliest demonstration of the regular tetrahedral arrangement of carbon bonds was provided by the analysis of the crystal structure of diamond, Fig. 127. In this crystal each C atom is linked to four equidistant neighbours, so that the linking shown in Fig. 127 extends throughout the whole crystal. The bond angles and the C—C bond lengths (1·54 A.) are the same as in a simple molecule like $C(CH_3)_4$ or in any saturated hydrocarbon chain. As an example of a simple molecule which has been studied in the crystal we may mention that of pentaerythritol, $C(CH_2OH)_4$, to which we have already referred in the section on the hydrogen bond, p. 264.

CARBON FORMING THREE BONDS

The next simplest way in which carbon can complete its octet is by forming two single bonds and one double bond. Carbon atoms with this combination of bonds appear in the structural formulae of many molecules, but in few of these does the representation $::\dot{\underset{\cdot}{C}}:$ give an adequate idea of the behaviour of the eight valency electrons. For the arrangement



the bond angles should be as shown and the lengths of the bonds C=R_1, C—R_2, and C—R_3 should be those expected for one double and two single bonds respectively. In two simple unsaturated hydrocarbons the angles between the double bond and the two single bonds have been shown to have the above value to within the experimental error:

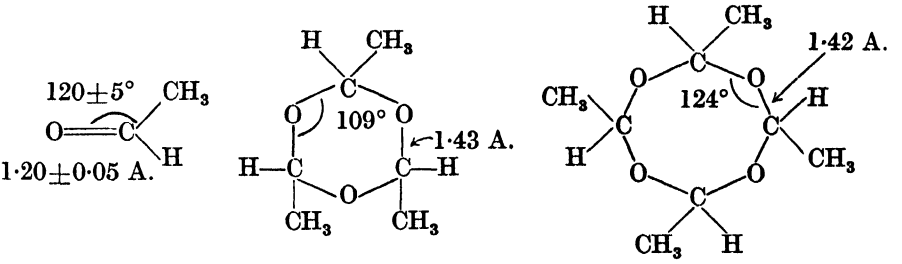


(tetramethylethylene) (isobutene)

Where atoms other than hydrogen are attached to the C atom, however, there arises the possibility of resonance with other structures in which the single and double bonds have been interchanged. We may distinguish two types of molecule (or ion) according to whether such resonance is (*a*) incomplete or (*b*) complete. In (*a*) there will be bond lengths intermediate between those for pure double or single bonds and the bond angles may be rather different from the ideal values given above. Where there is complete resonance all distinction between double and single bonds has vanished so that the bond lengths are all intermediate between those of single and double bonds and the bond angles are all 120°.

(*a*) As examples of molecules in which there is some resonance we shall take urea and phosgene, but before discussing these we must have some standard bond lengths with which to compare the values observed in these molecules. In aldehydes and ketones the C=O distance is found to be close to 1·24 A. As was explained in Chapter II, this distance is not to be regarded as the length of a pure double covalent bond between the two atoms because all bonds other than those between atoms of the same element will have some ionic character. In this particular case there is a fairly large difference between the electronegativities of the atoms and the structures $O:\ :CR_2$ and $:\ddot{\underset{\cdot\cdot}{O}}:C^+R_2$ must contribute nearly equally This is shown by the fact that the electric dipole moments of acetaldehyde, CH_3CHO, and of acetone, $(CH_3)_2CO$, are about 3×10^{-18} e.s.u. The structure $>C:\ :O$ would have a very small moment, whereas $C^+:\ddot{\underset{\cdot\cdot}{O}}:^-$

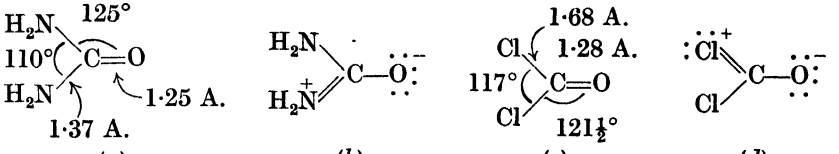
would have one of about 6×10^{-18} e.s.u. The single-bond C—O distance is 1·43 A. in $(CH_3)_2O$ and in paraldehyde and metaldehyde. The molecules of acetaldehyde and of its polymerized forms, paraldehyde, $(CH_3CHO)_3$, and metaldehyde, $(CH_3CHO)_4$, illustrate well these differences between bond lengths and between carbon interbond angles:



The carbon bond angles in the last two molecules have, of course, the normal tetrahedral values.

The single bond C—N length is 1·47 A. in $N(CH_3)_3$ and CH_3—N—N—N, so that for C=N we shall expect a value around 1·28 A.

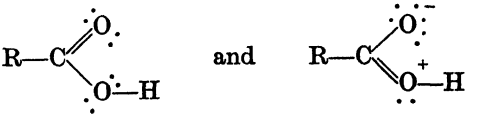
For urea the configuration (*a*) is found. The C=O distance is about that for a double bond, but the C—N distance is intermediate between that for C—N and C=N. If we assume that the carbon-nitrogen distance varies from C—N to C=N in the same way as the carbon-carbon distance



(*a*) (*b*) (*c*) (*d*)

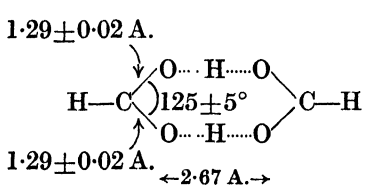
varies with percentage double-bond character (see p. 82), the bond in urea has about 20 per cent. double-bond character. For most purposes therefore the molecule is adequately represented by the formula (*a*), but there is some resonance with structures of the type (*b*), and since these structures are different from the 'normal' structure, resonance is not complete. Similarly in phosgene, $COCl_2$, with the configuration (*c*), there is only partial resonance with structures of type (*d*) as shown by the bond angles and bond lengths. (The single-bond length C—Cl is about 1·76 A.)

For a carboxylic acid R.COOH exact equivalence of the two carbon-oxygen bonds is not to be expected because it would require complete resonance between the forms

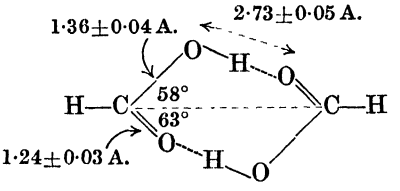


An electron diffraction study of the vapours of formic and acetic acids

in the monomeric form shows that the molecules are unsymmetrical, with C—O, 1·42±0·03 A., C=O, 1·24±0·03 A., and O—C=O bond angles 117±2° and 130±8° respectively. These acids also form dimeric molecules in the vapour state. An early study of the formic acid dimer indicated the symmetrical structure (*a*), but according to the results of later work the molecule is less symmetrical (*b*).



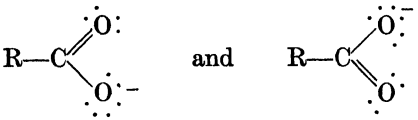
(*a*)



(*b*)

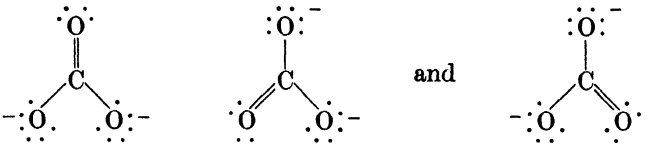
Similar unsymmetrical configurations were found for the dimers of CH_3COOH and CF_3COOH. The two carbon-oxygen bonds from a particular carbon atom are unequal in length, the difference being rather smaller in the dimeric forms than in the monomeric molecules. If the O—H—O bonds were symmetrical (see p. 252) we should expect a symmetrical structure of type (*a*), so that the structure (*b*) would appear to support the view that long O—H—O bonds, of lengths 2·70 A. or more, are different in nature from the very short O—H—O bonds found in acid salts (e.g. 2·55 A. in KH_2PO_4).

In the ions of carboxylic acids complete resonance is possible between



leading to equivalence of the two C—O bonds—compare the nitro group. In sodium formate the ion is reported to have the expected symmetrical structure, with both C—O distances 1·27±0·01 A. and O—C—O bond angle 124±4° (theoretical 125° 16′).

(*b*) We now come to systems in which all three bonds from the carbon atom become equivalent by resonance. In the carbonate ion the three resonating forms



are identical. Careful study of calcite ($CaCO_3$) has shown the carbonate ion to be planar with interbond angles of 120° and three equal C—O bonds of length 1·31±0·01 A.

Guanidine, $(NH_2)_2C{=}NH$, combines with the halogen acids HX to

form salts $C(NH_2)_3X$, which have been studied by X-ray methods. These salts contain guanidinium ions $C(NH_2)_3^+$ in which there is resonance of exactly the same kind as in the CO_3^{2-} ion, leading to a symmetrical planar ion.

Graphite and Benzene

We now have to consider briefly certain cyclic systems of carbon atoms. By forming three coplanar bonds carbon can form molecules built up of

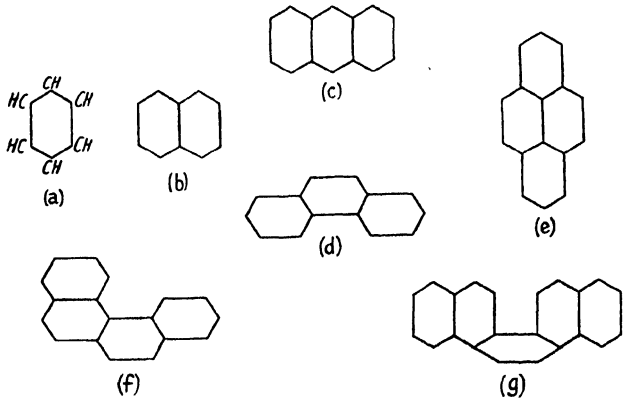


FIG. 128. Some molecules containing planar C_6 rings: (*a*) benzene, C_6H_6; (*b*) naphthalene, $C_{10}H_8$; (*c*) anthracene, $C_{14}H_{10}$; (*d*) phenanthrene, $C_{14}H_{10}$; (*e*) pyrene, $C_{16}H_{10}$; (*f*) chrysene, $C_{18}H_{12}$; and (*g*) picene, $C_{22}H_{14}$. The H atoms are omitted except in (*a*).

hexagonal C_6 rings. The simplest molecule of this type is the benzene molecule C_6H_6, and some other more complex ring systems are shown in Fig. 128. The remaining valencies of the outermost carbon atoms are, in the hydrocarbons, satisfied by bonds to hydrogen atoms, for which other atoms or groups may be substituted as, for example, in hexachlorobenzene, C_6Cl_6. The limit of this condensation of C_6 rings is the formation of a sheet of carbon atoms in which each is linked to three others. Graphite, one form of crystalline carbon, is composed of such sheets, and a portion of the structure of graphite is illustrated in Fig. 129. The wide separation of the sheets (3·4 A.) indicates relatively feeble binding between the atoms of different layers which can therefore slide over one another, conferring on graphite valuable lubricating properties.

The great difference between the binding within and between the layers leads to the formation of a number of interesting compounds in which atoms are introduced between the graphite layers, and we shall describe some of these shortly. The structural relationship between the simple benzene ring and the graphite layer is illustrated by the oxidation of graphite or charcoal (see below) by fuming nitric acid to mellitic acid, $C_6(COOH)_6$, which consists of a benzene ring with six carboxyl groups replacing the H atoms in C_6H_6. Distillation of this acid with lime yields

benzene itself. As a matter of interest we may mention two simple syntheses in which benzene or its derivatives are produced from simple

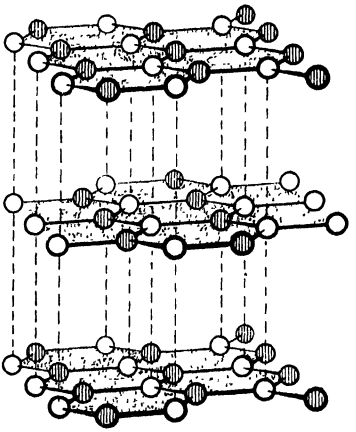
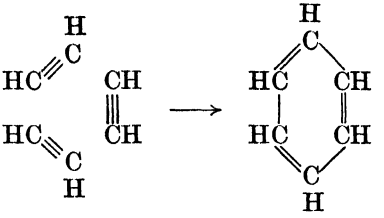


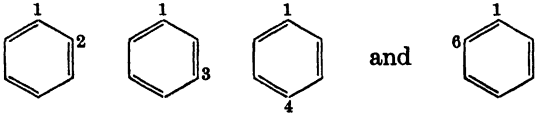
FIG. 129. The crystal structure of graphite. The diagram also represents the structure of BN, the shaded circles then being B atoms.

carbon compounds. The first is the pyrolysis of acetylene to give benzene:



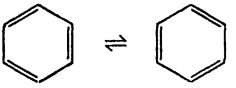
and the second is the action of carbon monoxide on metallic potassium, producing the potassium salt of hexahydroxybenzene, $C_6(OK)_6$.

Much attention has been devoted for many years to the problem of the structure of the benzene molecule. In the formula just given we have shown alternate double and single bonds, but a simple formula of this sort is unsatisfactory for a number of reasons. The H atoms in C_6H_6 may be replaced by other atoms or groups such as halogens, CH_3, NO_2, and many others, and the existence of only one mono-substituted derivative shows the equivalence of all six carbon atoms. Also, every di-substituted product exists in three isomeric forms only—whether the two substituting groups be similar or different—but according to the above formula we should expect four isomers:

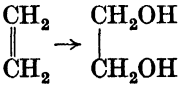


The figures indicate the positions of the substituents. The 1:6 compound should differ from the 1:2 isomer, since in one case there is a double bond

and in the other case a single bond between the substituents. Kekulé therefore suggested that the molecule oscillated in some way between the two forms



which are often referred to as the Kekulé structures. This is still not entirely satisfactory, since C_6H_6 has not the properties of aliphatic compounds containing C=C. For example, the addition of halogens to the molecule takes place much less readily than to the latter compounds, and benzene is also unaffected by alkaline potassium permanganate solution, which converts ethylene into the dihydric alcohol:

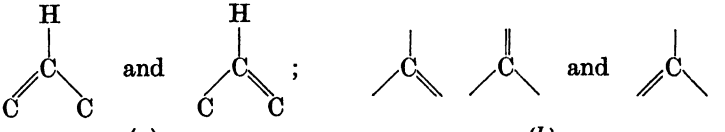


Various other formulae have been suggested to account for the unexpected stability of the benzene nucleus, such as those of Dewar, of type (*a*), and the centric formula of Armstrong, Baeyer, and Claus (*b*), but these, involving bonds between widely separated carbon atoms, will not be further considered here.



(*a*) (*b*)

The observed distance between adjacent carbon atoms in the symmetrical hexagonal benzene ring is 1·39 A., which may be compared with the length of a C—C bond, 1·54 A., and with C=C, 1·34 A. The modern view of the structure of the molecule is that there is resonance, chiefly between the two equivalent Kekulé forms (though other forms may be involved to a smaller degree), and that each bond has accordingly about 50 per cent. double-bond character. The molecule is stabilized by a considerable resonance energy—37 k.cals./mole—and the additional strength of the bonds is shown by the fact that their length is not midway between the lengths of C—C and C=C but much closer to the latter value. In benzene the double-bond from any one atom resonates between two positions (*a*), but in graphite between three (*b*). It is reasonable to assume



(*a*) (*b*)

that in graphite each bond has $\frac{1}{3}$ double-bond character, leading to a rather larger carbon-carbon distance (1·42 A.) than in benzene, and on this basis Pauling constructed the curve relating C—C distances with percentage double-bond character to which we referred in Chapter III.

Derivatives of Graphite

All forms of so-called amorphous carbon are graphitic in character, from lamp-black and coke to charcoal. They are composed of portions of the graphite structure without, however, the regular 3-dimensional periodicity characteristic of a crystal. On account of its structure, with its extensive internal surfaces and unsatisfied valencies, charcoal possesses the property of adsorbing gases and vapours to a remarkable extent and therefore also of catalysing reactions by bringing together the reacting gases. Graphite is far less reactive in this way since the layers of carbon atoms are complete and there is only a weak residual attraction between them, but nevertheless it undergoes a number of reactions in which atoms or radicals are taken up between the layers. The graphite crystal retains its original form except that it expands in one direction, perpendicular to the layers. A number of these reactions have been studied in recent years, with the following results.

Graphitic Oxide

This name is applied to the product of the action of strong oxidizing agents, such as nitric acid and potassium chlorate, on graphite. The graphite swells in one direction forming a material the colour of which varies from green to brown according to the conditions. The metallic lustre and conductivity of graphite are lost. This variation in colour, and the accompanying variation in composition, led to the belief that a number of compounds was formed—called graphitic oxides—to which formulae such as $C_{11}H_4O_5$ were assigned. Measurements of the distance between successive graphite sheets in these compounds show that it increases from the value 3·45 A. in graphite itself to values between 6 and 11 A., and that this expansion in spacing follows the increasing oxygen content. It appears that oxygen atoms are attached to both sides of the sheets, the C : O ratio varying between 2·9 and 3·5 : 1, and that water may be adsorbed on these 'graphite oxide' sheets. The limit of the swelling is reached when there are two layers of water molecules between all successive layers, but in alkaline solution the material may be converted into a colloidal suspension, probably owing to the final separation of the sheets and complete breakdown of the original graphite structure. With this behaviour of graphite compare that of certain clay minerals mentioned in Chapter XIV.

Graphitic 'Salts'

If graphite is suspended in concentrated sulphuric acid to which a small quantity of oxidizing agent (HNO_3, $HClO_4$, CrO_3, etc.) is added, it swells up and develops a steel-blue lustre and blue or purple colour in transmitted light. These products are stable only in the presence of the concentrated acid, being decomposed by water with the regeneration of graphite which, however, always contains some strongly held oxygen. By washing out the sulphuric acid with phosphoric acid the excess is removed,

but about 0·32 g. H_2SO_4 per gram of graphite is left. This may be removed by the action of reducing agents, and the reduction apparently proceeds in well-defined stages. In the sulphuric acid compound the maximum separation of adjacent graphite layers is 4·55 A., and in the material

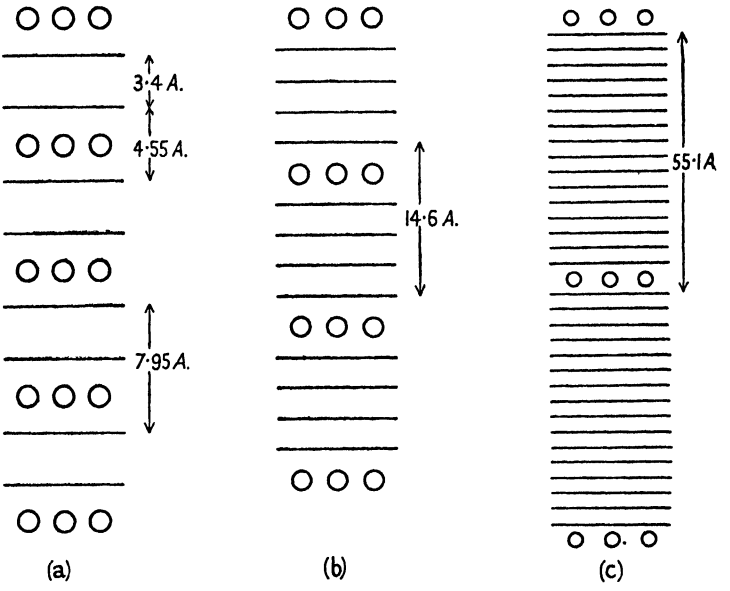


FIG. 130. Structures proposed for 'graphitic salts' (diagrammatic). The circles represent radicals such as SO_4^{2-} or ClO_4^-.

richest in H_2SO_4, with the composition approximately $(C_{24}.SO_4H_2)_n$, there is a layer of SO_4^{2-} ions between alternate pairs of graphite layers (*a*). The other products intermediate between this and graphite have structures of types (*b*) and (*c*). In Fig. 130 a circle represents SO_4^{2-} or ClO_4^-. In the nitric acid and selenic acid compounds the distances corresponding to 4·55 A. are 4·44 and 4·85 A. respectively. The detailed structures of these compounds have not been determined. For example, it is not known whether the graphite layers become charged in the presence of the oxidizing agent or whether the positive charges necessary for electrical neutrality are provided by H^+ ions also adsorbed between the layers.

Carbon Monofluoride

When graphite, previously degassed, is heated in fluorine to temperatures around 400–450° C. fluorine is taken up quietly with the formation of a grey solid with the approximate composition CF. The expansion of the interlayer separation to 8·17 A. shows that the fluorine is contained between the carbon sheets. Here again the characteristic lustre and conductivity of graphite are absent, the material having a specific resistance about 10^5 times that of graphite. On heating to higher temperatures no

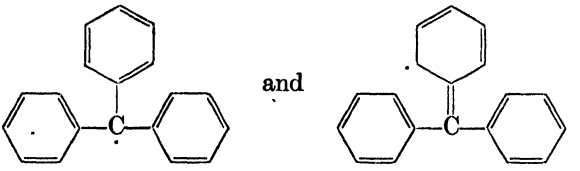
further fluorine enters the lattice, which eventually decomposes into a mixture of various carbon fluorides together with graphite soot—compare the final disruption of 'graphitic acid' into mellitic acid, $C_6(COOH)_6$.

Graphite-potassium 'Alloys'

Finally we may mention the absorption of molten metallic potassium by graphite. As in all the other cases, the graphite layers remain intact but their separation is increased. Two definite compounds may apparently be distinguished: one, the potassium-rich material, copper-red or bronze coloured, of composition C_8K, and the other, steel-blue in colour, of composition $C_{16}K$. The metal may be removed from either by treatment with mercury, leaving graphite. In the former compound there are potassium atoms between all successive graphite layers and in the latter only between alternate pairs of layers.

Free Radicals

The constitution of these compounds presents a problem very similar to that of the stability of the benzene nucleus. Corresponding to the simple ethane molecule, $H_3C—CH_3$, there are numerous substituted ethanes, from $RH_2C—CH_3$ to $R_3C—CR_3$. Certain of these compounds have the remarkable property of dissociating into two free radicals $—CR_3$, in which the carbon atom has a group of seven valency electrons. This dissociation takes place to an appreciable extent only if the substituting groups R are aromatic nuclei, and the stability of the free radical is attributed to resonance with other structures in which the odd electron is situated on other atoms. The radical $(C_6H_5)_3C—$, for example, may resonate between structures of the types

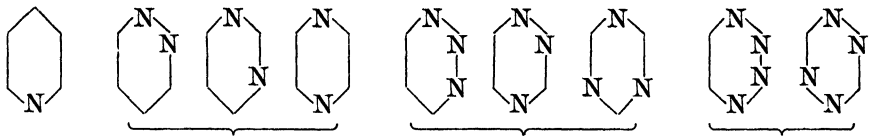


Calculations show that the resonance energy of each free radical $—C(C_6H_5)_3$ is of the order of one-half the C—C single-bond energy, so that little energy is required to break the central C—C bond in $(C_6H_5)_3C—C(C_6H_5)_3$ and form two radicals $—C(C_6H_5)_3$. As would be expected, these free radicals are very reactive owing to the strong tendency of the carbon atom to complete its octet of valency electrons. In the interesting reaction of tri-phenyl-methyl with ether, the octets of the two carbon atoms are completed in different ways:

$$2(C_6H_5)_3C— \rightarrow [(C_6H_5)_3C{:}\ddot{O}{:}C_2H_5]^+ + [(C_6H_5)_3C{:}]^-$$
$$\qquad\qquad\qquad

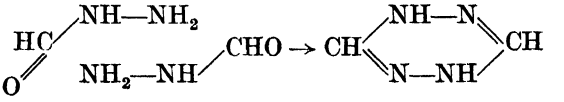
Cyclic Carbon-Nitrogen Compounds

Corresponding to the benzene molecule there are analogous 6-ring molecules in which one or more of the carbon atoms is replaced by nitrogen. In the formulae given below the CH groups at the remaining corners of the rings are omitted.



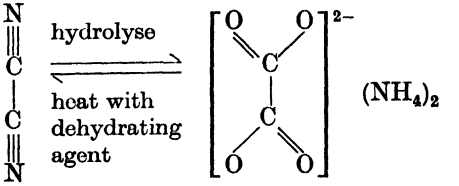
Pyridine Diazines Triazines Tetrazines

A general method of preparing derivatives of these compounds is to condense together molecules of open-chain compounds containing the required C—N skeleton. For example, if formyl hydrazine is heated to 150–200° C. a dihydrotetrazine is formed:



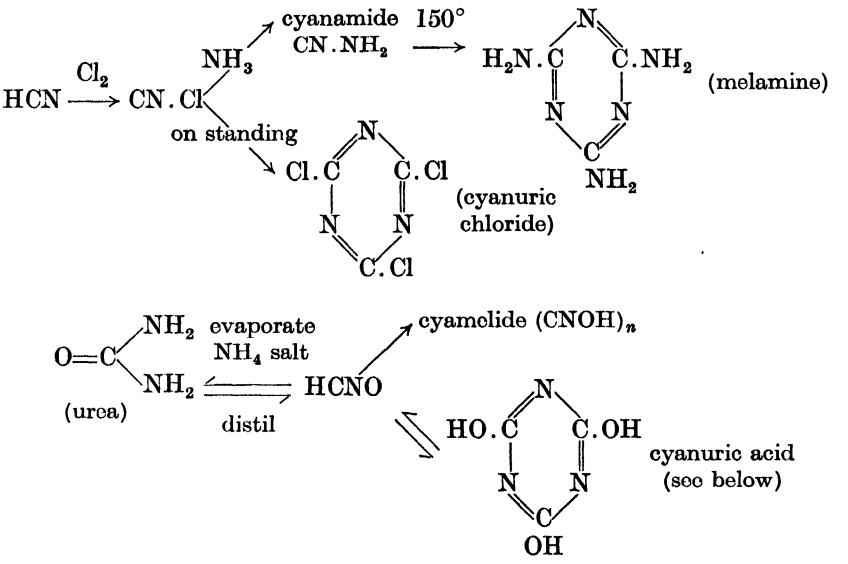
and examples of the formation of molecules containing the cyanuric ring will be found below. The molecules of pyridine, C_5H_5N, and pyrazine, $C_4H_4N_2$, have been shown by electron diffraction to be planar, like the benzene molecule, and the interatomic distances C—C = 1·40 A. and C—N = 1·36 A. show that there is resonance of the same type as in benzene.

The symmetrical cyanuric ring, with alternate CH and N, is of particular interest on account of its connexion with simple cyanogen compounds. Cyanogen $(CN)_2$ and its derivatives show a very strong tendency to polymerize to molecules containing the cyanuric nucleus. Cyanogen itself is often represented with one single and two triple bonds, N≡C—C≡N, but the length of the central C—C bond, 1·36 A., shows that this bond is more nearly a double than a single bond. When cyanogen is prepared by heating (to 450° C.) mercuric cyanide, preferably with the chloride, there is also obtained a quantity of a solid polymer, paracyanogen $(CN)_n$, of which the structure is unknown. In aqueous solution cyanogen hydrolyses to ammonium oxalate, among other products, and it may be prepared by heating this salt with a dehydrating agent:

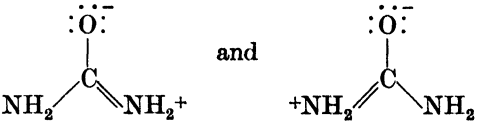


The cyanogen halides polymerize on standing to the 3-fold polymers, the cyanuric halides. Cyanamide is converted into the corresponding

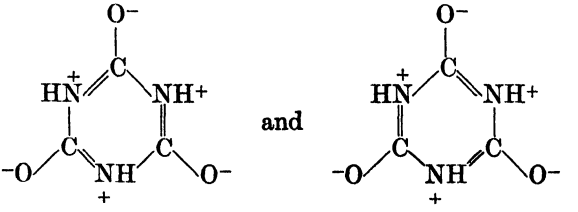
polymer, melamine, on heating to about 150° C. Cyanic acid, however, polymerizes far more readily. If urea is distilled, cyanic acid is formed but polymerizes to cyanuric acid, $(CNOH)_3$, which is a crystalline solid. By rapidly cooling the vapour of the latter cyanic acid may be obtained as a liquid which, above 0° C., polymerizes explosively to cyamelide, a white porcelain-like solid. This latter material is converted into salts of cyanuric acid by boiling with alkalis. These reactions may be summarized as follows:



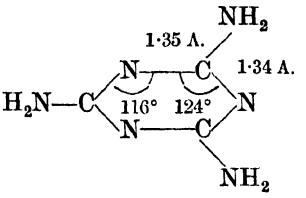
Cyanuric derivatives may be interconverted. Thus if cyanuric bromide is warmed with water, cyanuric acid is formed. The structure of the cyanuric ring has been studied in cyanuric acid, in the azide, and in the cyanuric tricyanamide ion, $[C_3N_3(NCN)_3]^{3-}$. It has the form of a plane hexagon, the C—N distance (*c.* 1·37 A.) indicating resonance of the Kekulé type. Just as in urea we have resonance with the structures



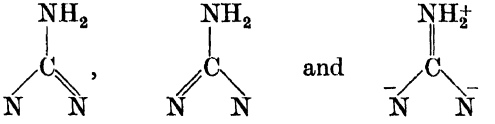
so in cyanuric acid (which is formed from urea) we have



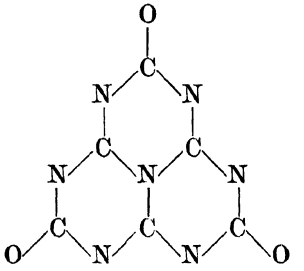
The fact that the C—N distances within and outside the ring are all equal in melamine (cyanuric triamide, $C_3N_6H_6$)



is taken to indicate that there is complete resonance between structures of the types



A more complex C—N ring system, the cyameluric nucleus, is found in the cyamelurate ion, $[C_6N_7O_3]^{3-}$, which is presumably built up of rings



of the same type as the cyanuric ring, but structural studies have so far been confined to the simple C_3N_3 ring.

CARBON FORMING ONE OR TWO BONDS

In this section we have to discuss first the oxides, oxysulphide and disulphide of carbon, and then the metallic cyanides, carbonyls, and carbides.

The Oxides of Carbon

We said in Chapter II that the calculations of resonance energies provided strong support for the idea of resonance between different possible electronic structures of a molecule or other system of atoms. The resonance energy is the difference between the observed heat of formation of the molecule and the heat of formation calculated for a particular bond structure of the molecule on the assumption that bond energies are additive. Carbon monoxide provides a good example of this kind of calculation and is worth considering in some detail. In the original formulation of the molecule as C=O (or $:C::\ddot{O}:$) it is clear that one of the unshared pairs of electrons on the oxygen atom could also be used,

making a triple instead of a double bond: $:\overset{-}{C}:::\overset{+}{O}:$ ($C\overset{\leftarrow}{=}O$, or $\overset{-}{C}\equiv\overset{+}{O}$). The objection to this structure is that it makes the bond polar, whereas the CO molecule has an extremely small (possibly zero) dipole moment.

Now the ordinary C=O in ketones is not simply $-C::\dot{O}:$, for the energy of this bond is 152 k.cals./mole, compared with the estimated value of 98 k.cals./mole for a *normal* C=O bond. We recall that the term normal covalent bond is applied to the hypothetical bond which would be formed between the atoms if there were no difference between the electronegativities of the atoms. The actual C=O bond has some ionic character, and the difference of 54 k.cals./mole between the energy of the actual C=O bond and the hypothetical normal covalent bond is interpreted as resonance energy arising from resonance between $-C::\dot{O}:$ and the ionic form $-\overset{+}{C}:\dot{\overset{\cdot\cdot}{O}}:^{-}$. In carbon monoxide therefore we expect two of the resonating structures to be

$$:\overset{+}{C}:\dot{\overset{\cdot\cdot}{O}}:^{-} \qquad \text{and} \qquad :C::\dot{O}:$$

A third structure mentioned above, $:\overset{-}{C}:::\overset{+}{O}:$, must also be important, for the dipole moment has still to be accounted for. Moreover, the heat of formation of CO from atoms is 210 k.cals./mole, 58 k.cals./mole greater than the C=O bond energy in ketones. The total resonance energy of CO relative to the *normal* C=O bond is therefore 112 k.cals./mole, so that the stability of this molecule is attributed to the resonance between

$$(1)\ :\overset{+}{C}:\dot{\overset{\cdot\cdot}{O}}:^{-}, \qquad (2)\ :C::\dot{O}:, \qquad \text{and} \qquad (3)\ \overset{-}{C}:::\overset{+}{O}:$$

The interatomic distance in CO is 1·13 A., compared with 1·43, 1·24, and 1·11 A. for single, double, and triple bonds respectively, but if, as Pauling suggested, the first two of these three values are reduced by 0·18 and 0·09 A. respectively to allow for the fact that the carbon valence shell is incomplete (giving values 1·25 and 1·15 A. for structures (1) and (2)), then the observed distance would be accounted for as well by (2) or (3) separately as by the resonating structure. The arithmetic mean of 1·25, 1·15, and 1·11 A. is 1·17 A., not far from the observed distance.

In the linear CO_2, CS_2, and COS molecules the interatomic distances are: C—O, 1·15±0·02 A., and C—S, 1·55±0·02 A. These distances also indicate resonance between various forms involving multiple bonds. For CO_2 these would include

$$:\overset{+}{O}:::C:\dot{\overset{\cdot\cdot}{O}}:^{-} \quad \text{and the corresponding} \quad :\dot{\overset{\cdot\cdot}{O}}:^{-}C:::\overset{+}{O}:$$

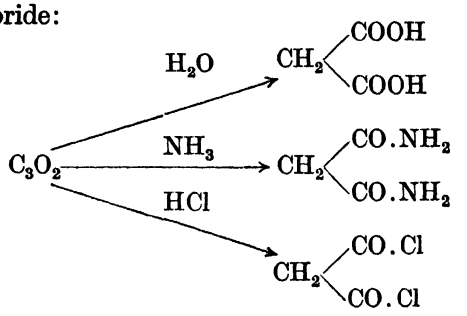
and the structures

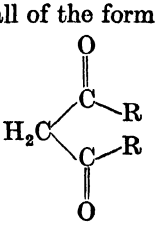
$$:\dot{O}::C:\dot{\overset{\cdot\cdot}{O}}:^{-} \qquad \text{and} \qquad :\dot{\overset{\cdot\cdot}{O}}:^{-}\ \overset{+}{C}::\dot{O}:$$

as in CO, in addition to the simple structure $:\dot{\overset{\cdot\cdot}{O}}::C::\dot{\overset{\cdot\cdot}{O}}:$. Isoelectronic

with these molecules are the nitrogen analogues [N—C—O]⁻ and [N—C—S]⁻. The CN^- ion, isoelectronic with the CO molecule, is dealt with below.

The third oxide of carbon, the so-called suboxide C_3O_2, is an interesting compound. It is a gas at ordinary temperatures (it boils at +6° C.) and may be prepared by heating malonic acid or its diethyl ester with a large excess of phosphorus pentoxide at 300° C. Its preparation from, and conversion into, compounds containing the —C—C—C— nucleus are consistent with its structure, O—C—C—C—O. The action of water regenerates malonic acid, ammonia yields malonamide, and HCl malonyl chloride:





The molecule of C_3O_2 is linear, and the observed interatomic distances suggest resonance of the simple form $:\ddot{O}=C=C=C=\ddot{O}:$ with $:\overset{+}{O}\equiv C-C\equiv C-\overset{\cdot\cdot\ -}{\underset{\cdot\cdot}{O}}:$ and $:\overset{-\ \cdot\cdot}{\underset{\cdot\cdot}{O}}-C\equiv C-C\equiv\overset{+}{O}:$. It is noteworthy that resonance with structures of this type could occur in carbon oxides of the general formula C_nO_2 only if n is odd, and this has been suggested as the reason for the existence of CO_2, C_3O_2, and possibly C_5O_2 rather than C_2O_2, C_4O_2, and so on.

CYANIDES

The last three sections in this chapter will deal with compounds containing the isoelectronic groups CC^{2-}, CN^-, and CO, though not in this order. The C_2^{2-} ion occurs in a number of carbides; the CO molecule utilizes the unshared pair of electrons on the carbon atom to form bonds to metals, giving rise to the metallic carbonyls. The CN^- ion is found in the ionic cyanides of the alkali metals, but we also find the CN group attached by a covalent bond either from the carbon or from the nitrogen atom: —C≡N: or :C≡N—. In this way, for example, the organic cyanides and isocyanides, R.CN and R.NC, arise. There is the further possibility that the CN group is attached at both ends by covalent bonds, —C≡N—, and this may be the case in a number of metallic cyanides.

We shall discuss the metallic cyanides in the following groups:

(*a*) Simple ionic cyanides.

(*b*) Essentially covalent cyanides $M(CN)_n$.

(*c*) Complex cyanides containing discrete $[M(CN)_n]$ ions.

(*d*) Other complex cyanides.

We should remark here that it is not yet possible to give a very satisfactory survey of the structures of cyanides owing to the scarcity of experimental data on these compounds.

(a) Simple Ionic Cyanides

The only metals known to form ionic cyanides are the alkali metals, Na to Cs, and thallium (Tl^I). The structures of the alkaline earth cyanides have not yet been investigated. The general structural relations between

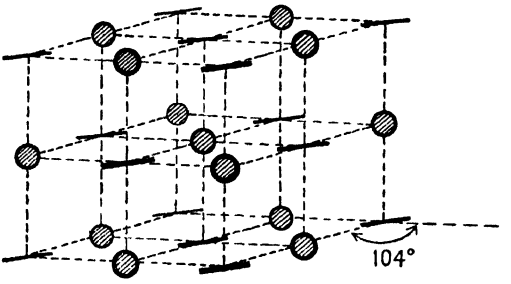


FIG. 131. The structure of the low-temperature form of NaCN. The CN^- ions are indicated by short straight lines.

metallic cyanides would appear to be similar to those between halides. The only halides of metals other than the alkalis which form essentially ionic 3-dimensional complexes are the fluorides. The chlorides, bromides, and iodides form more covalent chain, layer, or molecular lattices. These changes in structure type may be attributed, at least in part, to the decreasing electronegativity of the halogens as we go from F to I. An analogous change in structure type is found in cyanides, going from the most electropositive metals, the alkalis, to the metals of later groups or B sub-groups. Unfortunately very little is known of the structures of these cyanides, but it is likely that chain, layer, and molecular types will be found (see (*b*)).

At ordinary temperatures NaCN, KCN, and RbCN crystallize with the rock-salt structure and CsCN and TlCN with the caesium chloride structure. The supposition that in these crystals the CN^- ion is freely rotating, thereby acquiring spherical symmetry, has been checked by measurements and calculations of the intensities of the X-ray reflections. The effective radius of the rotating CN^- ion is about 1·92 A., intermediate between those of Cl^- (1·81 A.) and Br^- (2·00 A.). Accordingly, NaCN, for example, forms continuous series of mixed crystals with NaCl or with NaBr, but it does not form mixed crystals with NaI.

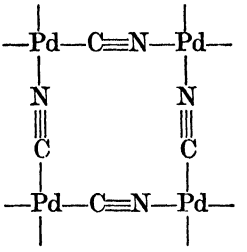
At lower temperatures rotation of the CN^- in this way ceases—rotation about the C—N bond would not, of course, be detectable—and the structure of the low-temperature form of NaCN has been studied in detail. This salt changes, reversibly, at about −10° C. into a form with lower (monoclinic) symmetry, in which the C—N groups are all arranged parallel to one another. The structure of this form is illustrated in Fig. 131, and

its close relation to the rock-salt structure is evident. It is interesting to compare with this structure that of CaC_2 (p. 457), which is related to the rock-salt structure in a similar way. The C—N distance in the CN^- ion was determined as 1·05 A.

(b) Essentially Covalent Cyanides

The structure of only one non-ionic metallic cyanide appears to have been studied, that of silver cyanide. In this crystal there are infinite chains of alternate Ag atoms and CN groups so that the cyanide group is attached at both ends to metal atoms. These chains are arranged parallel in hexagonal packing. The Ag—Ag distance along the chains (5·26 A.) is consistent with this —Ag—C—N—Ag— bonding, for if we take the C—N distance to be about 1·15 A. (as in $K_4Mo(CN)_8.2H_2O$), we should have 4·11 A. for the sum of the Ag—C and Ag—N distances. Now the radius of 2-covalent Ag is given by Pauling as 1·39 A., being derived from the Ag—O distance of 2·05 A. in Ag_2O using 0·66 A. as the tetrahedral radius of oxygen. Using for the latter, however, the value 0·74 A. (see p. 81), we should obtain 1·31 A. for 2-covalent Ag, which with the values 0·77 A. and 0·74 A. for C and N respectively would give 4·13 A. as the sum of Ag—C and Ag—N, in good agreement with the observed value. (See also the ion $[NC—Ag—CN]^-$, below.)

Simple layer structures are possible for the cyanides of metals like Pd^{II}, Pt^{II}, Ni^{II}, and Cu^{II} which form four planar bonds. With the suggested arrangement shown below for $Pd(CN)_2$ compare the structures of the gold



cyano-compounds of the type $[R_2AuCN]_4$ referred to on p. 509. It is preferable to defer further discussion of these simple metallic cyanides until more structural investigations have been made.

(c) Complex Cyanides containing Discrete $M(CN)_n$ Ions

Many metallic cyanides redissolve in the presence of excess CN^- ions with the formation of complex metallo-cyanide ions $[M^x(CN)_m]^{-(m-x)}$— compare the formation of ammino-ions $[M^x(NH_3)_m]^{+x}$ in the presence of excess ammonia. In the metallo-cyanide complexes one extra electron is required for each CN group, and since the coordination number m is greater than the electrovalency x of the metal, these ions carry a negative charge of $(m-x)$. The ammino-ions carry the same positive charge as the free M^x ions, both electrons for the M—NH_3 bond being provided by

the N atom. A number of crystalline salts containing metallo-cyanide ions have been studied by the X-ray method, and the following examples illustrate some of the possible arrangements of 2-, 4-, 6-, and 8-covalent bonds.

In $K[Ag(CN)_2]$ there are linear $[NC—Ag—CN]^-$ ions with the same configuration of silver bonds as is found in the $[H_3N—Ag—NH_3]^+$ ion in tetrammino-silver sulphate, $[Ag(NH_3)_2]_2SO_4$. The bond lengths in the cyanido-ion are:

$$[N—C—Ag—C—N]^-.$$
$$2{\cdot}13 \quad 1{\cdot}15 \text{ A.}$$

The salt $K_3[Cu(CN)_4]$ is interesting from the point of view of the stereochemistry of 4-covalent cuprous copper. The $[Cu(CN)_4]^{3-}$ ion has a tetrahedral configuration like the $Ni(CO)_4$ molecule with which it is isoelectronic. In the isomorphous tetrahydrates of $BaPt(CN)_4$, $BaPd(CN)_4$, and $BaNi(CN)_4$ the complex ions are planar, the metals forming coplanar dsp^2 bonds (see p. 86).

Many salts containing ions of the type $[M(CN)_6]$ have been prepared, the best known being the simple ferro- and ferri-cyanides. The ferrocyanides of the alkali and alkaline-earth metals form transparent pale yellow crystals soluble in water, containing the simple $[Fe(CN)_6]^{4-}$ ion which exists in the free acid $H_4Fe(CN)_6$, but the ferrocyanides of the transition metals are highly coloured insoluble compounds which are structurally quite different from the simple soluble ferrocyanides. These form the subject of the next section. No simple ferrocyanide has yet been thoroughly studied, but the octahedral configuration of certain hexacyanido-ions has been demonstrated in a number of cobaltammines. The salts $[Co(NH_3)_6][Co(CN)_6]$, $[Co(NH_3)_6][Cr(CN)_6]$, and $[Co(NH_3)_5H_2O][Fe(CN)_6]$ all crystallize with the same structure as $[Ni(H_2O)_6][SnCl_6]$ which has already been mentioned (p. 375), in which the octahedral ions pack together in much the same way as the Cs^+ and Cl^- ions in caesium chloride.

Molybdenum and tungsten are notable for forming complex octocyanides of the type $K_4M(CN)_8.2H_2O$, and the structure of the molybdenum compound has been determined by X-ray methods. The eight CN groups in the $Mo(CN)_8^{4-}$ complex ion are arranged at the apices of a dodecahedron around the metal atom, as shown in Fig. 132. The C—N bonds are collinear with the Mo—C bonds, their mean lengths being: Mo—C, 2·15, and C—N, 1·15 A. The orbitals used in these octa-covalent complexes are presumably the four $4d$, one $5s$, and three $5p$ orbitals, but this spatial arrangement of bonds had not been predicted and no theoretical treatment of such dodecahedral bonds has been given. It is of interest that the same

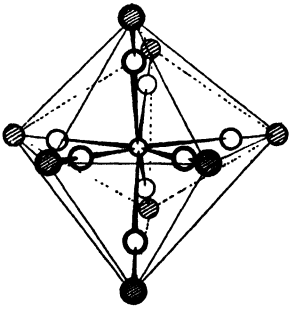


FIG. 132. The configuration of the $[Mo(CN)_8]^{4-}$ ion. The shaded circles represent N atoms.

geometrical arrangement of eight neighbours is found in $ZrSiO_4$, in which each Zr^{4+} ion is surrounded by eight O neighbours.

(d) Other Complex Cyanides

When cyanides of certain metals, e.g. Fe, Co, Mn, Cr, are redissolved by the addition of excess alkali cyanide solution, complex ions $[M(CN)_6]$ are formed. The alkali and alkaline-earth salts of these complexes are fairly soluble in water and crystallize well. The ferrocyanides and chromocyanides (e.g. $K_4Fe(CN)_6$ and $K_4Cr(CN)_6$) are pale yellow in colour. The ferricyanides and manganicyanides, e.g. $K_3Fe(CN)_6$ and $K_3Mn(CN)_6$, are deeper in colour and are made by oxidation of the $M(CN)_6^{4-}$ salts. Solutions of the manganese and cobalt $M(CN)_6^{4-}$ ions oxidize spontaneously in the air to the $M(CN)_6^{3-}$ salts. When solutions of these complex cyanides are added to solutions of salts of transition metals or Cu^{II}, insoluble compounds are precipitated in many cases. Thus addition of potassium ferrocyanide to ferric salt solutions gives a precipitate of Prussian blue, and cupric salts produce brown cupric ferrocyanide. These precipitates are usually flocculent and may form colloidal solutions on washing. When dried they are very stable towards acids, whereas alkali ferrocyanides yield the acid $H_4Fe(CN)_6$ on treatment with dilute HCl. Such compounds are obviously quite different in structure from the simple soluble ferrocyanides.

All the compounds variously described as Turnbull's blue, from a ferrous salt and ferricyanide, Prussian blue, from a ferric salt and ferrocyanide, and 'soluble Prussian blue', have the composition $KFeFe(CN)_6.H_2O$, though there may be more water associated with the material if it is in colloidal form. On account of their methods of preparation Turnbull's blue was originally formulated $KFe^{II}[Fe^{III}(CN)_6]$ and Prussian blue as $KFe^{III}[Fe^{II}(CN)_6]$, but there was no conclusive chemical evidence for these formulae. For example, the action of NaOH on Prussian blue gives ferric hydroxide and $Na_4Fe(CN)_6$, whereas ammonium carbonate yields $(NH_4)_3Fe(CN)_6$. It appears that there is only one compound $KFeFe(CN)_6$, and we shall refer to it as Prussian blue.

The reactions of the brown copper ferrocyanide, $Cu_2Fe(CN)_6.nH_2O$ (n probably 7 or 10), formed from a cupric salt and $K_4Fe(CN)_6$, show that it is not a simple salt. For example,

$$Cu_2Fe(CN)_6.nH_2O \xrightarrow{\text{boil with } Ca_2Fe(CN)_6} CaCuFe(CN)_6$$

$$Cu_2Fe(CN)_6.nH_2O \xrightarrow{\text{dilute } NH_4OH} [Cu(NH_3)_4][CuFe(CN)_6].H_2O$$

suggesting that the brown copper compound is a salt of a $[CuFe(CN)_6]^{2-}$ anion, viz. $Cu[CuFe(CN)_6]$.

A preliminary X-ray study of Prussian blue and some related com-

pounds has been made. In ferric ferricyanide (Berlin green), $FeFe(CN)_6$, Prussian blue, $KFeFe(CN)_6$, and the white insoluble potassium ferrous ferrocyanide, $K_2FeFe(CN)_6$, there is the same arrangement of Fe atoms on a cubic face-centred lattice. In Fig. 133 (*a*), (*b*), and (*c*), ferrous atoms are distinguished as shaded and ferric as open circles—see, however, the

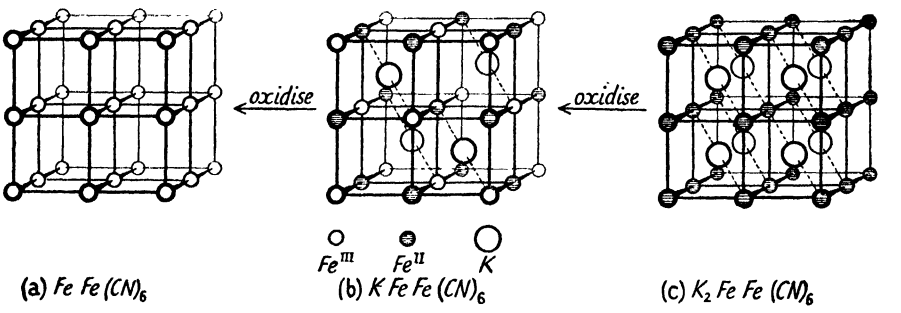


FIG. 133. The relationship between (*a*) Berlin green, (*b*) Prussian blue, and (*c*) potassium ferrous ferrocyanide.

remarks below. In (*a*) all the iron atoms are in the ferric state. In $KFeFe(CN)_6$, (*b*), one-half the atoms are Fe^{II} and the others Fe^{III}, and alkali atoms are taken up to maintain electrical neutrality. These are at the centres of alternate small cubes, and the water molecules presumably occupy similar positions. Lithium and caesium, with very small and very large ions respectively, do not form compounds with this structure. In (*c*), with all the iron in the ferrous state, every small cube contains an alkali metal atom. Compounds with the Prussian blue structure include $KCuFe(CN)_6$, $Cu_2Fe(CN)_6$—which contains no alkali ions—$KMnFe(CN)_6$, $KCoFe(CN)_6$, $KNiFe(CN)_6$, and $KFeRu(CN)_6$ (ruthenium purple). The compound with the empirical formula $KMn(CN)_3$, prepared from a manganous salt and KCN, is green in colour and very insoluble, suggesting that it is really $K_2[MnMn(CN)_6]$ with the same type of 3-dimensional complex as $[FeFe(CN)_6]$ in Prussian blue.

It must be remembered that we cannot distinguish between ferric and ferrous atoms by X-ray methods and also that the CN groups were not definitely located. It is reasonable, however, to assume that the CN groups lie along the cube edges, and if both the C and N are linked to Fe atoms we should have an infinite 3-dimensional complex based on Fe—C—N—Fe rather than discrete Fe atoms and $Fe(CN)_6$ groups. This would seem to be in accord with the insolubility of these complex cyanides and the fact that both ferri- and ferro-cyanides can be obtained from Prussian blue (see above). Magnetic data on Prussian blue have been interpreted to mean that half of the iron atoms form essentially covalent and the others ionic bonds—the former being presumably the iron atoms joined to carbon. A more detailed study of the structures of these compounds is desirable.

METALLIC CARBONYLS

A number of metals form compounds with carbon monoxide, $M(CO)_n$, termed carbonyls, and there are also compounds to which the rather unsatisfactory names of carbonyl hydrides and carbonyl halides are applied. The compounds of the alkali metals and the alkaline-earths (Li, Na, K, Rb, Ca, Sr, Ba) are apparently quite different in structure from those of the elements of the sixth, seventh, and eighth Periodic Groups, and little is known of their constitution except in the case of $K_6(CO)_6$. This compound, long known as a by-product in the old method of preparation of metallic potassium by reduction of the carbonate with carbon, is actually the potassium salt of hexahydroxybenzene, which is produced from it by treatment with dilute HCl. Certain of the salts of the elements of the I B sub-group combine with CO to form, for example, $CuCl(CO).2H_2O$, $Ag_2SO_4.CO$, and AuCl(CO), of which the latter is a comparatively stable volatile compound. In what follows we shall confine our attention to the carbonyls and related compounds of the metals of the later Periodic Groups. The following table gives some idea of the formulae of these compounds.

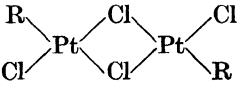
TABLE 24

Periodic Group	*Element*	*Carbonyls*	*Carbonyl hydrides*	*Carbonyl halides*
VI	Cr, Mo, W	$M(CO)_6$	..	..
VII	Re	$[Re(CO)_5]_2$	..	$Re(CO)_5X$
VIII	Fe	$Fe(CO)_5$	$Fe(COH)_2(CO)_2$	$Fe(CO)_5X_2$
		$Fe_2(CO)_9$	..	$Fe(CO)_4X_2$
		$[Fe(CO)_4]_3$	..	$Fe(CO)_2X_2$
				$Fe(CO)_2X$
				$[Fe(CO)_3X_2]_3$
	Co	$[Co(CO)_4]_2$	$Co(COH)(CO)_3$	$Co(CO)X_2$
		$[Co(CO)_3]_4$	..	..
	Ni	$Ni(CO)_4$	..	..

In the formulae of the carbonyl halides X represents Cl, Br, or I; the fluorides have not yet been prepared. Carbonyls of Ru, Os, and Ir also are known, and also carbonyl halides of these elements and of Rh, Pd, and Pt. We cannot give here any preparative details or describe the properties and reactions of these compounds. For information of this kind the reader is referred to the accounts by Blanchard and Welch, in which references will be found to the numerous original papers. Suffice it to say that the carbonyls may be prepared by the direct action of CO on the metal. Special preparation of the metal may be necessary and in some cases a catalyst, and in general the CO must be at a considerable pressure. Nickel carbonyl is exceptional in that it is prepared by the action of CO at atmospheric pressure on metallic nickel, a reaction utilized in the Mond process for the purification of nickel. The polynuclear carbonyls are prepared photosynthetically, by heating the simple

compounds, or indirectly (see below). The carbonyl hydrides are prepared either from the carbonyls or sometimes by the action of a mixture of CO and hydrogen on the metal. Cobalt in this way gives $Co(CO)_3COH$.

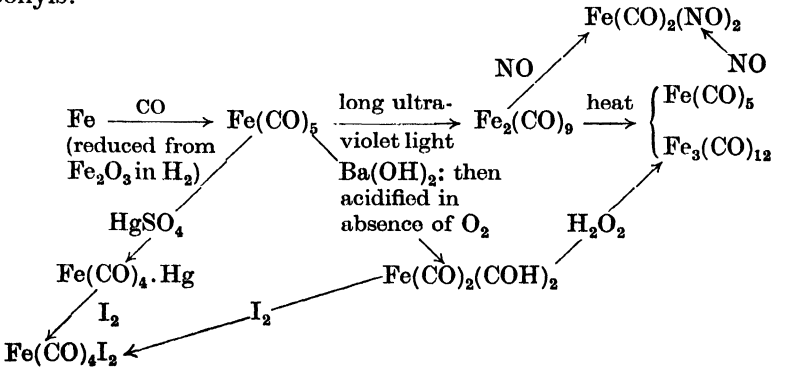
There are numerous compounds containing halogens and CO. They may be formed directly from the halides by the action of CO (e.g. CO and anhydrous CoI_2 give $Co(CO)I_2$) or, in the case of iron, indirectly from the carbonyls or carbonyl hydrides. All the elements of Group VIII except Ni are known to form carbonyl halides (see Table 24, above). Although carbonyls of Pd and Pt are not known, the lower halides of these elements combine with CO to form compounds with the empirical formulae $PdCl_2.CO$, $PtCl_2.CO$, and $PtCl_2(CO)_2$. The latter compound is monomeric and a non-electrolyte, but $PtCl_2.CO$, which is a solid melting at 195° C., is probably dimeric and analogous to the compounds of $PtCl_2$ with arsines and phosphines, of the general type



All the carbonyl halides are decomposed by water, but their stability towards water increases from the chloride to the iodide.

A further group of compounds, the nitrosyl carbonyls, results from the action of NO on the polynuclear carbonyls of iron and cobalt. Like the carbonyls the nitrosyl carbonyls react with neutral molecules such as organic nitrogen compounds and with halogens, and in such reactions CO, and not NO, is replaced. Thus $Fe(CO)_2(NO)_2$ with iodine gives $Fe(NO)_2I$. No reaction has yet been detected between NO and the much more stable hexacarbonyls of Cr, Mo, and W. Whereas Co and Fe form respectively $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$, $Ni(CO)_4$ does not form a nitrosyl carbonyl of this type—for the reason see below—and reacts with NO only in the presence of water. A blue compound, Ni(NO)OH, is then formed which is soluble in water and possesses reducing properties. It is regarded as a compound of univalent nickel and is obviously quite different in type from the nitrosyl carbonyls of cobalt and iron.

The following scheme summarizes some of the reactions of the iron carbonyls:



The Structures of the Carbonyls and Related Compounds

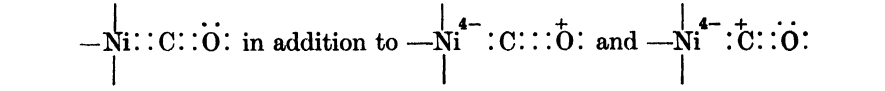
Considerable theoretical interest attaches to the structures of these compounds on account of their peculiar formulae, e.g. $Fe(CO)_5$, $Fe_2(CO)_9$, and so on. The formulae of the simple carbonyls are easily accounted for if we assume that the CO is directly attached to the metal atom and contributes the two electrons required for the single covalent bond. We then find that the effective atomic numbers of the metals become those of inert gases, thus:

$Ni(CO)_4$ . .	$28+8=36$ (krypton)
$Fe(CO)_5$ . .	$26+10=36$
$Cr(CO)_6$ . .	$24+12=36$
$Mo(CO)_6$ . .	$42+12=54$ (xenon)
$Ru(CO)_5$ . .	$44+10=54$
$W(CO)_6$ . .	$74+12=86$ (radon)

We also see why cobalt, with an odd atomic number (27), forms no mononuclear carbonyl but only $Co_2(CO)_8$ and $Co_4(CO)_{12}$. This simple idea, that the metal atom acquires a share in sufficient additional electrons to acquire an inert gas configuration, may be extended to the nitrosyl carbonyls and carbonyl hydrides. The NO and COH groups each contain eleven valency electrons, i.e. one more than CO, and if we assume that the metal acquires a share in three electrons for each NO or COH attached to it, their formulae are such as to give the Co and Fe atoms the krypton configuration as in $Ni(CO)_4$:

$Ni(CO)_4$	$28+8=36$
$Co(CO)_3NO$, $Co(CO)_3COH$ . .	$27+6+3=36$
$Fe(CO)_2(NO)_2$, $Fe(CO)_2(COH)_2$ . .	$26+4+6=36$

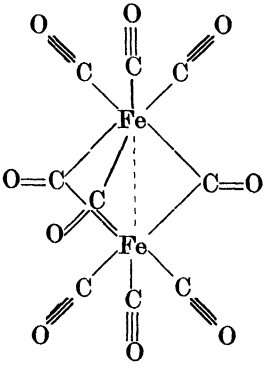
It has been shown by elcctron diffraction measurements that in all these molecules the four groups attached to the metal atoms are arranged tetrahedrally. This eliminates the old formulae $Co(CO)_4H$ and $Fe(CO)_4H_2$ for the carbonyl hydrides. The molecule $Ni(CO)_4$ may be regarded as derived from a neutral Ni atom with a filled $3d$ shell and not from a Ni^{2+} ion. The bonds therefore utilize hybrid $4s4p^3$ orbitals and are thus tetrahedrally arranged as in $[Zn(CN)_4]^{2-}$. The zero dipole moment of $Ni(CO)_4$ shows that the atoms Ni—C—O are collinear, for if there were free rotation of bent groups there would be a resultant dipole moment, as in $C(OC_2H_5)_4$. The interatomic distances in this and similar molecules suggest, however, that the above view of their structures is an over-simplification. Whereas the C—O distance is 1·15 A., agreeing well with that in CO itself (1·13 A.), the Ni—C distance is only $1{\cdot}82\pm0{\cdot}03$ A. compared with the value 2·00 A. to be expected if the tetrahedral radius of Ni is taken as 1·23 A. To account for this short Ni—C distance Pauling suggests that structures involving double bonds from Ni to C are to be taken into consideration:



In a previous chapter we have seen that there is probably resonance between a number of structures in the NO molecule, and this is likely to be the case also in the nitrosyl carbonyls.

The carbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ have all been shown to possess regular octahedral configurations. They form colourless crystalline solids which are appreciably more stable towards chemical reagents and heat than the simple Fe and Ni carbonyls, and they may be sublimed without decomposition. In iron pentacarbonyl, $Fe(CO)_5$, it has been shown by electron diffraction that the CO groups are arranged around the metal atom at the apices of a trigonal bipyramid.

Of the more complex carbonyls only $Fe_2(CO)_9$ has been studied in detail. This compound is a solid, and its structure has been determined by means of X-ray diffraction. It had previously been suggested that in the polynuclear carbonyls both the unshared pairs of electrons in :C:::O: were utilized to join together the metal atoms, forming a linear arrangement —M:C:::O:M—. This is not, however, so in $Fe_2(CO)_9$ where the carbon atoms of three of the CO groups form bonds $\begin{matrix}Fe\\Fe\end{matrix}\!\!>\!C{=}O$ as in ketones, and the C—O distance in these groups (*c.* 1·3 A.) is comparable with that in ketones, and much larger than that (1·15 A.) in the remaining six CO groups. Although at first sight the Fe atoms in this molecule would appear to be forming six bonds, it is fairly certain that there is also a



bond between the two Fe atoms, for the following reasons. The effective atomic number of the Fe atoms would be 35 (26+6+3) without such an Fe—Fe bond, but 36 if the odd electrons on the Fe atoms are shared. This would account both for the diamagnetism of the compound and for the short Fe—Fe distance of 2·64 A. which is exactly twice the 'metallic radius' of iron for coordination number 8 (see Chapter XVII). The orbitals used will presumably be seven d^3sp^3, the fourteen bonding electrons being those shown below.

1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*
2	2	6	2	6	4+	6	2	6

The arrangement of seven bonds found in $Fe_2(CO)_9$ is similar to that found for the Zr—F bonds in $(NH_4)_3ZrF_7$ and for the metal-oxygen bonds in oxides with the A—La_2O_3 structure (see p. 113).

METALLIC CARBIDES

Many metals form carbides M_xC_y which are prepared either by direct union of the elements, by heating the metal in the vapour of a suitable hydrocarbon, or by heating the oxide or other compound of the metal with carbon. A study of their chemical and physical properties shows that these carbides may be divided into three main groups, and we shall show that this classification is in accord with what is known of their structures. Since these substances exist only in the solid state they provide a good illustration of the way in which X-ray crystallography can supplement purely chemical studies. We may recognize the following groups of carbides:

(1) The interstitial carbides of transition metals, particularly of the IVth, Vth, and VIth Periodic Groups.

(2) A less well-defined group of carbides comprising those of metals of Groups VII and VIII and also some of those of elements of Group VI.

(3) The salt-like carbides, chiefly those of metals of the earlier Periodic Groups (I to III, including the rare-earths).

We shall not deal here with the interstitial carbides. As their name implies, these compounds are derived from metals by placing the small carbon atoms in the interstices of the (usually close-packed) metal lattice. They have certain of the characteristic properties of metals together with extraordinary hardness and infusibility. On account of the close relation between their structures and those of the parent metals, and also because interstitial hydrides, borides, and nitrides are precisely similar structurally to the carbides, we shall find it more convenient to describe the interstitial structures in Chapter XVII after we have considered the structures of the metals themselves. It will be clear that if the carbon atoms are to fit into the holes between the atoms in a metal without seriously distorting its structure there will be a lower limit to the radius of the metal atom. In a close-packed structure the largest holes for the interstitial atoms are those between six metal atoms ('octahedral holes'), and just as in ionic crystals the radius ratio of two ions must lie between certain values for 6-coordination, so similar considerations will apply to these interstitial compounds. Accordingly we should expect interstitial carbides to be formed by the larger metals, with radii greater than about 1·3 A., but that metals with smaller atomic radii would form carbides with structures not simply related to those of the pure metals. The Goldschmidt radii (for coordination number 12) of a number of metals are set out in the accompanying table. The metals to the left of the vertical line form interstitial carbides; those to the right (Fe, Co, Ni, Cr, and Mn)

form carbides with structures which are not closely related to those of the metals.

Ti	1·47	V	1·35	Mo	1·40	Cr	1·29 A.
Zr	1·60	Nb	1·47	W	1·41	Mn	1·37*
Hf	1·59	Ta	1·47			Fe	1·26
Th	1·80					Co	1·25
						Ni	1·25

* The crystal structures of the forms of Mn are complex. The interatomic distances are very varied, and the distances to the twelve nearest neighbours range from 2·24–2·90 A. in α-Mn and from 2·365–2·675 in β-Mn.

The carbides of these latter metals do not possess the extreme properties of the interstitial carbides. Whereas, for example, titanium carbide is not attacked by water or HCl even at 600° C., these carbides dissolve in dilute acids or in some cases are attacked by water. Thus Mn_3C is decomposed by water yielding equal volumes of methane and hydrogen, while Fe_3C and Ni_3C with HCl yield mixtures of hydrogen and hydrocarbons—both gaseous, liquid, and solid—and even free carbon. It is not known why a carbide like cementite (Fe_3C) should yield such a complex mixture of products on hydrolysis since the carbon is present in the crystal as discrete atoms (see the structure, p. 570). We shall return to the question of the relation of the products of breakdown of the crystal to its structure when we come to the third class of carbides. The carbide Cr_3C_2 has a rather interesting structure in which every carbon atom is surrounded by six Cr atoms forming a trigonal prism around it (C—Cr = 2·02–2·07 A.) and is also at a distance of only 1·665 A. from two other C atoms. The carbon atoms thus form a sort of chain throughout the crystal with C—C distances only a little larger than those in an ordinary aliphatic carbon chain. In this respect Cr_3C_2 resembles FeB, in which there are rather similar boron chains embedded in a lattice of iron atoms, and $CoSi_2$, in which silicon chains may be distinguished. The carbon chains in Cr_3C_2 may be compared with the C_2^{2-} ions in certain carbides to be described shortly and also with the graphite layers in the peculiar potassium-graphites described on p. 440.

The carbides of the third class are entirely different in nature from the above compounds which in their opacity, conductivity, and other physical properties have so much in common with metals and alloys. The more electropositive metals form carbides which have many of the properties associated with ionic crystals. They form colourless, transparent crystals which, at ordinary temperatures, do not conduct electricity. They are decomposed by water or dilute acids, and since the negative ions are unstable, hydrocarbons are evolved. According to the type of C_x^{n-} ion present in the crystal we may divide these carbides into two main groups:

(*a*) Those containing discrete C atoms (or C^{4-} ions).

(*b*) Those in which C_2^{2-} ions may be distinguished.

(There is no proof yet of more complex carbon anions in ionic carbides, but the fact that Mg_2C_3 on hydrolysis yields chiefly allylene,

CH_3—C≡CH, has been taken to suggest the presence of C_3^{4-} ions in this crystal. It is interesting that MgC_2, which may be prepared by the action of acetylene on $Mg(C_2H_5)_2$ and yields acetylene on hydrolysis, is unstable at high temperatures and breaks down into Mg_2C_3 and carbon.)

Carbides of type (*a*) yield CH_4 on hydrolysis. Examples are Be_2C, with the anti-fluorite structure, and Al_4C_3. The structure of the latter is rather

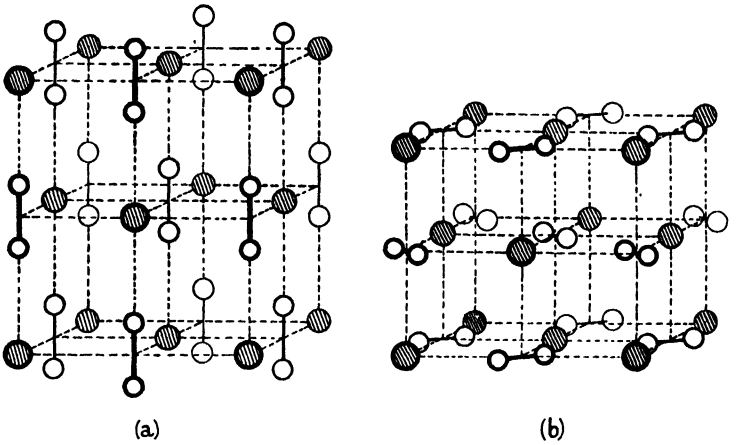


FIG. 134. The CaC_2 (*a*) and ThC_2 (*b*) structures.

more complex and its details do not concern us here. It is sufficient to note that each carbon atom is surrounded by Al atoms at distances from 1·90 to 2·22 A., the shortest C—C distance being 3·16 A. As in Be_2C therefore there are discrete C atoms, accounting for the hydrolysis to CH_4.

The carbides MC_2 of class (*b*) which have been studied up to the present crystallize with one of two structures, illustrated in Fig. 134. Both of these structures may be regarded, from the geometrical point of view, as derived from the rock-salt structure by replacing the Cl^- ion by the C_2^{2-} ion. In each case the symmetry is lowered to tetragonal, in the one case with axial ratio greater than, and in the other less than, unity. The presence of the C_2^{2-} ions in CaC_2 obviously accounts satisfactorily for the formation of C_2H_2 on hydrolysis and of $Br_3C.CBr_3$ on bromination, but it is not clear why we get products other than acetylene from other carbides with these structures. An approximate idea of the composition of the products of hydrolysis of the rare-earth carbides and of ThC_2 is given by the following figures:

	CaC_2 *structure*	ThC_2 *structure*
	LaC_2 CeC_2 PrC_2 NdC_2	ThC_2
C_2H_2	*c.* 70%	50%
C_2H_4	← Small quantity →	
CH_4	20–30%	30%
H_2	None	20%

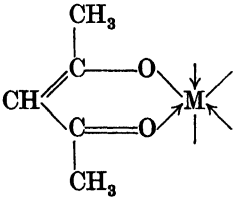
A reasonable suggestion is that if the valency of the metal in the carbide is different from that in the resulting hydroxide (e.g. $Ce(OH)_3$, $Th(OH)_4$), then hydrogen may be liberated and other hydrocarbons arise from secondary reactions between C_2H_2 and H_2. This is consistent with the formation of C_2H_2 alone from CaC_2, since the calcium is divalent both in the carbide and after hydrolysis, and with the fact that the carbides $Al_2(C_2)_3$ and $Ce_2(C_2)_3$ also give pure C_2H_2. Other carbides with the CaC_2 structure include UC_2 and VC_2. In view of the fact that the rare-earth elements are never divalent in their normal compounds, it would appear remarkable that their carbides, which behave so abnormally on hydrolysis, should have structures similar to the compounds of the divalent metals Mg, Ca, Sr, and Ba. It is possible that the structures of these carbides need further study, for it is difficult to locate, by X-ray methods, atoms as light as those of carbon in crystals containing heavy metal atoms—witness, for example, the difficulty which has been experienced in determining the precise structure of Fe_3C. The carbides of Group I metals, such as Na_2C_2 and K_2C_2, which on hydrolysis also give acetylene, presumably also contain C_2^{2-} ions, but their structures are not yet known. It is interesting that the hydrolysis of CaC_2 to acetylene is exactly paralleled by that of BaO_2 (or SrO_2), with the same type of structure, to hydrogen peroxide. Thus

$$C_2^{2-} \rightarrow \begin{matrix} C{-}H \\ \vdots\vdots \\ C{-}H \end{matrix} \quad \text{and} \quad O_2^{2-} \rightarrow \begin{matrix} O{-}H \\ | \\ O{-}H. \end{matrix}$$

CHAPTER XIV

SILICON

THE silicon atom has the same outer electronic structure as carbon but differs from that element in many ways, which we may summarize as follows. Firstly, silicon does not exhibit a covalency of less than four. Unlike carbon it does not complete its octet of valency electrons by forming a small number of multiple bonds, as does carbon in CO, CO_2, —CN, etc. Silicon forms only the one oxide SiO_2 which exists in a number of crystalline forms, in all of which there is the same tetrahedral arrangement of four bonds from each silicon atom, and in every case the silicon and oxygen atoms form an infinite 3-dimensional network. The infinite chains in the SiS_2 crystal have already been described in Chapter XI; in these also the silicon atoms form four tetrahedral bonds. The structures of SiO_2 and SiS_2 bear no relation to those of the simple molecules of CO_2 and CS_2. The fact that silicon does not at ordinary temperatures form simple molecules like O=Si=O or S=Si=S with double bonds (the structures of the vapours of these compounds are not known) does not mean that the element never forms double bonds, and we have seen in Chapter IX when discussing the interatomic distances in the SiO_4^{4-}, PO_4^{3-}, SO_4^{2-}, and ClO_4^- ions that the Si—O bonds in the orthosilicate ion may have some double-bond character. In these elements of the second short period there is the possibility that the valency group can expand beyond the octet, but the situation is complicated by the considerable (50 per cent.) ionic character of the Si—O bonds. This brings us to the second difference between carbon and silicon. Whereas carbon is known not to form more than four covalent bonds, the covalency of silicon can rise to six. There are no carbon analogues of the silicofluorides, which contain the SiF_6^{2-} ion and are stable crystalline salts. A rather similar difference is found between nitrogen and phosphorus, for the latter forms salts containing PF_6^- ions, whereas nitrogen forms no halogen ions NX_n. The formulae of the acetylacetone derivatives of the Group IV elements are of interest in this connexion. Acetylacetone forms compounds in which its two oxygen atoms form bonds to the central atom, thus



Silicon, titanium, and zirconium all form derivatives of the type $[MAc_3]AuCl_4$ in which the central atom is surrounded by six oxygen atoms. Zirconium also forms $ZrAc_4$ (Ac represents a molecule of acetyl-

acetone); compare the 8-coordination of zirconium by oxygen in $ZrSiO_4$ (see below).

The third point we have to mention is the great difference in stability between pairs of carbon and silicon compounds. In contrast to the stable CCl_4 and CS_2 the corresponding silicon compounds are decomposed by water to form 'silicic acid' (and, of course, HCl and H_2S respectively), a term applied to the colloidal silica which may be obtained hydrated to varying degrees. Again, silicon forms a number of hydrides, and although these are stable towards pure water they are hydrolysed by dilute alkali, which has no action at all on the corresponding hydrocarbons. In view of the ease with which silicon compounds are converted into the oxide or other oxy-compounds, it is not surprising to find that silicon occurs in nature exclusively as oxy-compounds, and we shall devote most of this chapter to a review of the extensive chemistry of the silicates.

We have mentioned in the previous chapter the two crystalline forms of carbon: diamond and graphite. The latter structure is unique among the elements, but a number of other elements of Group IV crystallize with the diamond structure; silicon, germanium, and tin (grey modification). In the B sub-group only lead has a typical metallic structure (cubic close-packed), whereas all the elements of the A sub-group crystallize with close-packed structures.

Carborundum (SiC) is of interest because it crystallizes in at least three forms which are structurally related in a simple way to diamond and the forms of zinc sulphide (blende and wurtzite). The atomic positions in zinc-blende are the same as in diamond, alternate atoms being Zn and S. The structures of zinc-blende and wurtzite are not layer structures in the sense in which we use this term, but we may dissect these structures into layers of types (*a*) and (*b*) as shown in Fig. 135 (where alternate circles represent Si and C or Zn and S atoms as the case may be). It will be seen that the zinc-blende structure is built up of layers of type (*a*) only, while in wurtzite (*a*) and (*b*) layers alternate. More complex sequences are possible, and some of these are found in the three forms of carborundum which have been studied. These sequences are as follows:

	Repeat unit
Zinc-blende . .	. *a*
Wurtzite . .	. *a b*
Carborundum III .	. *a a b b*
„ I .	. *a a a b b*
„ II .	. *a a a b b b*

The first three structures are illustrated in Fig. 135. We should, perhaps, point out that the *crystallographic* repeat unit is, in general, a multiple of that shown above because we have disregarded the relative translations of the layers. Thus in blende the unit cell contains three (*a*) layers and in carborundum I, fifteen layers (i.e. three sets of *aaabb*).

Before proceeding to silica and the silicates there are two other groups of compounds to be mentioned. Hydrides from SiH_4 to Si_6H_{14} are known

and may be prepared by the action of 20 per cent. hydrochloric acid on magnesium silicide in an atmosphere of hydrogen. The mixture of gases evolved is cooled in liquid nitrogen and fractionated as in the case of the boron hydrides. All the above hydrides are obtained in this way in

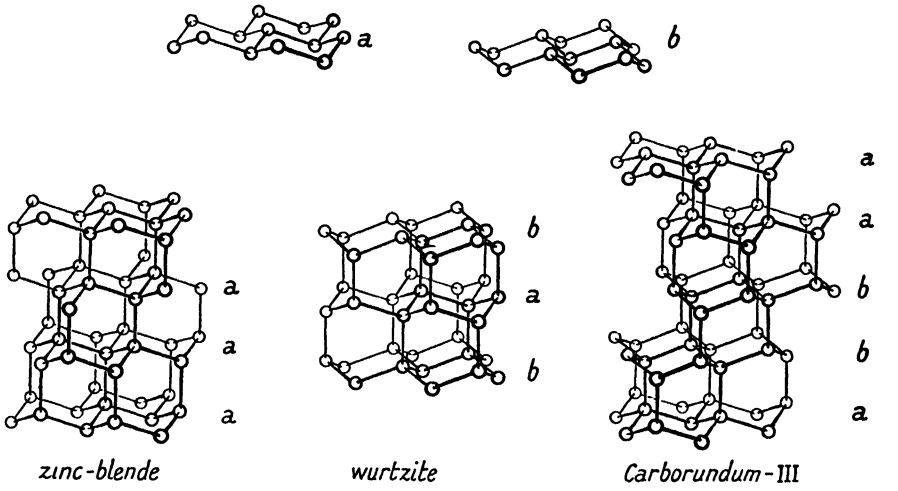


FIG. 135. The geometrical relationship between the structures of zinc-blende, wurtzite, and carborundum III.

regularly decreasing amounts from SiH_4 to Si_6H_{14}. The thermal stability of these compounds decreases with increasing molecular weight and the higher members break down on heating into mixtures of the lower hydrides —compare the 'cracking' of hydrocarbons, which is a similar process. The silicon hydrides are not attacked by water but are hydrolysed by dilute alkali solutions, hydrogen being evolved and a silicate formed. Like the hydrocarbons they may be halogenated, and the hydrolysis of the products is described below. In marked contrast to carbon, silicon appears to form no simple unsaturated hydrides corresponding to the olefines, acetylenes, and aromatic hydrocarbons. Only solid unsaturated hydrides such as $[SiH_2]_n$, of unknown constitution, have been isolated. Structurally the silicon hydrides are not of any particular interest since they are presumably similar to the saturated hydrocarbons.

By hydrolysis of alkyl substituted or halogenated silicon hydrides, oxy- and hydroxy-compounds are produced which are in many cases formally analogous to the corresponding carbon compounds. The silicon compounds, however, bear little resemblance, as regards chemical or physical properties, to their carbon analogues, being in general highly polymerized. Examples of the formation of these compounds by hydrolysis are:

$$SiH_3(CH_3) \rightarrow [SiO(OH)CH_3]_n$$

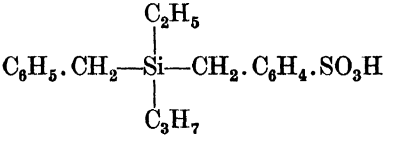
(in which reaction it is interesting to note that the Si—H and not the Si—C bonds are broken) and

$$SiH_3Cl \rightarrow (SiH_3)_2O \rightarrow [SiOH_2]_6 + SiH_4.$$

The polymerized $[SiOH_2]_6$ is also formed by the hydrolysis of SiH_2Cl_2. In all these reactions the hydrolysis must be carefully controlled, for the final product with excess water is always hydrated silica. Silico-chloroform, $SiHCl_3$, is converted by ice-cold water into the unstable silicoformic anhydride, $(H.SiO)_2O$, while silico-oxalic acid, $(SiO.OH)_2$, is formed from Si_2Cl_6. In spite of its name and empirical formula this compound bears little resemblance to oxalic acid, for it is a white powder which is insoluble in water and possesses no acidic properties. No salts or esters are known and it dissolves in alkalis with evolution of hydrogen. It is obviously a complex polymer. The silico-mesoxalic acid, $(H_4Si_3O_6)_n$, formed by the action of moist air on Si_3Cl_8, has rather similar properties to silico-oxalic acid. Another series of compounds, also of unknown constitution, includes siloxene and its derivatives. Siloxene, $(Si_2H_2O)_n$, is a white solid produced by the action of HCl in alcohol on calcium silicide. It is spontaneously inflammable in air; it is a reducing agent and is rapidly decomposed by hot water. It forms flakes of the same shape as the calcium silicide from which it was formed, which is reminiscent of the graphite derivatives described in the last chapter.

THE STEREOCHEMISTRY OF SILICON

This calls for little discussion since silicon is only known to form either four or six bonds and these bonds are arranged tetrahedrally and octahedrally respectively. The classical method of demonstrating the tetrahedral disposition of the four bonds was to resolve into its optical antimers an optically active compound. The laborious preparation and resolution of feebly active compounds such as



may be compared with the demonstration, by X-ray methods, of the structure of elementary silicon and the proof of the tetrahedral configuration of simple molecules like $SiCl_4$ and $Si(CH_3)_4$ by electron diffraction experiments. The octahedral arrangement of six atoms around silicon has been shown by the analysis of the crystal structures of various silicofluorides (K_2SiF_6 is a simple example, for this salt has the same structure as K_2PtCl_6). In silica and in almost all silicates silicon is surrounded tetrahedrally by four oxygen atoms, but in SiP_2O_7 it is surrounded octahedrally by six oxygen atoms. It will be observed that silicon is found octahedrally coordinated only by the most electronegative atoms, F and O—the chlorine, bromine, and iodine analogues of silicofluorides are not known—so that these octahedral bonds have very considerable amounts of ionic character. This, however, does not necessarily mean that silicon can form six bonds only if they are appreciably ionic in character, for the

most electronegative atoms in a Periodic Group are at the same time the smallest, and for a given coordination number there is a limit to the size of the atoms surrounding the central atom.

THE CRYSTALLINE FORMS OF SILICA

Silica exists in three crystalline forms, which are stable in the temperature ranges indicated below:

$$\xrightarrow{} 870° \xleftarrow{} 1470° \xleftarrow{} 1710° \text{ C. (m.pt.)}$$

Quartz Tridymite Cristobalite

Crystallization of the liquid is difficult, and it usually solidifies to a glass which has great value on account of its extremely small coefficient of thermal expansion and high softening-point (in the region of 1,500° C.). Silica in this glassy form is found in nature as the mineral obsidian. The three polymorphic forms of silica are not readily interconvertible, as is shown by the fact that all three are found as minerals, though tridymite and cristobalite are rare in comparison with quartz. Furthermore, each of the three forms exists in a low- and high-temperature modification (α and β respectively) with the following transition points: α-β quartz, 573°, α-β tridymite, 120–160°, and α-β cristobalite, 200–275° C. The fact that in the last two cases these transitions can be studied at temperatures at which the particular polymorphic forms are metastable is a further indication of the difficulty of changing one of the three varieties of silica into another. The general structural relations between these crystalline forms of silica are as follows, though the detailed structures of all six crystals are not yet known. The three main forms, quartz, tridymite, and cristobalite, are all built up of SiO_4 tetrahedra linked together so that every oxygen atom is common to two tetrahedra (thus giving the composition SiO_2), but the arrangement of the linked tetrahedra is quite different in the three crystals. The difference between, for example, tridymite and cristobalite is like that between wurtzite and zinc-blende, the two forms of ZnS. On the other hand, the α and β forms of one of the three varieties differ only in detail, there being, for example, slight rotations of the tetrahedra relative to one another without any alteration in the general way in which they are linked together. The change from quartz to tridymite thus involves the breaking of Si—O—Si bonds and the linking together of the tetrahedra in a different way and accordingly is a very sluggish process, whereas the conversion of $\alpha \rightarrow \beta$ quartz merely involves a small distortion of the structure without any radical rearrangement and is an easy and reversible process. Quartz is optically active, in contrast to the other varieties, and the fact that a crystal of left-handed α-quartz remains left-handed after conversion into the β form is further evidence of the relatively small change in structure at the transition point.

In β-quartz, the structure of which is illustrated in Fig. 136, there may

be distinguished spirals of linked tetrahedra, and in a given crystal the spirals are all either left- or right-handed, the crystal being laevo- or dextro-rotatory. Some idea of the relation between the α and β forms of quartz may be obtained from Fig. 137, which shows, in plan, the arrange-

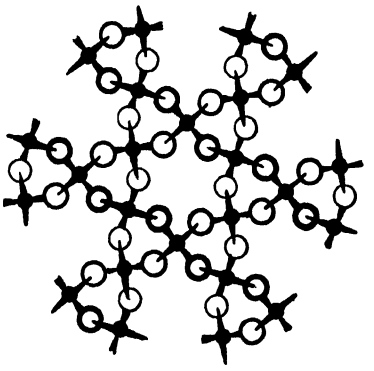


FIG. 136

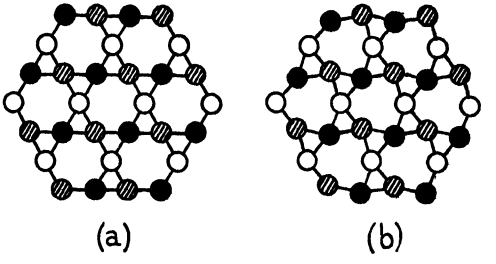


FIG. 137

FIG. 136. Plan of the structure of β-quartz. Small black circles represent Si atoms. The oxygen atoms lie at different heights above the plane of the paper, those nearest the reader being drawn with heaviest lines. Each atom is repeated at a certain distance above (and below) the plane of the paper along the normal to that plane so that the 3-membered rings in the plan represent spiral chains.

FIG. 137. The arrangement of the Si atoms (in plan) in (*a*) β-quartz and (*b*) α-quartz.

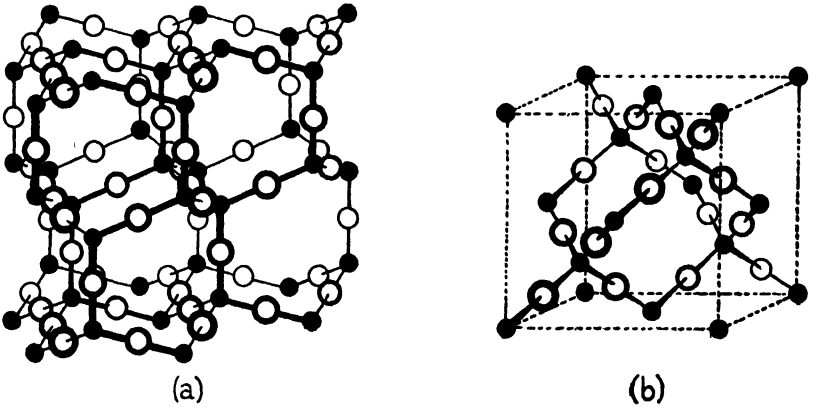


FIG. 138. The idealized structures of (*a*) β-tridymite and (*b*) β-cristobalite (see text). Small black circles represent Si atoms.

ment of the silicon atoms in the two crystals. It will be seen that the α form is a distorted version of the β form, but that the general scheme according to which the tetrahedra are linked together is the same in the two forms. The structures of β-tridymite and of β-cristobalite are shown in Fig. 138, according to Gibbs and Wyckoff respectively. In these diagrams the oxygen atoms are placed midway between, and on the straight

lines joining, the pairs of silicon atoms. This linear arrangement of oxygen bonds gives, however, in cristobalite a Si—O distance of only 1·54 A. which is smaller than the usual value. Later work by Barth suggests that the oxygen atoms actually rotate about the lines joining pairs of nearest silicon atoms, giving non-linear oxygen bonds and a more satisfactory Si—O distance of 1·63 A.

SILICATES

The earth's crust is composed almost entirely of silicates and silica, which constitute the bulk of all rocks and of soils, clays, and sands, the breakdown products of rocks. All inorganic building materials, ranging from natural rocks such as granite to artificial products like bricks, cement, and mortar, are silicates, as also are ceramics and glasses. Metallic ores and other mineral deposits form an insignificant proportion of the mass of the earth's crust. The following table, due to Goldschmidt, gives the average composition of the lithosphere; that of the hydrosphere is given for comparison.

TABLE 25

Compositions of the Lithosphere and Hydrosphere

Lithosphere					*Hydrosphere*	
Element	% (*weight*)	% (*atomic*)	*Radius* (A.*)	% (*volume*)	*Element*	% (*weight*)
O	46·59	62·46	1·32	91·77	O	85·89
Si	27·72	21·01	0·39	0·80	H	10·80
Al	8·13	6·44	0·57	0·76	Cl	1·93
Fe	5·01	1·93	0·82	0·68	Na	1·07
Mg	2·09	1·84	0·78	0·56	Mg	0·13
Ca	3·63	1·93	1·06	1·48	S	0·09
Na	2·85	2·66	0·98	1·60	Ca	0·04
K	2·60	1·43	1·33	2·14	K	0·04
Ti	0·63	0·28	0·64	0·22		
All other elements are present in smaller amounts					All others less than 0·01%	

* These ionic radii differ slightly from those given in Chapter III, since Goldschmidt based his values on O = 1·32 A.

It is seen that more than nine-tenths of the volume of the earth's crust is occupied by oxygen. In many silicates the oxygen atoms are close-packed, or approximately so, and the more electropositive ions, which are nearly all smaller than oxygen, are found in the interstices between the close-packed oxygen atoms. We have already discussed the relation between radius ratio and coordination number in Chapter III and oxygen coordination numbers in Chapter IX. Here we need only remind

the reader of the usual oxygen coordination numbers of the ions commonly found in silicate minerals:

Be, Li	4
Si	4
Al	4, 6 (rarely 5)
Mg, Ti, Fe	6
Na	6 (8)
Ca	8
K	6–12

Since there are a number of ions of similar size which can occupy, for example, octahedral holes (i.e. coordination number 6), and since atoms of many kinds were present in the melts or solutions from which the minerals crystallized, isomorphous substitution is very common in the silicates, which rarely have the 'ideal' composition of a simple chemical compound. The analysis of a typical specimen of hornblende illustrates this point well. Hornblende belongs to the group of silicate minerals called amphiboles (see below), and their ideal composition is represented by the following formula: $(OH)_2Ca_2Mg_2(Si_4O_{11})_2$. The numbers of atoms present for every twenty-four oxygen atoms, i.e. $O_{22}+(OH)_2$, are:

Si	5·98	Ti	0·13		Na	0·37	
Al	2·32	Fe^3	0·90		K	0·66	2·87
8·30		Mg	0·46	4·75	Ca	1·84	
		Fe^2	3·16				
		Mn^2	0·10				

Firstly, some of the silicon in tetrahedral positions is replaced by Al, for this atom may occupy either tetrahedral or octahedral holes. Some, however, of the Al atoms (0·30) must be in octahedral holes since in this particular structure there is room for only eight atoms in tetrahedral positions. The realization that aluminium can play this dual role in silicates was an important result of X-ray studies, for previously it was very difficult to interpret correctly analytical figures which gave only total Al without distinguishing between that which was replacing Si in the 'acid radical' part of the formula and that which was behaving like Fe^{3+}, Mg^{2+}, etc., as a simple positive ion. Secondly, we see that in this particular hornblende most of the magnesium in the above formula is replaced by divalent iron. From the list of elements in octahedral positions (second group) it will be seen that size is more important than valency in determining which elements may replace others by isomorphous substitution. Any substitution of an ion of one valency by one of another valency must, of course, be accompanied by some other adjustment in the structure to maintain electrical neutrality. The replacement of silicon by aluminium, which is very commonly found, requires the presence of extra positive ions, usually alkali or alkaline-earth, in the structure, and the micas provide good examples of this type of substitution.

We saw in Chapter VIII, when considering the structures of halides, that in a close-packed assemblage of halogen atoms we may distinguish

complex ions or molecules M_xX_y according to the arrangement of the metal atoms in the interstices. Now although it is important to remember that most silicates consist of close-packed oxygen atoms with positive ions in the interstices, this way of regarding these compounds is not the most convenient either when illustrating their structures or for comparing the different types of complex ion which are found in them. When discussing Pauling's rules for complex ionic structures it was pointed out

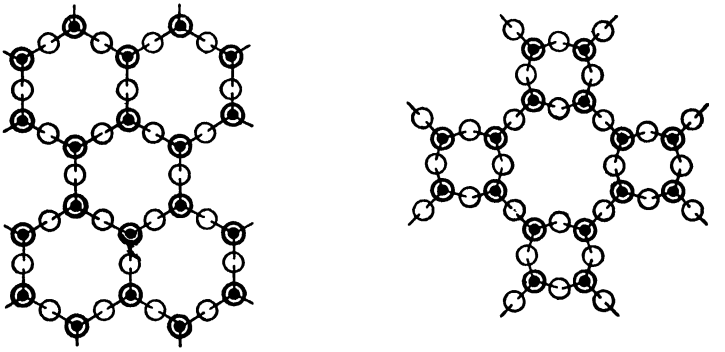
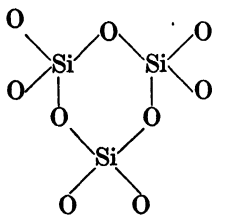


FIG. 139. Two types of silicon-oxygen sheet (idealized). Oxygen atoms lying above the Si atoms (small black circles) are drawn more heavily.

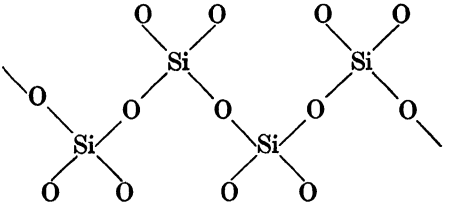
that we may focus our attention on the coordination polyhedra around the various positive ions and on the way in which these polyhedra share corners, edges, and faces to build up larger complexes. Accordingly, silicates are conveniently classified according to the way in which the SiO_4 tetrahedra are linked together. In some silicates there are discrete SiO_4 groups, i.e. no oxygen atom is common to two such groups. In others the SiO_4 tetrahedra are joined up to form larger groups Si_xO_y of which we may distinguish the following types:

(*a*) One O atom of each SiO_4 is shared with another SiO_4 giving the pyrosilicate ion $Si_2O_7^{6-}$.

(*b*) Two O atoms of every SiO_4 are shared with other SiO_4 tetrahedra, resulting in closed rings or infinite chains, as in



and larger rings, and



These complexes are all of the type $(SiO_3)_n^{2n-}$.

(*c*) Three O atoms of each SiO_4 are shared with other SiO_4 tetrahedra leading to sheets of composition $(Si_2O_5)_n^{2n-}$. Two kinds of sheet actually found in silicates are shown, in idealized form, in Fig. 139. The 6-ring sheets are characteristic of the micas and the clay

minerals, and the sheet with alternate 4- and 8-rings is found in the mineral apophyllite.

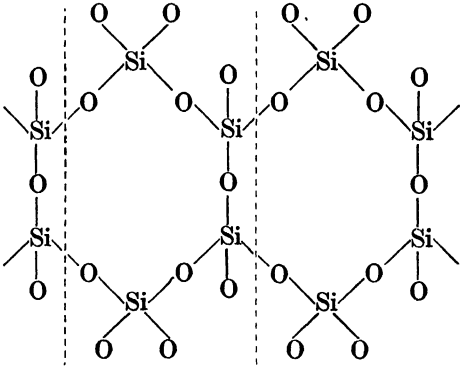
(*d*) Sharing of all corners of each SiO_4 tetrahedron leads to infinite 3-dimensional frameworks as in the various forms of silica, SiO_2. If some of the Si is replaced by Al the framework—always of composition $(Si, Al)O_2$—is negatively charged, and positive ions must be accommodated in the holes in the structure. We shall mention below the felspars and zeolites as examples of silicates with infinite 3-dimensional framework structures. Replacement of Si by Al to different extents is illustrated by the formulae of the following minerals:

		Si:Al *ratio*
The various forms of silica:	SiO_2	∞
Orthoclase	$K[AlSi_3O_8]$	3:1
Analcite	$Na[AlSi_2O_6].H_2O$	2:1
Natrolite	$Na_2[Al_2Si_3O_{10}].2H_2O$	3:2
Anorthite	$Ca[Al_2Si_2O_8]$	1:1

In the groups (*a*)–(*d*) above we have considered only those Si_xO_y complexes in which there are the same numbers of shared and unshared oxygen atoms around every Si atom, viz.

3	unshared,	1	shared	Si_2O_7
2	„	2	„	SiO_3
1	„	3	„	Si_2O_5
		4	„	SiO_2

There are other possible complexes in which the environment of every Si atom, in terms of shared and unshared O atoms, is not the same. The only complex of this kind so far discovered is the amphibole chain, which is intermediate between the pyroxene chain, $(SiO_3)_n$, and the infinite sheet,



$(Si_2O_5)_n$. By counting up the atoms in the repeat unit, marked off by the dotted lines, it is seen that this double chain has the composition $(Si_4O_{11})_n^{6n-}$. On account of the close structural relation between the pyroxenes and the amphiboles we shall consider these two groups of minerals together.

From this brief survey we see that in many silicates there are infinite Si_xO_y ions—chains, sheets, and frameworks. These complex ions can exist only in the crystalline state, so that when the crystal is broken down, for example by fusion with alkali, the complex characteristic of the particular crystal is destroyed. There is therefore no foundation for postulating series of fictitious silicic acids from which these silicates might be supposed to be derived. We shall now describe briefly some of the more important silicate structures,* dealing in turn with the following groups:

1. Orthosilicates, containing discrete SiO_4^{4-} ions.
2. Silicates with $Si_2O_7^{6-}$ ions.
3. ,, ,, ring $(SiO_3)_n^{2n-}$ ions.
4. ,, ,, chain complexes (pyroxenes and amphiboles).
5. ,, ,, layer structures—clay minerals and micas.
6. ,, ,, framework structures—felspars and zeolites.

Orthosilicates

These include such minerals as olivine and those of the chondrodite series, phenacite, the garnets, zircon, and the aluminosilicates Al_2SiO_5 (cyanite, sillimanite, and andalusite). In general the metal atoms occupy positions of higher coordination than does the silicon, though the smaller metal ions Be^{2+} and Al^{3+} are found in 4-fold coordination (see below).

Olivine and related compounds have the general formula M_2SiO_4, where M is a divalent metal (Mg, Fe, Mn) or a mixture of such metals. Olivine itself may be written $9Mg_2SiO_4.Fe_2SiO_4$ so that about one in every ten Mg atoms in Mg_2SiO_4 is replaced by Fe^{2+}. The olivine structure may be described either as an assembly of SiO_4^{4-} groups with Mg^{2+} ions between them in holes between six oxygen atoms, or as an infinite array of approximately close-packed oxygen atoms with Si in tetrahedral and Mg (or Fe) in octahedral holes. The idealized structure with the oxygen atoms shown in perfect hexagonal close-packing is illustrated, in plan, in Fig. 140 (*a*). It will be recalled that in certain metallic hydroxides with layer structures the oxygen atoms are close-packed. The plan of a layer of the $Mg(OH)_2$ structure is shown in Fig. 140 (*b*), in which are shown two layers of oxygen atoms with the smaller Mg atoms in between these layers surrounded octahedrally by six oxygen atoms. Owing to the similar packing of the oxygen atoms in Mg_2SiO_4 and in $Mg(OH)_2$ portions of the two structures fit together perfectly, giving rise to a series of minerals of general formula $m[Mg_2SiO_4].n[Mg(OH)_2]$—the so-called chondrodite series. If we compare the compositions of the horizontal rows of atoms in the plans of Fig. 140 (*a*) and (*b*) we see that they are of two kinds, x and y, the former containing Mg and O and the latter Mg, O, and Si. In brucite, $Mg(OH)_2$, the rows are all of the type x; in olivine x and y alternately. Other

* For a much fuller account see *The Atomic Structure of Minerals*, by W. L. Bragg.

sequences are possible and those found in the chondrodite minerals are as follows:

Repeat unit		
xxy	norbergite,	$Mg_2SiO_4.Mg(OH)_2$
xy, xxy	chondrodite,	$2\,Mg_2SiO_4.Mg(OH)_2$
xy, xy, xxy	humite,	$3\,Mg_2SiO_4.Mg(OH)_2$
xy, xy, xy, xxy	clinohumite,	$4\,Mg_2SiO_4.Mg(OH)_2$

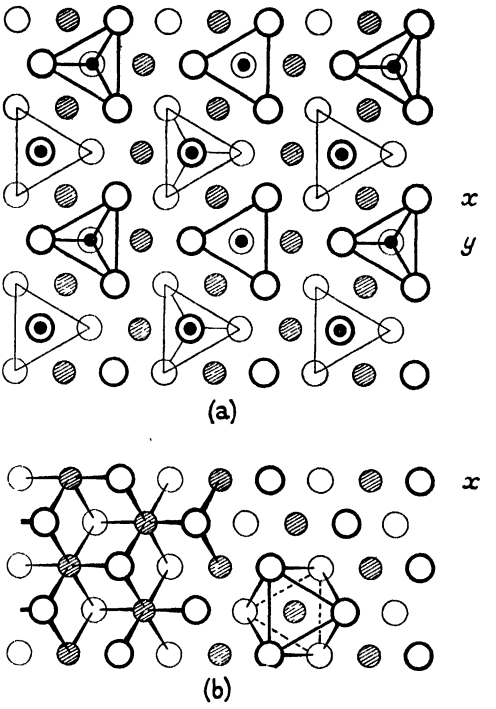


FIG. 140. Plans of the structures of (*a*) Mg_2SiO_4 and (*b*) $Mg(OH)_2$. Small black circles represent Si, shaded circles Mg, and open circles O atoms. In (*a*) light and heavy lines are used to distinguish between SiO_4 tetrahedra at different heights. To the left in (*b*) the Mg—OH bonds are shown, and to the right an octahedral coordination group is outlined.

Plans of portions of the norbergite and chondrodite structures are shown in Fig. 141 (*a*) and (*b*). We have neglected the difference between OH^- and simple O^{2-} ions in these figures. Those atoms belonging to the octahedral coordination groups around Mg ions and which do not belong to SiO_4 groups are OH, as in $Mg(OH)_2$, and these are replaceable by fluorine. The general formula of these minerals is therefore

$$m[Mg_2SiO_4].n[Mg(OH, F)_2].$$

Phenacite, Be_2SiO_4, has a structure quite different from that of Mg_2SiO_4 owing to the small size of the Be^{2+} ion, which is found in tetrahedral holes. A number of salts, including Li_2MoO_4, Li_2WO_4, and Li_2BeF_4 are

isomorphous with phenacite. The garnets are a group of orthosilicates of the general formula $R^{II}_3R^{III}_2(SiO_4)_3$, where R^{II} is Ca, Mg, or Fe^{2+}, and R^{III} is Al, Cr, or Fe^{3+}, as in grossular, $Ca_3Al_2(SiO_4)_3$, uvarovite, $Ca_3Cr_2(SiO_4)_3$, and andradite, $Ca_3Fe_2(SiO_4)_3$. We have already mentioned that the com-

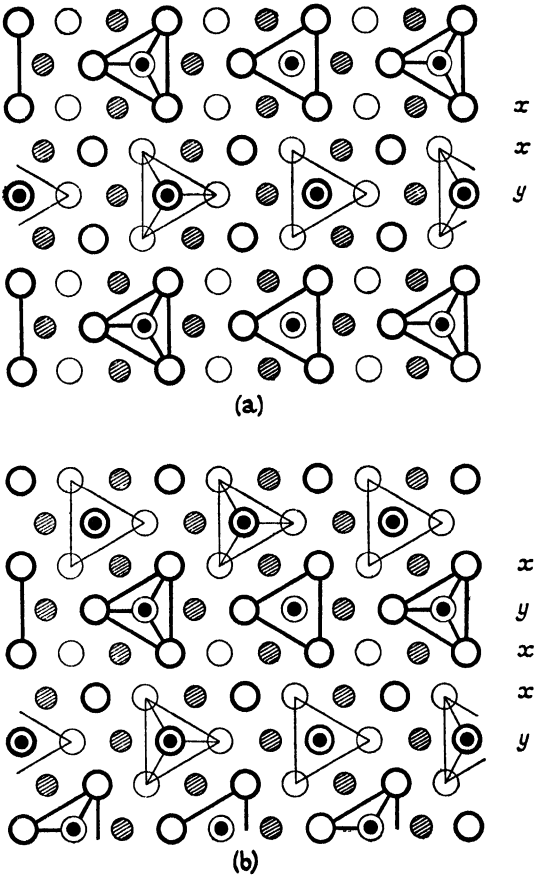


FIG. 141. Plans of the structures of (*a*) norbergite and (*b*) chondrodite.

plex fluoride $Na_3Al_2Li_3F_{12}$ crystallizes with the garnet structure. In this structure SiO_4^{4-} ions are packed together with R^{II} ions in positions of 8- and R^{III} ions in positions of 6-coordination. Eight-coordination of the metal ions is also found in zircon, $ZrSiO_4$, though all the eight oxygen neighbours are not equidistant, there being four at 2·05 and four at 2·41 A. It is interesting that YPO_4 is isomorphous with $ZrSiO_4$.

The compound Al_2SiO_5 exists in three polymorphic forms, cyanite, sillimanite, and andalusite. From their formulae these compounds would not appear to be simple orthosilicates, but it is not necessary that all the oxygen atoms in an orthosilicate should be attached to silicon. In each of the three forms of Al_2SiO_5 one-half of the Al atoms are 6-coordinated

and the other half are in positions of 4-, 5-, and 6-coordination in sillimanite, andalusite, and cyanite respectively. The latter is accordingly the most compact of the three forms, the oxygen atoms being cubic close-packed. Just as the structures of the minerals of the chondrodite series are closely related to those of olivine and brucite, so we find a more complex mineral, staurolite—with the ideal composition $H_2FeAl_4Si_2O_{12}$—

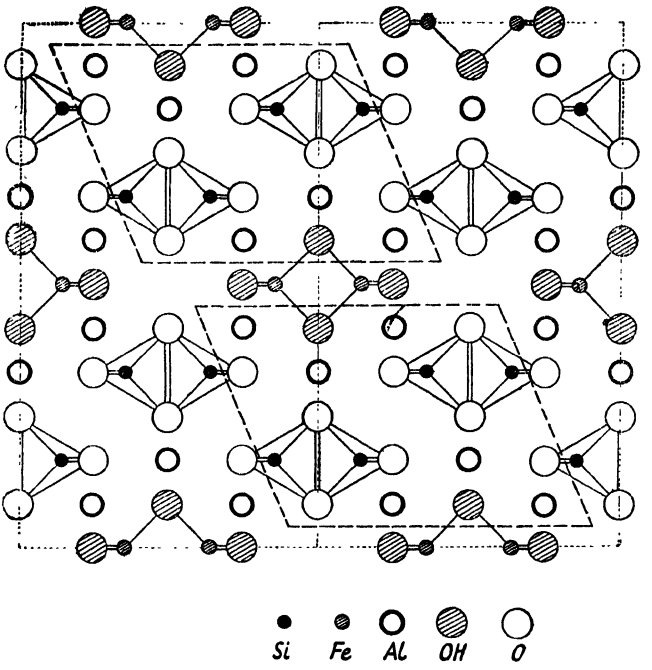


FIG. 142. Relation between the structures of staurolite, $H_2FeAl_4Si_2O_{12}$, and cyanite, Al_2SiO_5.

related in a rather similar way to cyanite. Two unit cells of the staurolite structure are shown, in plan, in Fig. 142, and the broken lines outline cyanite unit cells. It may be seen that the cyanite structure is interrupted by the insertion of Fe atoms, surrounded tetrahedrally by OH groups, so that the formula of staurolite may be written $Fe(OH)_2.2Al_2SiO_5$; compare chondrodite, $Mg(OH)_2.2Mg_2SiO_4$.

Silicates containing $Si_2O_7^{6-}$ Ions

Silicates of this type are rare. They include thortveitite, $Sc_2Si_2O_7$, composed of $Si_2O_7^{6-}$ ions held together by Sc^{3+} ions lying within octahedra of oxygen atoms, and hemimorphite. The latter, an important zinc ore, is of particular interest as an example of the way in which X-ray studies assist in the assignment of correct structural formulae. It was formerly written $H_2Zn_2SiO_5$, but one-half of the hydrogen in this empirical formula is in the form of water molecules which may be removed by moderate

heating of the crystal, whereby its form and transparency are not destroyed. The removal of further water, at temperatures above 500° C., results in destruction of the crystal. These facts are consistent with the crystal structure, which shows that the composition is $Zn_4(OH)_2Si_2O_7 . H_2O$, the crystal containing both OH^- and $Si_2O_7^{6-}$ ions in addition to the Zn^{2+} ions and discrete water molecules.

Silicates containing Cyclic $(SiO_3)_n^{2n-}$ Ions

Of the various possible cyclic silicon-oxygen complexes only the $Si_3O_9^{6-}$ and $Si_6O_{18}^{12-}$ ions are known to exist as discrete ions in silicates. The

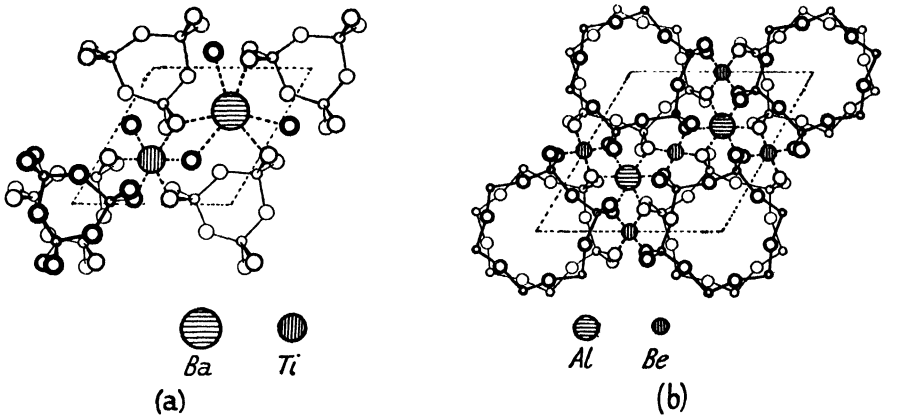


FIG. 143. Plans of the structures of (*a*) benitoite, $BaTiSi_3O_9$, and (*b*) beryl, $Be_3Al_2Si_6O_{18}$. Atoms belonging to complex ions lying at different heights above the plane of the paper are shown as heavy and light circles in order to show the nature of the coordination groups around the metal ions. Only one of the upper complex ions is shown in (*a*) and many oxygen atoms are omitted from (*b*) for the sake of clarity.

former occurs in benitoite, $BaTiSi_3O_9$, and wollastonite, $CaSiO_3$, and the latter in beryl (emerald), $Be_3Al_2Si_6O_{18}$. The structures of benitoite and beryl are very similar in general type, as can be seen from the plans in Fig. 143. In each case the ring ions are arranged in sheets with their planes parallel, but the structures are not layer structures, as might appear from these plans, for the metal ions lie between the sheets and bind together the rings in different sheets. Both the Ti^{4+} and Ba^{2+} ions in $BaTiSi_3O_9$ are 6-coordinated (the Ba—O distance being greater than the Ti—O), but in beryl the Be^{2+} ions are in tetrahedral and the Al^{3+} in octahedral holes.

Silicates containing Chain Ions

This group includes two large classes of minerals, the pyroxenes and amphiboles. The former contain simple chains (*a*) of composition $(SiO_3)_n$, and the latter double chains (*b*) of composition $(Si_4O_{11})_n$—Fig. 144.

The pyroxenes include enstatite, $MgSiO_3$, diopside, $CaMg(SiO_3)_2$, and augite (which contains some Al and Fe^{3+}), and also such minerals as jadeite, $NaAl(SiO_3)_2$, and spodumene, $LiAl(SiO_3)_2$. In the latter minerals the two divalent ions in diopside have been replaced by one uni- and one tri-valent ion. The structure of diopside is shown in Fig. 145, where it

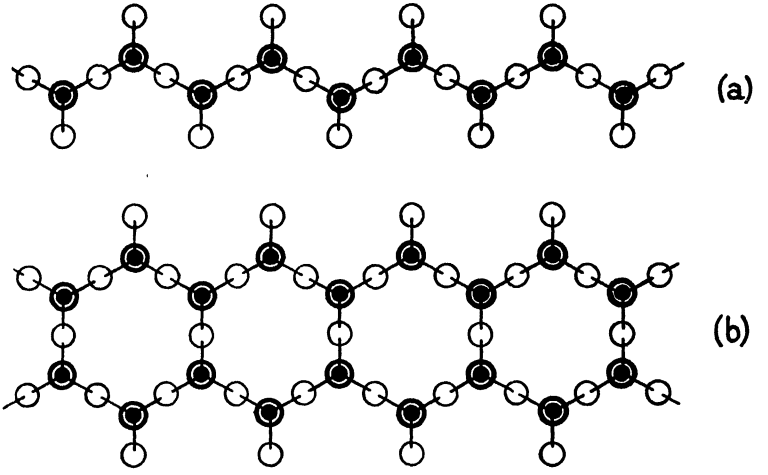


FIG. 144. The silicon-oxygen chain ions in pyroxenes (*a*) and amphiboles (*b*).

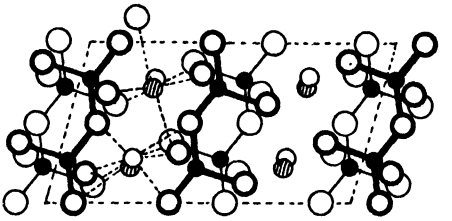


FIG. 145. The structure of diopside. Some of the metal ions are omitted, and those shown are displaced slightly to avoid superposition. Shaded circles represent magnesium ions (6-coordinated) and small open circles calcium ions (8-coordinated).

may be seen that the parallel SiO_3 chains are held together by the metal ions lying between them. The amphiboles are very similar in general type, the single chains being replaced by double chains, but they always contain some hydroxyl groups. These are attached to the metal atoms only and not to silicon. A typical member of the family is tremolite, $(OH)_2Ca_2Mg_5(Si_4O_{11})_2$, but isomorphous substitution is very widespread. Firstly, the total positive charge of $+14$ (Ca_2Mg_5) may be made up in various ways, e.g. $CaNa_2Mg_5$ in soda-tremolite and Na_3Mg_4Al in arfvedsonite, and the Ca or Mg is commonly replaced in part by Fe. Secondly, the silicon in the chains may be replaced by Al in 4-fold coordination up to $Si_6Al_2O_{22}$ in hornblende, which is the amphibole analogue of augite.

In this case the additional negative charge on the chains has to be compensated by the substitution of Al for some of the divalent metal ions (e.g. Mg) and also by the actual addition of alkali or alkaline-earth ions in positions between the chains which are unoccupied in the ideal tremolite structure.

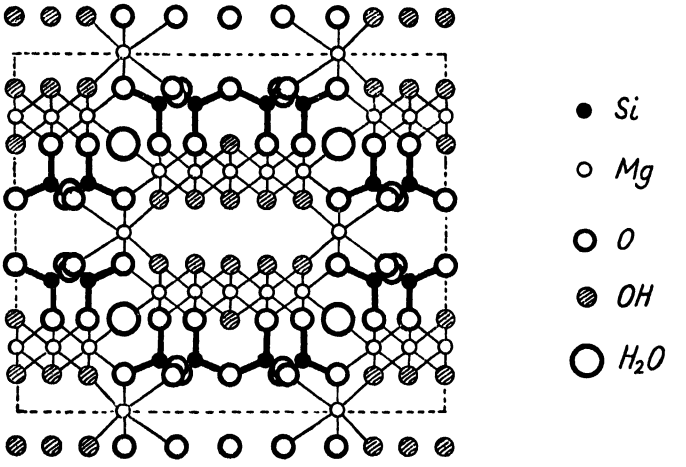


FIG. 146. The probable structure of chrysotile, $(OH)_6Mg_6Si_4O_{11}.H_2O$.

These structures are not of great interest from the standpoint of structural chemistry apart from the form of the silicon-oxygen chains. They are, however, important to mineralogists because they account for the cleavages of these minerals. The angles between the two prominent cleavage directions have long been used to distinguish amphiboles from pyroxenes. The analysis of the structures of amphiboles led to the revision of the old formulae. Tremolite, for example, was originally written $CaMg_3(SiO_3)_4$. If we double this formula, $Ca_2Mg_6Si_8O_{24}$, we have the same numbers of silicon and oxygen atoms as in the true structural formula, $(OH)_2Ca_2Mg_5Si_8O_{22}$, but from the environment of two of the oxygen atoms it is clear that they are OH groups. Each is attached to three Mg^{2+} ions, all lying to one side of it, and not to silicon. Since every Mg^{2+} ion is surrounded by six oxygen atoms, the Pauling electrostatic bond strength reaching such an oxygen is only 1, corresponding to OH^- and not to O^{2-}. If the additional Mg in the old formula (which contains Mg_6 as compared with Mg_5) were present in the structure it would have as nearest neighbours only two oxygen atoms, each of which is already bound to two silicon atoms. In fact, such Mg atoms are not present. This example of the revision of a formula is particularly interesting, as the old formulation would correspond to a metasilicate which should have either cyclic $(SiO_3)_n$ ions or chain ions of the pyroxene type, whereas the actual form of the silicon-oxygen complex is the double amphibole chain.

The asbestos minerals are amphiboles, and chrysotile, which is also

a fibrous mineral, is closely related to the amphiboles but contains more Mg and OH. Its formula is $(OH)_6Mg_6Si_4O_{11}.H_2O$ and its structure is probably of the type shown in Fig. 146, though the structure has not been confirmed in every detail. It will be seen that the Mg atoms lie between oxygen atoms of Si_4O_{11} chains and OH groups, so that the chains are in effect coated with hydroxyl groups. Whereas in pyroxenes and amphiboles the chains are directly bound together by the metal ions, here the lateral binding between the chains is almost wholly the weak attraction between the OH groups, just as in the $Mg(OH)_2$ and $Al(OH)_3$ layer structures. A structure of this kind would account for the ease with which the crystals may be split into bundles of parallel fibres.

Silicates based on Si_2O_5 sheets

We have already illustrated sheets formed of 6- and of 4- and 8-membered rings. In pyroxenes and amphiboles the SiO_3 and Si_4O_{11} chains respectively are directly linked together by metal ions, but the situation is not quite so simple in most silicates containing sheets of linked tetrahedra. In apophyllite the sheets (of 4- and 8-rings) are held together in this simple way, but the hexagonal sheets characteristic of clay minerals and micas are never found as simple structural units. Instead we find composite layers built up of one or two silicon-oxygen sheets combined with layers of hydroxyl groups firmly cemented to the silicon-oxygen sheets by Mg or Al atoms. These composite layers are then the units of structure, and we must first consider their internal structure before seeing how they are packed together in crystals. In Fig. 147 (*a*) is shown a portion of a sheet of linked SiO_4 tetrahedra, three oxygen atoms of every SiO_4 being shared with adjacent groups. The vertices of all the tetrahedra point upwards, in contrast to the apophyllite sheet of 4 and 8 rings which will be considered later. Fig. 147 (*b*) shows the arrangement of the OH groups in a layer of the $Mg(OH)_2$ or $Al(OH)_3$ structures. The distance between the upper oxygen atoms in (*a*), drawn with unbroken lines, is approximately the same as that between the corresponding OH groups in (*b*). It is therefore possible by turning (*b*) over and placing it on top of (*a*) to form a composite layer having these oxygen atoms in common. The remaining OH groups (one-quarter of the total in (*b*)) fit in at the centres of the hexagonal rings in (*a*). This composite layer is shown in elevation in Fig. 147 (*c*). It is possible to repeat this process of condensation on the other side of the (*b*) layer giving the more complex layer shown at (*d*). In illustrating structures based on these layers we shall use the diagrammatic forms shown to the right of (*c*) and (*d*) to represent layers of these types extending indefinitely in two dimensions, a simplification suggested by Pauling. Just as the $Mg(OH)_2$ and $Al(OH)_3$ layers have the same arrangement of OH groups and differ, from the geometrical point of view, only in the number of octahedral holes occupied by metal atoms, so in these composite layers there may be either Mg or Al ions or,

of course, other di- or tri-valent ions of appropriate size. The compositions of these layers are:

(*c*) $Mg_3(OH)_4Si_2O_5$ or $Al_2(OH)_4Si_2O_5$
(*d*) $Mg_3(OH)_2Si_4O_{10}$ or $Al_2(OH)_2Si_4O_{10}$

according to whether the octahedral holes are occupied by Mg or Al. The layer $Mg_3(OH)_4Si_2O_5$ has so far not been found in any mineral, but its aluminium analogue is the basis of the kaolin minerals. All the above

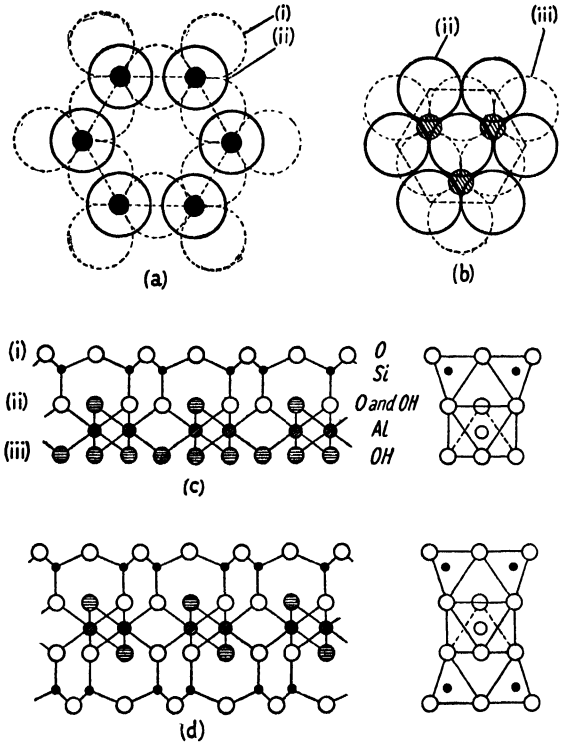


FIG. 147. The formation of composite silicon-aluminium-oxygen or silicon-magnesium-oxygen layers (see text).

layers are electrically neutral, so that in crystals built from them there are only feeble attractive forces between neighbouring layers. The crystals therefore cleave very easily, and talc, for example, finds applications (as french chalk) on account of its lubricating qualities. Of the four possible structures formed by superposition of layers of the above compositions, three are known (Fig. 148). There are actually three closely related minerals with the composition $Al_2(OH)_4Si_2O_5$ (or $Al_2O_3.2SiO_2.2H_2O$ as kaolin was originally formulated), kaolinite, dickite, and nacrite, which differ only in detail and are all based on the same kind of layer.

We have seen that the silicon in Si_xO_y complexes may be partly replaced by Al occupying tetrahedral holes. Replacement of this kind is possible

in the complex layers we are now considering, and while it has not been found in layers of the kaolin type, there is an important group of minerals derived in this way from the multiple layers (*d*), Fig. 147. These are the micas, typical formulae of which are:

$KMg_3(OH)_2Si_3AlO_{10}$	phlogopite
$KAl_2(OH)_2Si_3AlO_{10}$	muscovite
$CaAl_2(OH)_2Si_2Al_2O_{10}$	margarite

In phlogopite and muscovite one-quarter of the silicon atoms have been replaced, statistically, by aluminium, the layers as a result being negatively

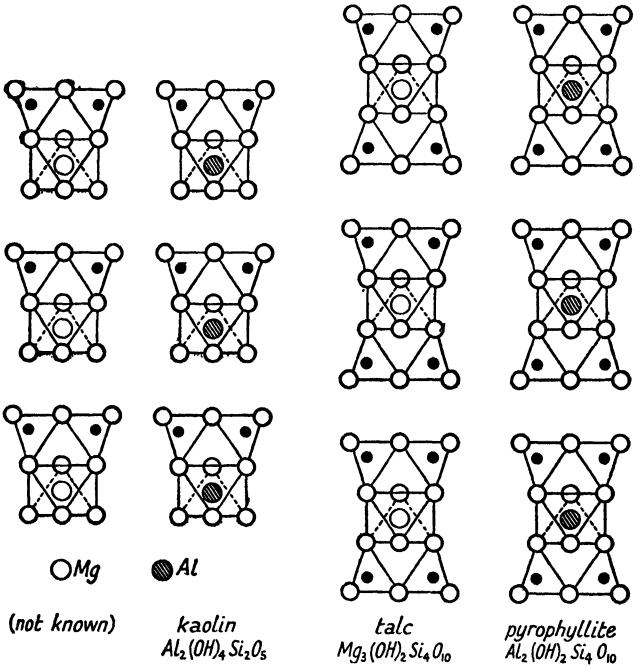


FIG. 148. The structures of some silicate minerals with layer structures (diagrammatic).

charged. They are held together by positive ions as shown diagrammatically in Fig. 149. These two minerals are therefore related in exactly the same way as talc and pyrophyllite. The potassium ions occupy large holes between twelve oxygen atoms so that the K—O electrostatic bond strength is only 1/12. These bonds are easily broken and the micas accordingly possess very perfect cleavage parallel to the layers. In the so-called brittle micas, typified by margarite (formula above), further substitution of Al for Si has taken place so that the negative charge on the layers is twice as great as in phlogopite and muscovite. The layers are therefore held together by divalent ions such as Ca^{2+}. The increased strength of the interlayer Ca—O bonds, with electrostatic bond strength

now equal to 1/6, results in greater hardness, as shown by the figures for the hardnesses on Mohs's scale:

	Hardness
Talc, pyrophyllite	1–2
Micas	2–3
Brittle micas	3½–5

In all these layer structures so far described all the layers in a given crystal are of the same kind. There are also more complicated structures

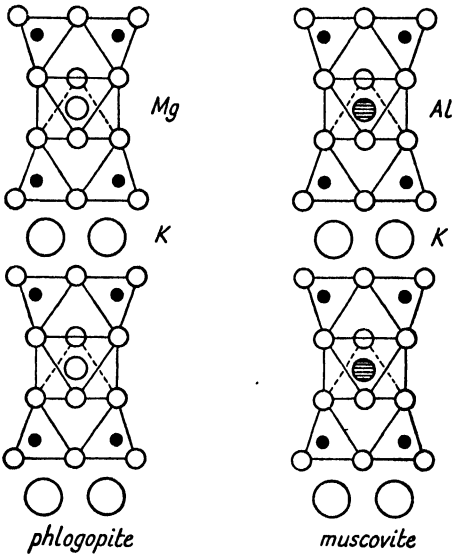


FIG. 149. The structures of the micas phlogopite and muscovite (diagrammatic).

with layers of two kinds, and the chlorite minerals are in this class. In kaolin, talc, and pyrophyllite the uncharged layers are held together by comparatively weak forces, and in the micas the negatively charged layers are cemented together by positive ions. In the chlorites another possibility is realized, the alternation of negatively charged layers of the mica type with positively charged layers, i.e. the structures contain infinite 2-dimensional ions of opposite charge. The mica-like layers have compositions ranging from $[Mg_3(AlSi_3O_{10})(OH)_2]^-$ to $[Mg_2Al(Al_2Si_2O_{10})(OH)_2]^-$. The positive layers result from the replacement by Al of one-third of the Mg in a brucite ($Mg(OH)_2$) layer, giving the composition $[Mg_2Al(OH)_6]^+$. The sequence of layers in the chlorites is compared with that in $Mg(OH)_2$ and phlogopite in Fig. 150. There is one other structure to be mentioned before leaving the 'layer' silicates, that of apophyllite. This contains sheets of silicon-oxygen tetrahedra linked to form 4- and 8-membered rings. In the hexagonal mica sheet the vertices of all the tetrahedra point to one side, but in the apophyllite sheet the vertices of the tetrahedra in

alternate 4-rings point in opposite directions. The cations are arranged in layers between the sheets. The formula of apophyllite may be written $KF.Ca_4Si_8O_{20}.8H_2O$, but it is considered unlikely that normal water molecules exist in the crystals. It has been suggested that there are hydroxyl groups linked by hydrogen to the vertices of SiO_4 tetrahedra.

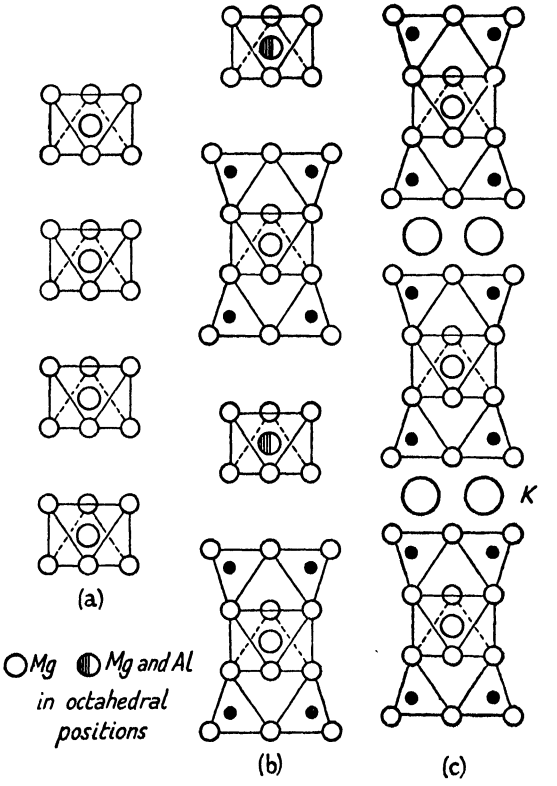


FIG. 150. The sequence of layers in (*a*) brucite, $Mg(OH)_2$, (*b*) chlorite, and (*c*) phlogopite.

Silicates with 'Framework' Structures

We shall deal with three groups of minerals based on infinite 3-dimensional silicon-oxygen frameworks, the felspars, zeolites, and ultramarines. In all these structures some (often about one-half) of the tetrahedral positions in the framework are occupied by Al so that positive ions are present to neutralize the negative charge of the $(Si, Al)O_2$ framework. The ratio of (Si+Al) to O must always be 1:2 since every Si or Al is surrounded tetrahedrally by four oxygen atoms and each of these is common to two tetrahedral groups. The felspar structures are relatively compact, but in the zeolites and ultramarines there are large spaces in the structures in which are accommodated water molecules (in the zeolites)

or finite negative ions (Cl^-, SO_4^{2-}, S^{2-}, etc.) in the ultramarines—in addition, of course, to the necessary numbers of positive ions.

The Felspars

These are the most important rock-forming minerals, comprising some two-thirds of the igneous rocks. Granite, for example, is composed of quartz, felspars, and micas. The felspars are subdivided into two groups according to the symmetry of their structures, typical members of the groups being:

(1) Orthoclase $KAlSi_3O_8$
Celsian $BaAl_2Si_2O_8$.

(2) The plagioclase felspars: Albite $NaAlSi_3O_8$
Anorthite $CaAl_2Si_2O_8$.

It will be noticed that in the first example in each group one-quarter of the tetrahedral positions are occupied by Al, requiring a monovalent ion to balance the charge on the $AlSi_3O_8$ framework. In celsian and anorthite further replacement of Si by Al necessitates the introduction of divalent ions. The plagioclase felspars, albite and anorthite, are of peculiar interest since they are practically isomorphous and many minerals of intermediate composition are known. The composition of labradorite, for example, ranges from AbAn to $AbAn_3$, where Ab = albite and An = anorthite. This isomorphous replacement of (K+Si) by (Ba+Al) or of (Na+Si) by (Ca+Al) is characteristic of felspars and other framework silicates. The felspars of the first group contain the large K^+ and Ba^{2+} ions (radii 1·33 and 1·35 A. respectively), whereas the plagioclase felspars contain the smaller Na^+ and Ca^{2+} ions (radii 0·95 and 0·99 A. respectively). The difference in symmetry of the two groups of felspars is due to this difference in size of the positive ions, for the framework is essentially the same in all felspars but closes in slightly in the first group around the smaller ions. We shall therefore not describe the minor differences in structure between felspars of the two groups but only the general nature of the $(Si, Al)_4O_8$ framework. It may be noted here that only the comparatively large positive ions (Na, K, Ca, Ba) are found in felspars. The smaller Fe, Mn, Cr, etc., so commonly found in chain and layer silicates do not occur in these minerals since the cavities in the frameworks are too large for them. Now although in the felspars the $(Si, Al)_4O_8$ framework extends uninterruptedly throughout the crystal in all directions, nevertheless it is convenient to describe the structure of the framework in terms of a characteristic chain of 4-membered rings. These chains are not discrete units like the pyroxene or amphibole chains, for they are all linked up laterally with other similar chains by Si—O—Si bonds of exactly the same type as those in the chains, but these cross-links are few in number compared with those within the chains. The idealized form of one of these felspar chains is shown in Fig. 151 (*a*). The shaded oxygen atoms are those which form the links to neighbouring chains, as shown in

Fig. 151 (*b*), which shows the plan of part of the structure of orthoclase, $KAlSi_3O_8$.

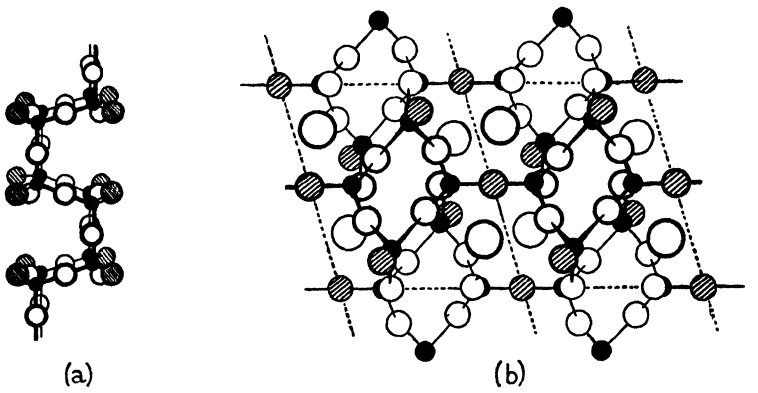


FIG. 151. Portions of (*a*) a felspar chain (idealized) and (*b*) the structure of orthoclase, $KAlSi_3O_8$. Large circles represent K^+ ions.

The Zeolites

The zeolites, like the felspars, consist of $(Si, Al)_nO_{2n}$ frameworks, substitution of Al for some of the Si in SiO_2 giving the framework a negative charge which is balanced by positive ions in the cavities. The structures are much more open than those of the felspars, and a characteristic property of the zeolites is the ease with which they take up and lose water, which is loosely held in the lattice. In addition to water, a variety of other substances can be absorbed, including gases like CO_2 and NH_3, alcohol, and even mercury. Also, the positive ions may be interchanged for others merely by soaking the crystal in a solution of the appropriate salt. The 'permutites' used for water-softening are sodium-containing zeolites which take out the calcium from the hard water and replace it by sodium, thereby rendering it 'soft'. The permutite is regenerated by treatment with brine, when the reverse process—replacement of Ca by Na—takes place, making the permutite ready for further use. In this interchange of positive ions the actual number of ions in the crystal may be altered provided the total charge on them remains the same. Thus one-half of the Ca^{2+} ions in the zeolite thomsonite, $NaCa_2(Al_5Si_5O_{20}).6H_2O$, may be replaced by $2Na^+$, thereby increasing the total number of positive ions from three to four, there being sufficient unoccupied positions in the lattice for the additional sodium ions.

A complete and systematic study of all the various kinds of zeolites has not yet been made, though the structures of some have been studied in considerable detail. It appears that three main types of zeolite framework occur. In the first, typified by analcite, $Na(AlSi_2O_6).H_2O$, there is no prominent concentration of atoms into chains or layers but instead a linking of the tetrahedra into 4- and 6-membered rings which are joined up to form a 3-dimensional framework rather like those in the

forms of silica itself. The second group contains the lamellar zeolites which have been comparatively little studied and of which heulandite, $Ca_2(Al_4Si_{14}O_{36}).12H_2O$, is an example. In these there are probably closely knit sheets of tetrahedra accounting for the cleavage into plates. Those of the third group, the fibrous zeolites, bear a general structural resemblance to the felspars in that chains of tetrahedra, of a characteristic kind, can be distinguished in their structures. As in the felspars, these chains are cross-linked to others by comparatively few bonds, giving the crystals a fibrous rather than a massive nature. We shall confine our remarks to zeolites of the first and third groups.

(1) *Analcite*, $(NaAlSi_2O_6).H_2O$. The structure of this mineral is not easily appreciated from a diagram, and like many other complex structures can be studied satisfactorily only from a scale model. The complex arrangement of linked SiO_4 and AlO_4 tetrahedra results in comparatively large channels through the structure in which the Na^+ ions and H_2O molecules are accommodated. The arrangement of the Si and Al atoms is statistical. Also, there is room in the unit cell of the structure, which contains 16 formula-weights of the above composition, for 24 Na, whereas only 16 are present. These Na ions are distributed at random in the twenty-four available positions, a conclusion which was checked by substituting Ag for Na and comparing the intensities of corresponding X-ray reflections. The Ag atoms can be located much more easily owing to their greater scattering power. (The replacement of Na by Ag is achieved simply by keeping the crystal in a hot concentrated solution of silver nitrate for several days.) It seems probable that the Na ions can move around from one place in the structure to another even at room temperature, so that exchange with Ag is a facile process. It is interesting to see why all the geometrically possible positions for Na are not occupied, since this would be possible if more Si were replaced by Al, giving the framework a greater negative charge. This question is apparently linked up with the environment of the water molecules. Each of these is situated between two Na and two other water molecules, and the nearest neighbours of each Na are four oxygen atoms of the framework and two water molecules. If all the twenty-four Na positions were occupied, this type of environment for the water molecules would not be possible. We have already discussed the tetrahedral charge distribution of the H_2O molecule in Chapter XI, and this model is in full agreement with the environment of water molecules in zeolites. These molecules are always found in close proximity to positive ions and either to other water molecules or to oxygen atoms of the $(Si, Al)O_2$ framework. If we consider these latter atoms to be negatively charged (owing to substitution of Al for Si) we have an electrostatic bond picture of the type (*a*) for H_2O surrounded by two monovalent ions and two O atoms, or of type (*b*) for H_2O with three neighbours—one divalent ion and two O atoms (see next page).

In (*a*) the arrangement of the atoms around the H_2O molecule is tetrahedral and in (*b*) triangular. In each case the O atoms of the framework

may be replaced by H_2O molecules, the negative regions of which would be pointing towards the central H_2O, as at (*c*). We see therefore that although the H_2O molecules are situated in the channels in the structure,

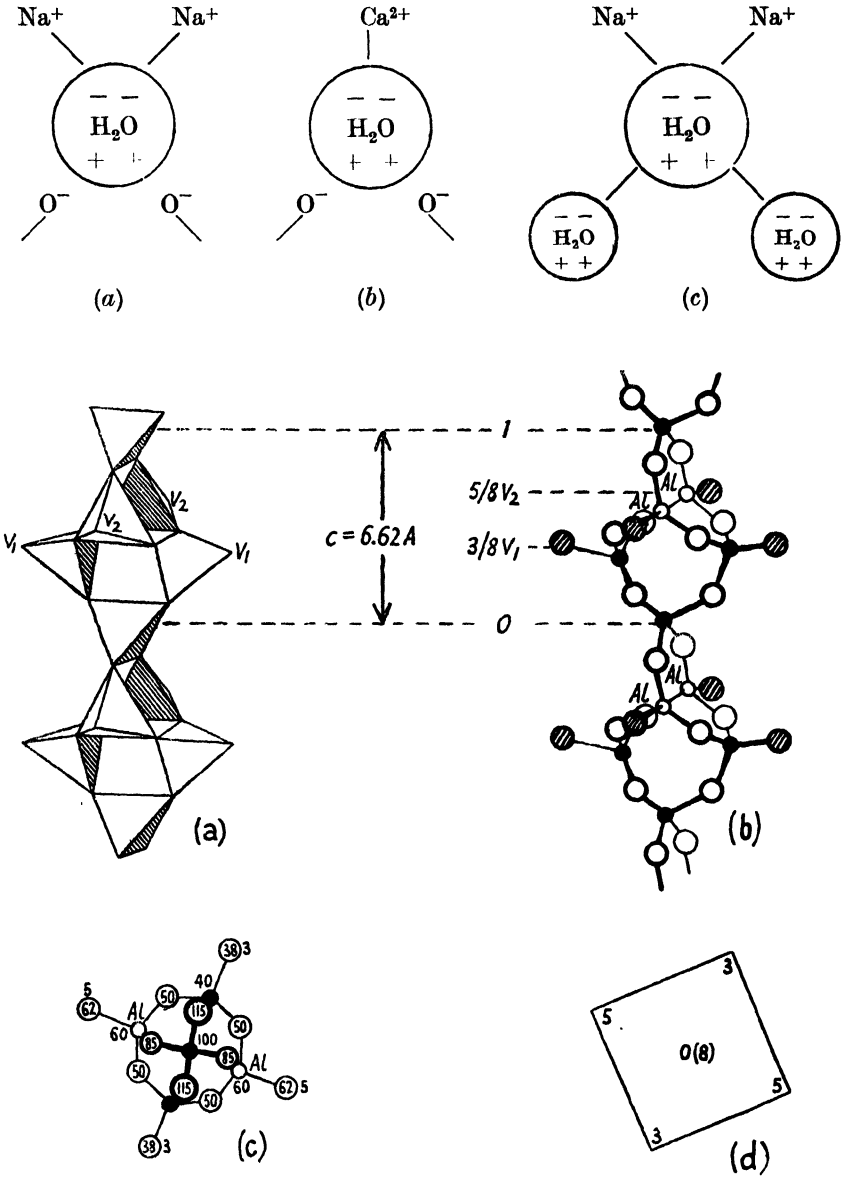


FIG. 152. The common structural feature of the fibrous zeolites. (*a*) The chain of linked tetrahedra. It is attached to neighbouring chains by the vertices V_1 and V_2. (*b*) The same chain showing the silicon-oxygen arrangement. The vertices V_1, V_2 occur at heights $\frac{3}{8}$, $\frac{5}{8}$ in the repeat of the pattern. (*c*) The chain viewed along its length. (*d*) A diagrammatic representation of the outline of the chain, with numbers 3, 5 to denote the heights of attachment. (After Pauling and Bragg.)

through which they and the positive ions can diffuse, nevertheless in the hydrated crystal these H_2O molecules have perfectly definite sets of neighbours owing to the requirements of their tetrahedral charge distribution.

(2) In the *fibrous zeolites* such as natrolite, $Na_2(Al_2Si_3O_{10}).2H_2O$, there

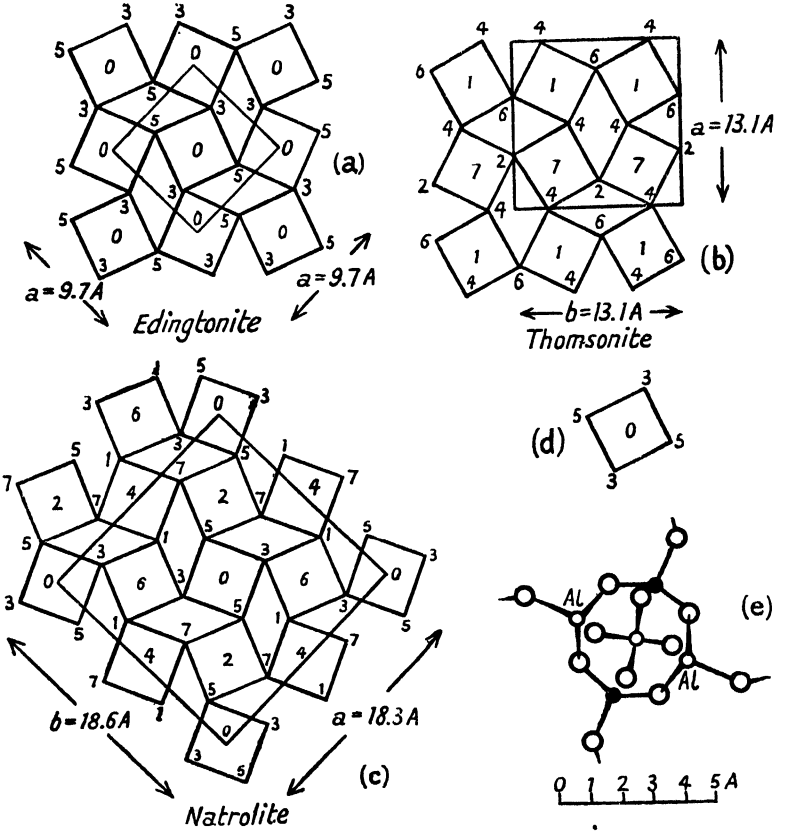


FIG. 153. A diagrammatic representation of the structural schemes in edingtonite, thomsonite, and natrolite. The squares represent chains as in Fig. 152. (After Pauling and Bragg.)

is a quite different arrangement of linked tetrahedra. Just as the felspars are built up of characteristic chains joined on all sides to other similar chains, so in the fibrous zeolites we can distinguish chains of the type shown in Fig. 152.

The chain is made up by the regular repetition of a unit of five tetrahedra so that the formulae of all these fibrous zeolites contain the unit $(Si, Al)_5O_{10}$ or a multiple thereof. The proportion of Al varies; compare the formulae of natrolite, $Na_2(Al_2Si_3O_{10}).2H_2O$, and thomsonite, $NaCa_2(Al_5Si_5O_{20}).6H_2O$. The chains are linked by the oxygen atoms which are shaded in Fig. 152, and these are $\frac{3}{5}$ and $\frac{5}{5}$ of the repeat distance from the silicon atom taken as origin. The structures of the various

minerals of this group can be conveniently shown by indicating the way in which neighbouring chains are linked. Representing the plan of a chain (i.e. viewed along its length) by a square, the heights of the linking oxygen atoms are shown as 3, 5, etc., indicating $\frac{3}{8}c$, $\frac{5}{8}c$, etc., above the plane of the paper, c being the repeat distance along the chain. The numeral in the centre of the square indicates in a similar way, in terms of $c/8$, the height above the plane of the paper of the silicon atom at the beginning of the repeat unit. The structures of edingtonite, $Ba(Al_2Si_3O_{10}).4H_2O$, thomsonite, and natrolite are shown diagrammatically in this way in Fig. 153. This method of representation is due to Pauling.

The Ultramarines

The last group of framework silicates which we shall mention includes the materials called ultramarines, the coloured silicates which are manu-

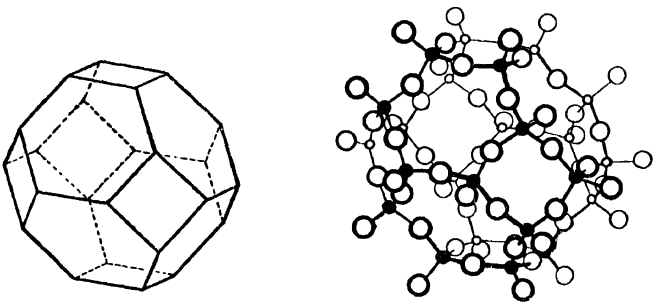


FIG. 154. The basket-like framework of linked SiO_4 tetrahedra which is the basis of the structures of the ultramarines. The silicon atoms are arranged at the vertices of the polyhedron shown on the left, and the Si—O framework extends indefinitely in three dimensions.

factured for use as pigments. The mineral lapis lazuli is of the same type, and since a number of colourless minerals such as sodalite are closely similar in structure, we shall for simplicity refer to all these silicates as ultramarines. Like the other framework silicates they are based on $(Si, Al)O_2$ frameworks with positive ions in the interstices, but a characteristic of the crystals of this group is that they also contain negative ions such as Cl^-, SO_4^{2-}, or S^{2-}. Like the felspars and in contrast to the zeolites the ultramarines are anhydrous. Formulae of representative members of the group are:

Ultramarine . .	$Na_8Al_6Si_6O_{24}.S_2$
Sodalite . .	$Na_8Al_6Si_6O_{24}.Cl_2$
Noselite . .	$Na_8Al_6Si_6O_{24}.SO_4$
Helvite . . .	$(Mn, Fe)_8Be_6Si_6O_{24}.S_2$

The last-mentioned is of considerable interest as a silicate in which one-half of the tetrahedral positions are occupied by beryllium.

All of these compounds contain essentially the same framework of linked

tetrahedra, which is best visualized as a system of baskets of the kind illustrated in Fig. 154. These are joined on all sides to other similar baskets through the projecting oxygen atoms. The positive and negative ions are situated in the numerous cavities in the resulting 3-dimensional framework. As in the zeolites, exchange of these ions for others is possible. For example, sodalite, which contains Cl^- ions, is converted into noselite by heating in fused sodium sulphate. Also, many ultramarines have been prepared containing ions such as Li^+, Tl^+, Ca^{2+}, and Ag^+ instead of Na^+ and with Se or Te replacing S. Considerable variations in colour, from nearly colourless to yellow, red, violet, and blue, result from these various replacements. It will be appreciated that the formulae assigned to the compounds in the above list are 'ideal' formulae and that considerable variation in composition is possible, subject always to the balancing of the total positive and negative charges.

CHAPTER XV

BORON

We shall deal here with only the first member of the third Periodic Group, boron. The structures of some of the compounds of the next member, aluminium, are described in other chapters, e.g. the halides (p. 285), oxide (p. 313), and aluminosilicates (p. 471). A short account of the chemistry of thallium, the heaviest element in this group, is given in Chapter XVI, since this element is of peculiar interest.

Boron has little in common with the other elements in Group III. It is, of course, the most electronegative element of the group and in general resembles the non-metals, particularly silicon, far more than the essentially metallic aluminium and the metals of the A and B sub-groups. Boron is the only element of Group III to form an extended series of hydrides. These bear no resemblance to the solid ionic hydrides of the alkali and alkaline-earth metals but are volatile compounds like the molecular hydrides of the non-metals of later groups. Moreover, as we have already mentioned in an earlier chapter, these boron hydrides are remarkable in that there are not sufficient valency electrons to join together the component atoms by electron-pair bonds, and in view of the interest of these and related compounds we shall give a short outline of their chemistry. Unlike aluminium, boron forms no oxy-salts (nitrate, sulphate,* etc.)—for the 'phosphate' and 'arsenate' see p. 337—but instead forms oxy-acid ions in which the boron is almost invariably attached to three oxygen atoms. Aluminium, on the other hand, forms ionic oxy-salts in which the Al atoms are usually surrounded by six oxygen atoms, though coordination numbers 4 and 5 occur in some crystals. The halides of boron are monomeric in the vapour in contrast to the double Al_2X_6 molecules of the aluminium halides. In its oxy-compounds boron usually forms three bonds, but in molecules like the halides and $B(CH_3)_3$ it has a very strong tendency to complete its octet of valency electrons by forming a fourth bond. Thus $B(CH_3)_3$ unites with NH_3 to form a stable solid $B(CH_3)_3.NH_3$ which can be distilled without decomposition, and the halides form similar compounds, e.g. $BF_3.NH_3$. In this respect the aluminium halides behave similarly with organic oxy-compounds—$AlCl_3$ reacts with many ketones to give $R_2C{=}O.AlCl_3$. Aluminium also forms volatile esters like boron, e.g. $Al(OC_2H_5)_3$.

The resemblance of boron to silicon is very marked. Its halides, like those of silicon but unlike those of carbon, are easily hydrolysed, boric acid, H_3BO_3, being formed. This is the only well-characterized acid of boron, though on heating, H_3BO_3 is said to dehydrate in stages via HBO_2

* An acid sulphate, $B(HSO_4)_3$, is said to be produced by the action of SO_3 on boric acid.

and $H_2B_4O_7$, the oxide B_2O_3 being the final product. As in the case of silicon (and carbon) there are also per-salts (the perborates), the constitution of which is not known, and there are also hypoborates (e.g. $KOBH_3$), but the corresponding acid is not stable. Like silicon, boron forms only one oxide, which is a solid (contrast the gaseous oxides of carbon), and when the fused oxide solidifies on cooling it forms a glass which, as in the case of SiO_2, can be crystallized only with difficulty.

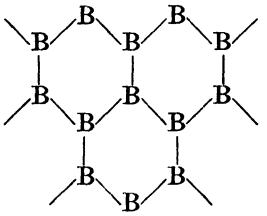
Boron rivals silicon in the number and complexity of its oxy-salts. Borates ranging in composition from CaB_2O_4 to $Mg_7Cl_2B_{16}O_{30}$ may be prepared or are found as minerals, and as was the case with silicates they were supposed to be derived from numerous hypothetical acids, from HBO_2 and $H_2B_4O_7$ to $H_6B_8O_{15}$ and $H_2B_{10}O_{16}$. As we saw in the case of the silicic acids in the previous chapter, such formulae are quite meaningless, as these borates exist only in the solid state and breakdown of the complex B—O groupings of the crystals leads to the formation of small finite complex ions such as BO_3^{3-}. It has been suggested that in an aqueous solution of a particular borate there may be different complex ions in equilibrium, for borates formed by double decomposition have various kinds of empirical formulae. For example, from solutions of the appropriate metal salts boric acid will produce $AgBO_2$, $Ca(H_2BO_2)_2$, or $Na_2B_4O_7$. This does not, however, imply the existence of different kinds of complex ions in a solution of H_3BO_3 since the BO_3^{3-} ions may link together in various ways when the crystals are being formed. In fact we know that the crystalline salts which are apparently derived from a hypothetical metaboric acid, HBO_2, having empirical formulae of the type $M_x(BO_2)_y$, actually contain complex ions of quite different sorts; see the structures of CaB_2O_4 and $K_3B_3O_6$ described below. Since it is impossible to predict the empirical formula of the borate which will be formed by double decomposition in aqueous solution, a salt of particular composition is best made by fusion of the metallic oxide (or carbonate) with B_2O_3 in the required proportions. Here again borates resemble silicates, for many metallic borates made in this way solidify as glasses, and mixed borosilicate glasses have special applications on account of their physical properties (e.g. low melting-points).

We have seen that boron readily forms a fourth bond by addition of various molecules to BF_3 and $B(CH_3)_3$. This tendency to complete its octet of valency electrons is also shown in the formation of the stable BF_4^- ion. The acid HBF_4 is formed, together with boric acid, when BF_3 reacts with water, and the salt $NaBF_4$ may be prepared from solutions of boric acid and $NaHF_2$. A quite analogous behaviour is shown by silicon, but here we have a change from SiF_4 to the SiF_6^{2-} ion.

THE STEREOCHEMISTRY OF BORON

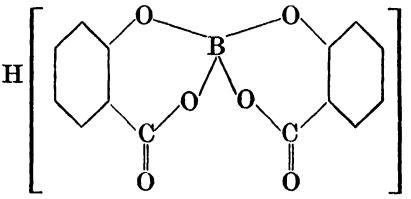
Boron forms either three coplanar bonds, with interbond angles of 120°, or four tetrahedral bonds. The three bonds utilize one $2s$ and two $2p$ orbitals, presumably as some kind of hybrid sp^2 orbitals. The planar

configuration of three bonds from a boron atom has been demonstrated in many molecules, e.g. the halides and $B(CH_3)_3$, in the nitride BN with the graphite structure (see p. 436), in AlB_2 in which there are layers of boron atoms forming a hexagonal network (see accompanying diagram) (the



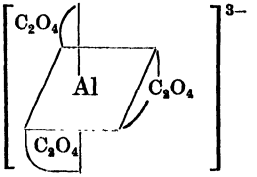
aluminium atoms occupying positions between these layers), in boric acid and various borates, and in certain hydrides and related compounds. The crystal structure of elementary boron does not appear to be known. The experimental evidence for the coplanar arrangement of three bonds from a boron atom in these compounds comes from X-ray studies of solids and from the study of gaseous molecules (halides, hydrides, etc.) by electron diffraction.

The tetrahedral disposition of the bonds from a 4-covalent boron atom was, however, established by the methods of classical stereochemistry. A molecule such as that of borosalicylic acid (I) would possess a plane of symmetry if the boron bonds were coplanar. The optical activity of this



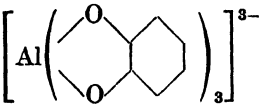
(I)

molecule was demonstrated by its resolution into optical antimers using strychnine as the active base. As we have already pointed out, this does not prove that the boron bond angles are strictly tetrahedral, but shows that a planar configuration for the whole molecule is impossible. The complexes formed by aluminium with such organic molecules are of a different kind, the metal atoms forming six octahedral bonds, as in the trioxalato or tricatechol derivatives, which are also optically active (II and III).



(II)

and



(III)

The fact that the covalency of boron cannot exceed four, whereas that of the later elements of Group III is usually six, is shown by the formulae of the acetylacetone derivatives of these elements:

$$[BAc_2]Cl \begin{cases} AlAc_3 & GaAc_3 & InAc_3 & TlAc \\ ScAc_3 & YAc_3 & Pr_2Ac_6 \end{cases}$$

(Ac represents an acetylacetone radical, $CH\begin{cases} C(CH_3)O- \\ C(CH_3)=O \end{cases}$)

The simplest complex containing a boron atom forming four bonds is the BF_4^- ion. The isomorphism of certain fluoborates with oxy-salts containing tetrahedral oxy-ions confirms the shape of the BF_4^- ion. Other examples of tetrahedrally coordinated boron atoms will be found in the two following sections, in which we shall discuss the oxygen and hydrogen compounds of boron.

THE OXYGEN CHEMISTRY OF BORON

Boron, like silicon, occurs in nature exclusively as oxy-compounds. Boric acid itself is present in certain natural steam jets of volcanic origin, but most of the boron compounds of commerce are obtained from the calcium borate deposits of South America and California and from the borax lakes of North America and India. The most important borate minerals include:

Borax	$Na_2B_4O_7.10H_2O$
Colemannite . .	$Ca_2B_6O_{11}.5H_2O$
Boracite . . .	$Mg_7B_{16}O_{30}Cl_2$
Borocalcite . . .	$CaB_4O_7.4H_2O$
Boronatrocalcite . .	$Na_2B_4O_7.Ca_2B_6O_{11}.16H_2O$

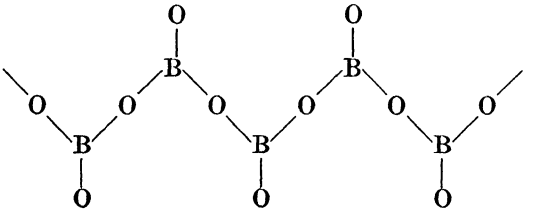
No systematic study of complex borates has yet been made, so that correct structural formulae analogous to the modern formulae for silicates cannot yet be assigned to many of these compounds. An outline of the structural plan according to which borates are built up can, however, be given. We shall assume first, for simplicity, that all boron atoms will be attached to three oxygen atoms forming planar BO_3 groups. The simplest borates will be orthoborates containing these discrete BO_3^{3-} ions, and an example is the mineral hambergite, $Be_2(BO_3)OH$. This crystal consists of an assembly of Be^{2+}, OH^-, and BO_3^{3-} ions so arranged that each Be^{2+} ion is surrounded tetrahedrally by oxygen atoms of BO_3^{3-} and OH^- ions. For the structure of boric acid see p. 355. Since oxygen can form two bonds, BO_3 groups can link together by sharing O atoms just as the extended silicon-oxygen groups arise by the sharing of O atoms between SiO_4 tetrahedra. We have therefore a number of possibilities:

(*a*) BO_3 *groups sharing one* O *atom only.* This gives the simple finite $B_2O_5^{4-}$ ion, which should properly be called the pyroborate ion:

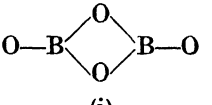


Its existence has not yet been proved in any crystalline borate.

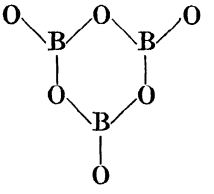
(*b*) BO_3 *groups each sharing two* O *atoms.* In this way two types of complex ion arise, the infinite chain ion of composition $(BO_2)_n^{n-}$



and finite closed rings with the same empirical composition. The simplest of the latter, (i), is unlikely to occur since it would require very considerable distortion of the oxygen bond angle from the usual value of about 150° in such compounds. Of the higher members of the series, the $B_3O_6^{3-}$ ion (ii) occurs in potassium and sodium metaborates, $K_3B_3O_6$



(i)



(ii)

and $Na_3B_3O_6$, which should therefore not be written with the simple empirical formula MBO_2. Sodium is usually surrounded by 6 and the larger potassium by 8–10 oxygen atoms in ionic crystals, and it is interesting that the presence of the rigid $B_3O_6^{3-}$ ions results in a compromise, both Na^+ and K^+ being 7-coordinated in these metaborates. Just as some metasilicates (with Si:O, 1:3) contain ring ions and others infinite chain ions, so calcium metaborate consists of infinite chain ions of the type shown above, held together by the calcium ions. The actual configuration of the boron-oxygen chain in CaB_2O_4 is shown in Fig. 155. This chain is the boron analogue of the pyroxene SiO_3^{2-} chain, but the analogue of the amphibole chain has not yet been discovered. It would have the empirical composition $B_4O_7^{2-}$, and it may occur in tetraborates such as borax, $Na_2B_4O_7.10H_2O$.

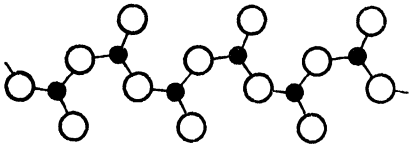
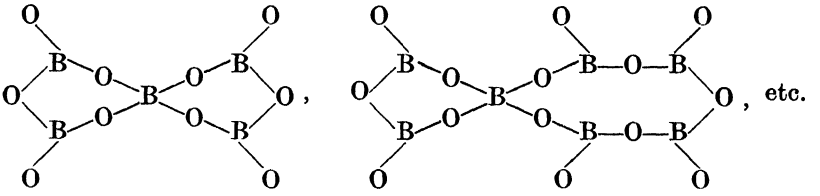


FIG. 155. Portion of the infinite $B_2O_4^{2-}$ chain ion in CaB_2O_4. Small black circles represent B atoms.

(*c*) BO_3 *groups sharing all their oxygen atoms.* Boron trioxide, B_2O_3, presumably consists of BO_3 groups linked up by sharing each O atom between two such groups. The crystalline oxide has only been obtained comparatively recently, for, like SiO_2, it readily forms a glass.

In addition to these arrangements built up entirely from planar BO_3 groups there are other boron-oxygen complexes in which some of the boron atoms are attached to three and some to four oxygen atoms. This suggests another set of possible borate ions consisting of a double-ring system:



An ion of this sort is found in the so-called potassium pentaborate, which could be formulated as an acid metaborate, $KH_4B_5O_{10}.2H_2O$. The structure of this salt has already been described in the section on hydrated acids (p. 375). Tetrahedrally coordinated boron has also been found in the mineral danburite, $CaB_2Si_2O_8$, and in the borotungstates (see p. 339).

BORON HYDRIDES AND RELATED COMPOUNDS

Preparation

The boron hydrides were originally prepared by the action of 10 per cent. HCl, or preferably 8N-phosphoric acid, on magnesium boride. The chief product of this method was B_4H_{10}, mixed with small quantities of B_5H_9, B_6H_{10}, and $B_{10}H_{14}$. This mixture was separated into its components by fractional distillation. B_2H_6 had to be obtained indirectly (with B_5H_9 and $B_{10}H_{14}$) by heating B_4H_{10} at 100° C. It is interesting to note that the action of acid on Mg_2Si gives the silanes from SiH_4 to Si_6H_{14} in decreasing amounts. The later method of preparing boron hydrides is to pass the vapour of BCl_3 (or BBr_3) with hydrogen in a rapid stream at low pressure (5–10 mm.) through an electric discharge between copper electrodes. The main boron-containing product of this reaction is monochlorodiborane, B_2H_5Cl, which decomposes when kept at 0° C. into B_2H_6 and BCl_3. From B_2H_6 many other boranes and related compounds can be prepared, as may be seen from the chart on p. 494. The following list includes all the well-characterized boranes, there being in addition certain solid compounds which are possibly polymerized products.

	B_2H_6	B_4H_{10}	B_5H_9	B_5H_{11}	B_6H_{10}	$B_{10}H_{14}$
State at ordinary temperature and pressure	Gas	Liquid	Liquid	Liquid	Liquid	Solid
Action on water	Very rapid	Slow	Slow	..	Slow	Very slow
General stability	High	Low	High	Very low	Low	Very high

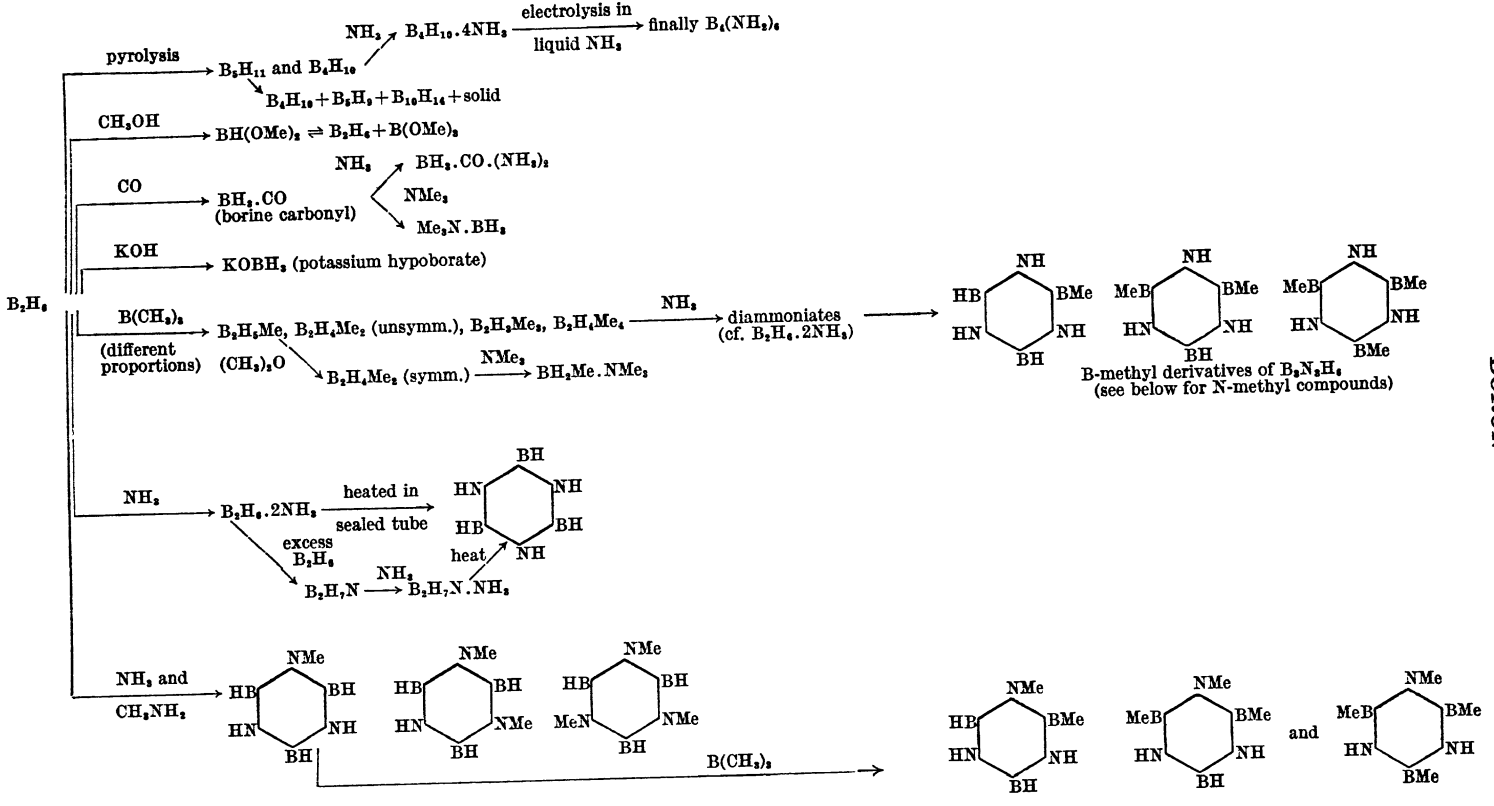


CHART. *The Reactions of Diborane*, B_2H_6

If B_2H_6 is passed through a glass U-tube heated to about 100° C. B_4H_{10} and B_5H_{11} are formed, and similar treatment of B_5H_{11} leads to the formation of B_5H_9 and $B_{10}H_{14}$. Apparently an equilibrium mixture of a number of hydrides is formed in this way so that interconversion of the various hydrides is possible. We shall not give here any preparative details, but the variety of reactions of B_2H_6 may be seen from the chart. We shall confine ourselves to a few general observations followed by notes on the structures of such of these compounds as have been studied by physical and chemical methods.

Theories of the Structure of Boron Hydrides

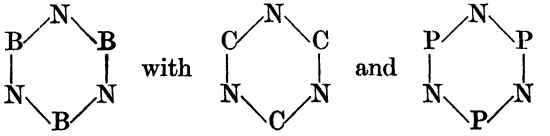
In some respects the hydrogen chemistry of boron resembles that of carbon and in others that of silicon. For example, monoiododiborane reacts with sodium in exactly the same way as does ethyl iodide in the Wurtz reaction:

$$2B_2H_5I + 2Na \rightarrow B_4H_{10} + 2NaI;$$

compare

$$2C_2H_5I + 2Na \rightarrow C_4H_{10} + 2NaI.$$

In their reactions with halogens and halogen hydrides, however, the boranes behave quite differently from hydrocarbons. Diborane, for example, reacts with HCl to give a chloro-derivative and hydrogen, and $B_{10}H_{14}$—which from its formula would appear to be an unsaturated compound—forms with a halogen a substituted derivative and not an addition product as is the case with C_2H_4 and other unsaturated hydrocarbons. In their low stability and vigorous reaction with water some of the boranes resemble silanes rather than hydrocarbons. Like carbon and phosphorus, boron forms heterocyclic compounds containing nitrogen; compare the nucleus

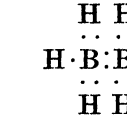


A characteristic feature of the boranes is that there are not sufficient valency electrons to bind together all the atoms by electron-pair bonds. Their constitutions have therefore aroused much interest, and we may note four suggestions. A theory due to Wiberg postulated double bonds between certain of the boron atoms, as in the formulae

$$H^+[H_2B{=}BH_2]H^+, \qquad \begin{matrix} & & H & H & \\ H_2\bar{B}{=}&B{-}&B{=}&\bar{B}H_2, \\ & H^+ & H^+ & H^+ & H^+ \end{matrix}$$

which would account for the compounds with ammonia as ammonium salts, e.g. $B_2H_6.2NH_3$ as $(NH_4)_2[H_2B{=}BH_2]$. However, the interatomic distances obtained from electron diffraction studies of certain boranes disprove the idea of double bonds between boron atoms and make Wiberg's theory untenable. Sidgwick suggested electron pair bonds between the B atoms and 1-electron bonds between some B and H atoms. Pauling

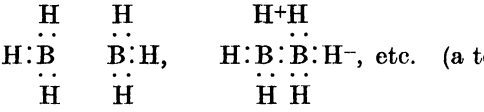
then pointed out that 1-electron bonds are to be expected between B and H, since these atoms have the same electronegativity (see p. 68), and that resonance of the 1-electron bonds among the various positions would stabilize the molecules. The structure of B_2H_6, for example, would then result from resonance between a number of structures of the type



The electron deficiencies, i.e. the differences between the numbers of valency electrons and twice the numbers of bonds, in some of the boranes are shown below:

	Number of bonds	*Number of valency electrons*	*Electron deficiency*
B_2H_6	7	12	2
B_4H_{10}	13	22	4
B_5H_9	14	24	4
B_5H_{11}	15	26	4

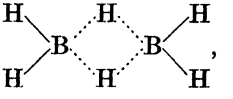
The third alternative is due to Lewis, who suggested that in B_2H_6 there are six electron-pair bonds resonating between the seven positions, so that each of the seven bonds has $\frac{6}{7}$ single-bond and $\frac{1}{7}$ 'no-bond' character. The structures involved in such resonance would be of the types:



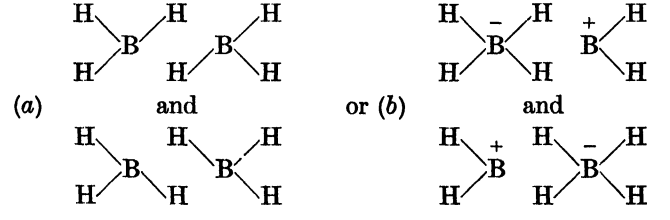
(a total of 7 structures)

It is possible that there is resonance between the Lewis structures and those involving 1-electron bonds, so that each bond is in effect regarded as a hybrid between a 2-electron bond, a 1-electron bond, and a state in which there is no covalent linkage between the atoms.

The last and perhaps most attractive theory of the structure of the boron hydrides postulates 'resonance bridges' between some of the boron atoms. The structure of diborane is represented



where the terminal B—H bonds are normal electron-pair bonds and the central bonds result from resonance between either covalent structures of type (*a*) or ionic structures of type (*b*):



With tetrahedral bonds from each boron atom the molecule of B_2H_6 is geometrically similar to those of the dimeric forms of halides of such metals as Al, Fe, and Ga (see p. 285). The nature of the B—H—B bonds is supposed to be essentially different from the ordinary hydrogen bonds, which are formed only between the most electronegative elements (N, O, and F) and are believed to be due to electrostatic attraction between a dipole such as $\overset{-}{O}—\overset{+}{H}$ and the unshared pair(s) of electrons on the other atom of the bond. The B—H bond will have a very small dipole moment, and there are no pairs of unshared electrons on the B atom in the hypothetical molecule BH_3. With regard to the small B—B distance (1·8 A.) as compared with the distances of 3 A. and upwards generally found between atoms not directly linked by electron-pair bonds, it is pointed out that these large distances are due to the repulsive forces between the pairs of unshared electrons on such atoms. In the boron hydrides, however, there are no pairs of unshared electrons on the B atoms. These considerations show also why the resonance bridge link should not occur between such molecules as NH_3, H_2O, or HF, owing to the presence of pairs of unshared electrons on the N, O, or F atoms. It should, however, occur in any covalent hydrides XH, XH_2, or XH_3 having no unshared electrons in the outer shell, i.e. in hydrides of elements of Groups I, II, or III of the Periodic Table or of the rare-earth or transition metals. Ruling out the salt-like hydrides of Li, Ca, etc., the only well-defined hydrides known in Group III are those of boron, a volatile gallium hydride Ga_2H_6 (aluminium hydride has not been prepared pure but is probably Al_2H_6), and the mixed hydrides BeB_2H_8 and AlB_3H_{12}. (The analogous $LiBH_4$ is an ionic compound.) These mixed hydrides may also be formulated with resonance bridges, see below.

The following evidence is adduced in support of the resonance bridge structures.

(1) All resonating forms, whether of type (*a*) or (*b*), contain only paired electrons, thus accounting for the diamagnetism of B_2H_6 and for the fact that all known hydrides of boron contain even numbers of electrons.

(2) The fact that there is no direct B—B bond in B_2H_6 accounts for the ease with which the boron hydrides are interconverted and for reactions such as

$$B_2H_6+2CO \rightarrow 2BH_3.CO$$
$$B_2H_6+2N(CH_3)_3 \rightarrow 2BH_3.N(CH_3)_3$$
$$B_2H_6+2NH_3 \rightarrow NH_4[BH_3.NH_2.BH_3].$$

(3) Of the six H atoms in B_2H_6 it has been found possible to replace only four by CH_3 and in these methylated compounds there are never more than two CH_3 groups on a particular B atom. The resonance bridge theory—but not the 1-electron bond structures—requires that there shall always be at least one H atom on each B atom. Also, $B(CH_3)_3$ is known, but not $BH(CH_3)_2$ or $BH_2(CH_3)$, which could obviously condense to $B_2H_2(CH_3)_4$ and $B_2H_4(CH_3)_2$ respectively.

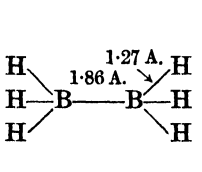
(4) The infra-red and Raman spectra of B_2H_6 have not been satisfactorily interpreted in terms of the ethane-like model, whereas a reasonable interpretation is possible in terms of the 'resonance bridge' structure.

The division of the boranes into two series, B_nH_{n+4} and B_nH_{n+6}, bears little relation to the physical and chemical properties of these compounds. Such general formulae mean very little until we know the structural scheme on which these molecules are based. Perhaps the most interesting problem in connexion with the boranes is to explain why particular members of the family exist and why others do not—or at least are so slowly formed or so unstable that they have not yet been isolated.

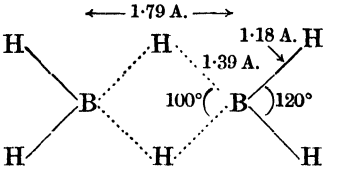
Results of Structural Studies

Boron Hydrides

B_2H_6 gives an electron diffraction photograph similar to that of ethane. The fact that the observed B—B distance is greater than the estimated single-bond length eliminates the formula of Wiberg with a double bond between these atoms. Although the electron diffraction results for this hydride have been interpreted to support the ethane-like structure (1), it appears uncertain whether the photographs eliminate the 'resonance bridge' structure (2). For the present it must be admitted that there is little to choose between these two interpretations of the data.

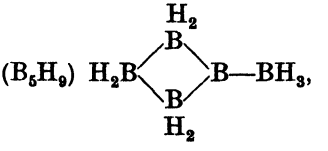


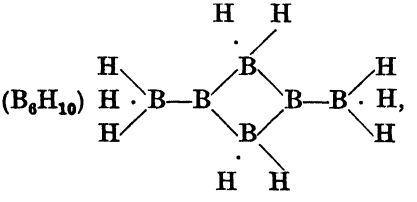
(1)

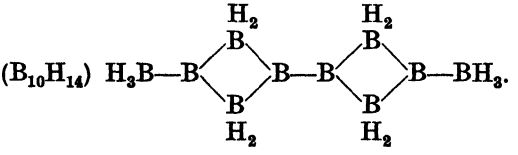


(2)

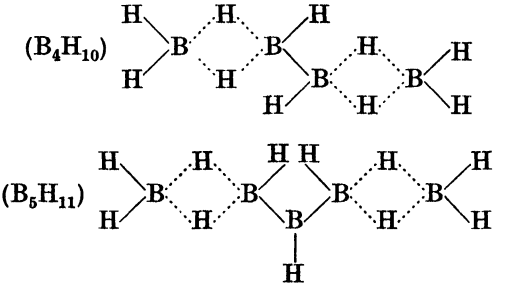
Electron diffraction studies have also been made of B_4H_{10}, B_5H_{11}, and B_5H_9. The photographs have been interpreted as indicating that B_4H_{10} and B_5H_{11} have configurations like those of the hydrocarbons butane and pentane (or isopentane), C_4H_{10} and C_5H_{12}. The borane B_5H_9 has been assigned a cyclic structure (the positions of the hydrogen atoms are assumed as being the most reasonable):







The structures of B_6H_{10} and $B_{10}H_{14}$ have not yet been determined, but since these compounds show a considerable resemblance to B_5H_9 in chemical properties, Bauer and Pauling suggest the above configurations based on the same 4-ring as in B_5H_9. It is interesting to note that the numbers of NH_3 molecules with which B_6H_{10} and $B_{10}H_{14}$ (and also B_5H_9 and B_2H_6) combine are equal to the numbers of H atoms attached by 1-electron bonds. These structures for higher boranes are based on the assumption of resonance involving structures containing 1-electron bonds, as in the ethane-like model for B_2H_6. Alternative structural formulae containing 'resonance bridges' have also been suggested and must still be considered possible. Examples are:

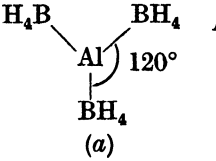


The interatomic distances determined in the borane molecules are given in the accompanying table. For a discussion of these see, for example, the papers of Bauer to which references are given. In the early X-ray crystallographic study of diborane the B—B distance was determined to be 1·82 A. The H atoms were not, of course, located.

	B–B	B–H
B_2H_6 . . .	1·86 A.	1·27 A. in general ±0·03–0·04 A.
B_4H_{10} . . .	1·84	1·28
B_5H_{11} . . .	1·81	1·26
B_5H_9 . . .	1·76	1·17
Single-bond radius sum	1·76*	1·21*

Mixed Hydrides

AlB_3H_{12}. A study of this volatile compound by the electron diffraction method shows that the boron atoms are arranged at the apices of an equilateral triangle around the Al atom. The current formulation of this



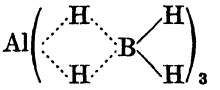
(*a*)

Al—B 2·14±0·02 A.
B—H 1·24±0·04 A.

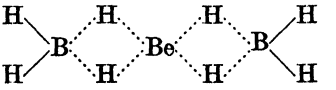
compound as a covalent compound involving resonance with structures containing 1-electron links implies 5-covalent boron, (*a*). The formulation

* The original Pauling-Huggins radius for B, 0·88 A., was obtained by extrapolation from those of C and F. Its value is doubtful (see pp. 82–4).

with resonance bridge links, giving Al six octahedral bonds, is consistent with these results (*b*), and the corresponding beryllium compound, BeB_2H_8, may be formulated with tetrahedral bonds from the Be atom—(*c*).



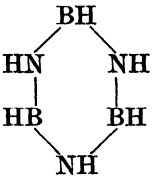
(*b*)



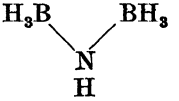
(*c*)

Boron-Nitrogen Compounds

We have already pointed out that the formulation of $B_2H_6.2NH_3$ as $(NH_4)_2[H_2B{=}BH_2]$ is unsatisfactory; a more likely formula is $NH_4^+[BH_3.NH_2.BH_3]^-$ which contains the B—N—B skeleton and is consistent with the formation of $B_3N_3H_6$ on heating. This compound, triborine triammine, gives an electron diffraction photograph like that of benzene and is therefore assigned the cyclic structure:



The B—N distance is $1{\cdot}44\pm0{\cdot}02$ A., compared with $1{\cdot}56\pm0{\cdot}03$ A. in B_2H_7N (see below). These distances may be compared with the C—C distance of 1·42 A. in benzene and 1·54 A. for a C—C single bond. The B—N—B angle in B_2H_7N is tetrahedral ($\pm4°$):



but the experimental evidence does not eliminate the possible formulation $BH_2.NH_2.BH_2$.

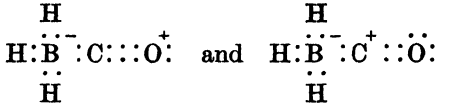
In $H_3B.N(CH_3)_3$ the distances observed are B—N = 1·62 A. and N—C = $1{\cdot}53\pm0{\cdot}06$ A. The molecule has a configuration similar to that of neopentane; there is, of course, no electron deficiency in this molecule.

Borine Carbonyl

Vapour-density measurements show $BH_3.CO$ to be monomeric. Electron diffraction studies show the molecule to be linear:

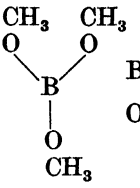
H_3B—C—O with B—C, 1·57, C—O, 1·13, and B—H $1{\cdot}20\pm0{\cdot}03$ A.,

distances which are compatible with resonance between



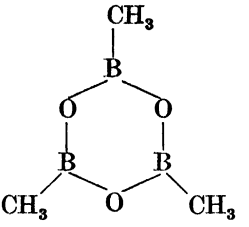
Other boron compounds which have been studied by electron diffraction

include methyl borate (1) and trimethyl-triborane-trioxane (2). In the latter all the atoms except H are coplanar.

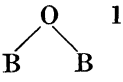


B—O 1·38±0·02 A.
O—C 1·43±0·03 A.

(1)



B—O 1·39±0·02 A.
B—C 1·57±0·03 A.



112±4°

(2)

An electron diffraction study of the compound $BF_3.O(CH_3)_2$ shows that in this molecule the boron atom forms four tetrahedral bonds. See the remarks on p. 488 on the addition compounds of BF_3 and of $B(CH_3)_3$.

CHAPTER XVI

THE STEREOCHEMISTRY OF CERTAIN METALS

As was pointed out in the introduction, our plan in this book has been to describe in some detail the structural chemistry of the non-metals, the later elements of the first and second rows of the Periodic Table. In this way we have covered much of the stereochemistry of the metals. There are, however, a number of metals which present points of particular interest and these form the subject of the present chapter. We propose to deal with three groups of metals:

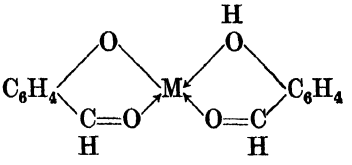
(1) The elements Cu, Ag, and Au of Group I B.

(2) Certain B sub-group elements, particularly Tl and Pb, in which a pair of electrons appears to behave as part of the core rather than as valency electrons—the 'inert pair'. We shall also summarize the stereochemistry of mercury.

(3) The elements of the three triads of Group VIII: Fe, Co, and Ni; Ru, Rh, and Pd; and Os, Ir, and Pt.

THE STEREOCHEMISTRY OF COPPER, SILVER, AND GOLD

The alkali metals, of Group I A, form few essentially covalent molecules. They do combine with molecules like salicylaldehyde to form complex molecules of the type



where M is any alkali metal. The larger alkali metals, K, Rb, and Cs, also form similar molecules with three molecules of the aldehyde, in which the metal is 6-coordinated. Apart from a few compounds of this type, the chemistry of the alkalis is almost entirely that of the ions formed from the atoms by the loss of the single electron in the outermost quantum shell. In the B sub-group, however, we find a quite different state of affairs. The electronic structures of the atoms are:

	K	*L*	*M*	*N*				*O*			*P*
				4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	6*s*
Cu . .	2	8	18	1							
Ag . .	2	8	18	2	6	10		1			
Au . .	2	8	18	2	6	10	14	2	6	10	1

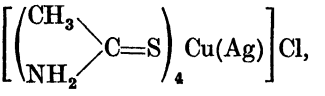
In the case of copper and gold the penultimate quantum groups (the third and fifth respectively) have just been completed—the fifth is never filled

beyond the 5*d* level—and in silver the fourth quantum group has just filled to the extent of eighteen electrons (4*s*, 4*p*, and 4*d*), a stable arrangement which persists until we reach the rare earths. Then it expands by the filling of the 4*f* shell to its full complement of thirty-two electrons. Each of these atoms follows a set of 'transition' elements with incomplete penultimate groups and possessing characteristic properties such as variable valency and the formation of coloured paramagnetic ions. Thus Cu, Ag, and Au follow Ni, Pd, and Pt respectively. In addition to forming the normal colourless singly-charged ions (see, however, below) the elements Cu, Ag, and Au also behave like transition elements in exhibiting higher valencies, electrons of the penultimate group being shared with other atoms in forming covalent bonds or ejected to form ions (e.g. Cu^{2+}, with the electronic structure, 2, 8, 17).

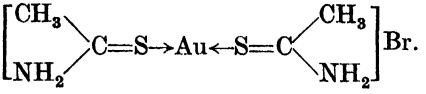
In spite of the general similarity in the electronic structures of their atoms, copper, silver, and gold differ very considerably in their chemical behaviour. First, whereas the first two elements exhibit divalency, gold exhibits only trivalency in addition, of course, in each case to univalency. Secondly, the more stable ion of copper is the cupric ion, Cu^{2+}, whereas that of silver is the argentous ion, Ag^{+}. Cuprous oxy-salts such as Cu_2SO_4 are decomposed by water, $2Cu^{+} \rightarrow Cu + Cu^{2+}$, and the simple nitrate is not known. The only stable cuprous compounds are the insoluble ones, in which the bonds have appreciable covalent character (the halides, Cu_2O, Cu_2S), and the halides and the cyanide are actually more stable in the presence of water than the cupric compounds. Thus CuI_2 and $Cu(CN)_2$ decompose in solution to the cuprous compounds. The cuprous state is, however, stabilized by coordination, and derivatives such as $[Cu(etu)_4]NO_3$ and $[Cu(etu)_3]_2SO_4$ are much more stable than the simple oxy-salts (etu = ethylene-thiourea). In general the cupric salts of only the stronger acids are stable, $Cu(NO_3)_2$ and $CuSO_4$ for example; those of weaker acids are unstable, and only 'basic salts' are generally known, as in the case of the carbonate, nitrite, etc. However, if a coordinated ion such as $[Cu(en)_2]^{2+}$ is formed, then stable compounds result, for example, $[Cu(en)_2](NO_2)_2$, $[Cu(en)_2]SO_3$, etc. Thus it is not so much that the cuprous or cupric states are unstable as that the simple ions are unstable in the presence of water or certain negative ions. The simple argentic ion is not known, and compounds of divalent silver can be prepared only in the presence of molecules which will coordinate on to the silver and form complex ions. The persulphate is formed by double decomposition in the presence of pyridine and isolated as $[Ag(py)_4]S_2O_8$, and the nitrate as $[Ag(py)_4](NO_3)_2$ by anodic oxidation of argentous nitrate solution in the presence of the same base. Many other coordinated compounds of divalent silver have been prepared. The third point to note is that the Au^{+} and Au^{3+} ions do not exist in aqueous solutions of gold salts, at least in any appreciable concentration. The only water-soluble compounds of gold—aurous or auric—contain the gold in the form of a complex ion, as, for example, in solutions of $K[Au(CN)_2]$ or $Na_3[Au(S_2O_3)_2].2H_2O$. As in the

case of copper and silver, coordination compounds of gold are considerably more stable than the corresponding simple salts. For example, AuCl is readily decomposed by hot water, which does not affect $[Au(etu)_2]Cl.H_2O$. Similarly, nitrates of gold have not been prepared, but $[Au(etu)_2]NO_3$ is a quite stable compound unaffected by a reducing agent like formaldehyde, and complex auric nitrates such as $K[Au(NO_3)_4]$ are known.

Finally, we may note differences between the coordination numbers preferred by these elements in the complexes in which they are univalent. In cuprous compounds the copper atom forms either two linear or four tetrahedral bonds, and the stereochemistry of univalent silver is similar, though this element shows a preference for 2- rather than 4-coordination. Thus we find $K[Ag(CN)_2]$ but $K_3[Cu(CN)_4]$. Aurous gold, however, as far as is known is invariably 2-coordinated. Four-coordination has been suggested in compounds like $(C_2H_5)_3P.(NH_3)_2AuCl$ and $(NH_3)_3AuCl$, but in no case has a structure determination been made. The most stable ammino derivatives of AuCl are $NH_3{\rightarrow}Au{-}Cl$ and $[NH_3{\rightarrow}Au{\leftarrow}NH_3]Cl$, and $KAu(CN)_2$ is analogous to the silver compound. Whereas Cu^I and Ag^I form coordination compounds containing 4-coordinated metal atoms, Au^I does not. For example, with thioacetamide copper and silver form



but gold forms only the rather unstable



With trialkyl phosphines and arsines, cuprous and argentous halides form the 4-fold molecules of the type $[R_3P(As){\rightarrow}CuI]_4$, the structure of which is described later, whereas gold gives only $R_3P(As){\rightarrow}AuI$.

The normal coordination number of these elements in their higher valency states (Cu^{II}, Ag^{II}, and Au^{III}) is four, though copper may apparently exhibit 6-coordination in such complexes as $[Cu(H_2O)_2en_2]^{2+}$. The tartrate of this complex was resolved by Wahl in 1928 and the active portions converted into optically active iodides. It is difficult to see how this complex could be enantiomorphous unless it contains 6-coordinated cupric atoms.

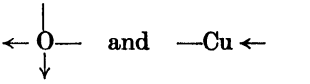
We shall now discuss the spatial arrangement of the bonds formed by copper, silver, and gold in their various valency states in terms of the electronic structures of the respective atoms.

Univalent Copper, Silver, and Gold

The stereochemistry of these atoms when exhibiting the normal valency of one is simple. They form either two linear or four tetrahedral bonds.

2-covalent Atoms

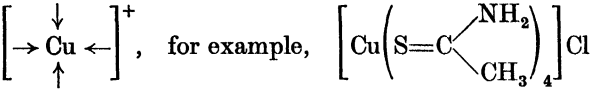
The atom here acquires a share in three additional electrons. It may simplify matters if we show the origin of the various shared electrons forming the bonds, assuming these to be simple electron-pair bonds. For this purpose we shall make use of Sidgwick's symbol (→) for a 'coordinate' covalent bond to indicate that the pair of electrons is supplied by the atom away from which the arrow points. No physical distinction between bonds indicated by → or — is implied. It is easily seen that in the $[Ag(CN)_2]^-$ ion the Ag atom acquires a share in three additional electrons, but it is not so obvious in the case of crystalline Cu_2O. In a crystal of cuprous oxide every oxygen atom is surrounded tetrahedrally by four Cu and every Cu has two oxygen neighbours. We could therefore represent the bond scheme as follows, maintaining the octet of valency electrons of the oxygen atom:



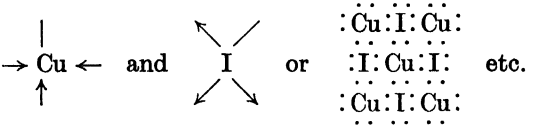
The electronic structure of the Cu atom in 2-coordination is therefore 2, 8, 18, $\underline{4}$, shared electrons being underlined. The orbitals used are hybrid *sp* orbitals, as described in Chapter III. The linear arrangement of bonds in 2-coordinated aurous compounds is accounted for in a similar way.

4-covalent Atoms

The atoms (Cu^I and Ag^I) here acquire seven additional shared electrons as in forming a singly charged complex of the type



or in the crystalline cuprous halides and AgI with the zinc-blende structure. In these crystals each atom is surrounded by four of the other kind, and we may represent the bond picture



The electronic structure of the 4-covalent Cu^I atom is accordingly 2, 8, 18, $\underline{8}$ (the krypton configuration). One 4*s* and three 4*p* orbitals are used in forming the four bonds which are therefore of the normal sp^3 tetrahedral type. Examples of compounds containing 2- and 4-coordinated cuprous, argentous, and aurous atoms are summarized in the following table.

Some of the compounds in this table are mentioned in other chapters as follows: Cu_2O, Ag_2O, p. 315; cuprous and argentous halides, p. 274; $KAg(CN)_2$, p. 448; $[Ag(NH_3)_2]_2SO_4$, p. 150; $Cs_2Au_2Cl_6$ and $Cs_2AgAuCl_6$,

p. 290. The 4-fold molecule $Cu_4I_4(AsEt_3)_4$ has a rather interesting structure (Fig. 156). This compound, with empirical formula $CuI.As(C_2H_5)_3$, was shown by the ebullioscopic method to have a 4-fold molecular weight in solution, and an X-ray study of the crystals showed that the structural

	2 linear bonds	*4 tetrahedral bonds*
Cu^I . .	Cu_2O	$K_2Cu(CN)_4$, $\left[Cu\left(SC\langle^{NH_2}_{CH_3}\right)_4\right]Cl$, $Cu_4I_4(AsEt_3)_4$ and the crystalline cuprous halides
Ag^I . .	Ag_2O, $K[Ag(CN)_2]$ $[Ag(NH_3)_2]_2SO_4$ $Cs_2AgAuCl_6$	$\left[Ag\left(SC\langle^{NH_2}_{CH_3}\right)_4\right]Cl$, $Ag_4I_4(AsEt_3)_4$ AgI (crystalline)
Au^I . .	$Cs_2Au^IAu^{III}Cl_6$	No example known

unit consists of a central tetrahedron of copper atoms surrounded by tetrahedral groups of iodine atoms and triethylarsine molecules.

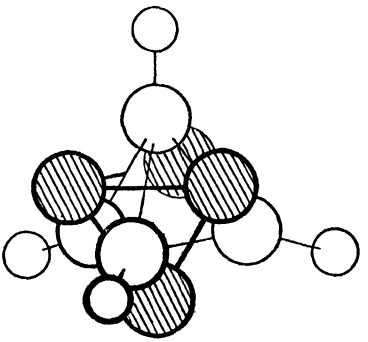


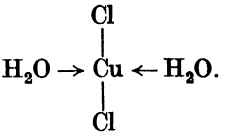
FIG. 156. The molecule $Cu_4I_4[As(C_2H_5)_3]_4$. The shaded circles represent I and the small circles As atoms, the ethyl groups being omitted.

Divalent Copper and Silver

The usual, possibly the only, number of covalent bonds formed by these atoms is four, the four bonds being coplanar. (An earlier demonstration of the tetrahedral configuration of the four bonds from a cupric atom—the resolution of the benzoyl pyruvic acid derivative—has since been disproved.) The stereochemistry of these divalent atoms is rather less simple than that of the univalent atoms. We have already seen (p. 86) that Ni^{II} forms four coplanar bonds using one $3d$, one $4s$, and two $4p$ orbitals which are hybridized to dsp^2 orbitals, the distribution of the electrons in the 4-coordinated Ni^{II} atom being

			3s	*3p*	*3d*	*4s*	*4p*
4-covalent Ni^{II}	2	8	2	6	8+2	2	4
						shared	

The neutral copper atom has one electron more than nickel and acquires a share in six additional electrons as in



There are two simple ways of distributing the resulting thirty-five electrons among the available orbitals, viz.

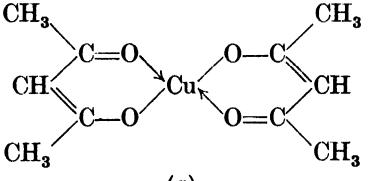
				3*s*	3*p*	3*d*	4*s*	4*p*
(*a*)	2	8		2	6	8+1	2	6
							shared	

i.e. with the odd unshared electron in the fifth 3*d* orbital and the four shared pairs in the 4*s* and three 4*p* orbitals. The bonds would then be tetrahedral sp^3 bonds with strength 2·0 (see p. 87). The alternative,

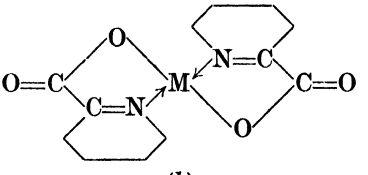
				3*s*	3*p*	3*d*	4*s*	4*p*
(*b*)	2	8		2	6	8+2	2	4+1
						shared		

is to place the unshared electron in a 4*p* orbital, when the bonds would be planar dsp^2 bonds of strength 2·694. The formation of these dsp^2 bonds rather than tetrahedral bonds is therefore due to the greater strength of the former. A similar explanation holds in the case of Ag^{II}. The coplanar arrangement of four covalent bonds from a cupric atom has been proved in a number of compounds, including the following:

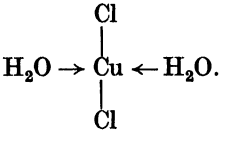
(1) Coordination complexes with organic molecules such as acetylacetone (*a*), phthalocyanine (see p. 526) and methyl-ethyl-glyoxime. The cupric compound of the latter is isomorphous with the nickel derivative. The planar configuration of the four metal bonds has also been demonstrated in the cupric and argentic compounds of picolinic acid (*b*).



(*a*)



(*b*)



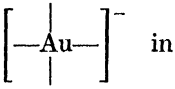
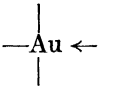
(*c*)

(2) In crystalline CuO the metal atoms form four coplanar bonds; for its structure see p. 315.

(3) In crystalline $CuCl_2.2H_2O$ the structural units are planar groups of the kind shown at (*c*) above, and the same groups are found in crystals of $K_2CuCl_4.2H_2O$. In this crystal we might have expected to find $(CuCl_4)^{2-}$ ions, but the nearest neighbours of a copper atom are two oxygen atoms (of H_2O molecules) at 1·97 A. and two chlorine atoms at 2·32 A. There are also two more chlorine atoms at 2·95 A., but this Cu—Cl distance indicates that these atoms are not covalently bound to the copper. The structure is therefore an aggregate of $(CuCl_2.2H_2O)$ groups, K^+ and Cl^- ions.

Trivalent Gold

As far as is known, gold in the trivalent state always forms four covalent bonds, which are coplanar like those of 4-covalent Cu^{II} and Ag^{II}. When forming these bonds the effective atomic number of the Au^{III} atom is 84, five shared electrons being added to the seventy-nine of the free atom, as is seen from the bond pictures

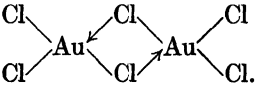

in $K[AuBr_4]$ or 
in Au_2Br_6 (see below).

The electronic structure of the 4-covalent Au^{III} atom is thus

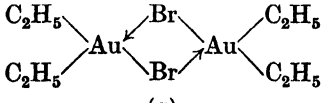
				5*s*	5*p*	5*d*	6*s*	6*p*
2	8	18	32	2	6	8+2	2	4
							shared	

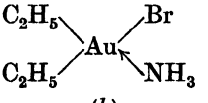
so that four coplanar dsp^2 bonds are formed.

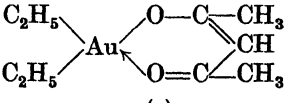
Of the trihalides of gold the chloride and bromide have been shown to form double molecules Au_2X_6. The vapour density of the chloride between 150° and 260° C. indicates Au_2Cl_6 molecules, and the elevation of the boiling-point of bromine by the bromide shows that this compound exists as molecules Au_2Br_6. Although the structures of these halides have not been determined, studies of closely related compounds show that they must be of the form



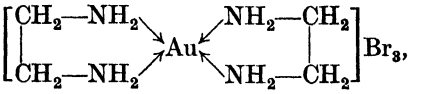
Compounds with empirical formulae $AuBr(C_2H_5)_2$ and $AuBr_2(C_2H_5)$ have been prepared. The determination of the molecular weight of the former in benzene and bromoform solutions shows that the molecules are $Au_2Br_2(C_2H_5)_4$, and an X-ray study of the crystals proves that the molecules are planar and of the form (*a*). In recent years many coordination


(*a*)


(*b*)


(*c*)

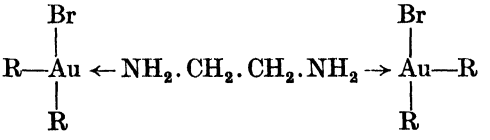
compounds of gold have been made, such as (*b*) and (*c*) above, and there are many stable 4-coordinated auric salts. Among these we may mention



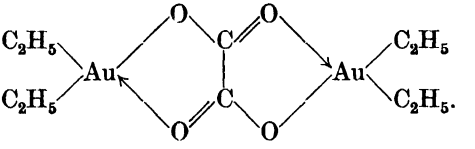
$[Au(NH_3)_4](NO_3)_3$
$(NO_3)SO_4$,
(PO_4)

$KAuCl_4$ and $KAuBr_4$.

Investigation of the structure of the crystalline dihydrate of the latter confirms the presence of planar $[AuBr_4]^-$ ions, and planar $AuCl_4^-$ ions occur in crystals of $Cs_2Au^IAu^{III}Cl_6$ (see p. 290). Molecules containing two gold atoms include, in addition to those already mentioned,

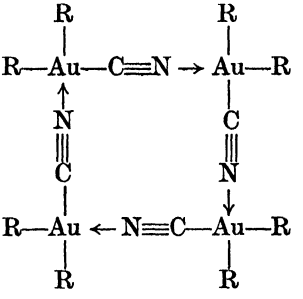


and



The latter is interesting on account of its similarity to the binuclear oxalato palladium compounds which are mentioned later.

By the action of silver cyanide on $[AuBr(C_2H_5)_2]_2$ there is produced the corresponding cyanide, but this compound has a 4-fold molecular weight, $[AuCN(C_2H_5)_2]_4$. Now the structure shown on p. 508 for the bromo-compound is possible because the angle between two bonds from a halogen atom must be approximately 90°, but a similar structure is not possible for the cyanide since the atoms linked by the CN group must be collinear with the C and N atoms. Accordingly this cyanide forms a square molecule with the structure shown below, R being an alkyl group (C_2H_5, nC_3H_7).



The determination, by X-ray methods, of the structure of the *n*-propyl compound added a further very interesting example to the list of molecules containing 4-coordinated auric atoms.

THE STEREOCHEMISTRY OF CERTAIN B SUB-GROUP ELEMENTS: THE INERT PAIR

The elements of the B sub-groups which follow copper, silver, and gold present several points of interest. We have seen that the latter elements exhibit valencies higher than one, the 'group valency', making use of electrons of the penultimate quantum group. Some of the elements we are now going to consider show a quite different behaviour. The pair of *s* electrons shows a reluctance or inability to ionize or to act as bonding electrons and on this account has been termed the 'inert pair'. This phenomenon is observed in the heavier elements of the B sub-groups and results in an element resembling, in some of its compounds, the element which is two places in front of it in the Periodic Table. Thus we find thallous compounds with resemblances to aurous (actually more to argentous), and Pb^{II} compounds like those of Hg^{II}. We repeat here the outer electronic structures of the B sub-group atoms, as we shall have occasion to refer to them.

				4*s*	4*p*						5*s*	5*p*							6*s*	6*p*
Cu				1		Ag					1		Au						1	
Zn				2		Cd					2		Hg						2	
Ga				2	1	In					2	1	Tl						2	1
Ge	2	8	18	2	2	Sn	2	8	18	18	2	2	Pb	2	8	18	32	18	2	2
As				2	3	Sb					2	3	Bi						2	3
Se				2	4	Te					2	4	Po						2	4
Br				2	5	I					2	5	..						2	5

Evidence for the Existence of the Inert Pair

In his discussion of the inert pair Sidgwick argued that evidence for its existence comes from

(1) The formation of ions with charge two less than the normal group valency.

(2) The existence of covalent compounds in which the metal atom has a 'mixed' valency group of more than eight electrons. We shall explain later what is meant by a mixed valency group. Let us review the available evidence under these two heads.

(1) Stable ions formed by the elements of the earlier Periodic Groups contain either eight or eighteen electrons in the outermost quantum group in the case of A and B sub-group elements respectively. Ions of transition elements have, of course, outer shells containing intermediate numbers of electrons. Some of the heavier B sub-group elements, however, in addition to forming the normal ions, e.g. Tl^{3+} (2, 8, 18, 32, 18), also form ions of the type (core) 2 as in Tl^{+} (2, 8, 18, 32, 18, 2), and this may be regarded as evidence for the inertness of the two *s* electrons. Now evidence for the existence of ions is by no means always clear-cut. It may come from the properties of compounds in solution or in the fused state or from the nature of their crystal structures. In this connexion the first elements we have to consider are those of Group III B, Ga, In, and Tl. (The formation

of a monatomic vapour by mercury may be interpreted as evidence for the inertness of the two *s* electrons, leading to a resemblance to the inert gases.) There is no evidence for the existence of the Ga^+ ion and that of In^+ is doubtful. Indium forms the chlorides InCl, $InCl_2$, and $InCl_3$, of which the first two are decomposed by water giving $In^{3+} + In\downarrow$. The vapour densities of all three chlorides are apparently normal. The structure of crystalline InCl is not known, and apparently the only evidence for the existence of the In^+ ion is the moderate conductivity of the fused salt. There would appear to be as much evidence for the existence of In^{2+}, for $InCl_2$ is said to be isomorphous with $SnCl_2$, but here again we do not know whether $SnCl_2$ is an essentially ionic crystal. Since we do not know why the divalent state is possible for indium, it is probably wise not to take the univalent state as evidence of an inert pair in this element. The thallous ion Tl^+, however, is certainly stable. The soluble hydroxide TlOH is a strong base like KOH, and the halides have typical ionic structures (see p. 274). In Group IV B tin is the first element to form a divalent ion, though Sn^{2+} is easily converted into Sn^{4+}, giving stannous compounds reducing properties. When we reach lead we find that the stable ion is Pb^{2+}. It has no reducing properties and there is no evidence that Pb^{4+} can exist in aqueous solution, though it presumably exists in crystalline PbO_2, which has the ionic rutile structure. From the existence of double nitrates such as $Mg_3[M^{III}(NO_3)_6]_2.24H_2O$ in which the trivalent metal may be Bi, La, Ce, etc., it seems likely that the Bi^{3+} ion exists. Let us now examine the other criterion for the inert pair.

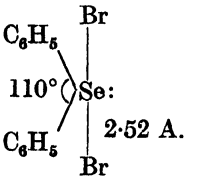
(2) The evidence from covalent compounds is based on the postulate that a mixed valency group, i.e. one containing both shared and unshared electrons, is never larger than eight, though wholly shared groups of up to sixteen electrons are commonly found. Thus while, for example, the valency groups in $SbCl_3$ (2, 6) and SbF_5 (10) are both normal, those in ICl_3 (4, 6) and IF_5 (2, 10) are consistent with the above hypothesis only if we write them (2) 2, 6 and (2) 10 respectively, assuming two electrons to be acting as if part of the core. Application of this idea to the electronic structures of covalent compounds of the elements, in addition to the evidence from the formation of ions, indicates the occurrence of the inert pair in all the elements in the lower part of the table given below.

Be	B	C	N	O	F
Mg	Al	Si	P	S	Cl
Zn	Ga	Ge	As	Se	Br
Cd	In	Sn	Sb	Te	I
Hg	Tl	Pb	Bi		

We shall not, however, accept the second criterion as evidence for the inertness of a pair of *s* electrons, for mixed groups of more than eight electrons certainly occur, for example, in the planar $[ICl_4]^-$ ion, where we have iodine with (2, 8, 18, 18) 4, 8 or with (2, 8, 18, 18, 2) 2, 8 if we incorporate the two 5*s* electrons in the core. While, therefore, there is no

doubt about the inertness of a pair of *s* electrons in certain elements, we shall prefer to confine the use of the term to cases where either an ion such as Tl^+ is formed or where structural investigations show that the pair of electrons is *stereochemically* inert.

In Chapter III we saw that the pyramidal and non-linear configurations respectively of molecules like NH_3, SH_2, etc., could be ascribed either to the use of *p* orbitals or to the formation of tetrahedral bonds with the pair(s) of unshared electrons occupying one or two of the tetrahedral bond positions. On the latter view the presence of the pairs of unshared electrons influences the angles between the bonds formed. No comprehensive answer can yet be given to the question: How is the stereochemistry of an atom affected by the presence of pairs of unshared electrons? Among compounds of the heavier atoms where the valency group often contains shared and unshared electrons there appear to be some cases where the configuration of the bonds is that to be expected if one or more pairs of unshared electrons occupied some of the bond positions and others where the arrangement of the bonds is that which we should expect if the unshared pairs of electrons were absent. In the latter case we may describe the pair of unshared electrons as stereochemically inert. When discussing the stereochemistry of iodine we found that the planar configuration of the ICl_4^- ion, in which the iodine atom has a valency group 2, $2+\underline{4}$, $\underline{4}$, could be simply accounted for if we assume the group to be derived from an octahedron with the two pairs of unshared electrons occupying two of the bond positions. The configuration of the linear ICl_2^- ion could similarly be derived from a trigonal bipyramid, three pairs of unshared electrons occupying the equatorial bond positions. The trigonal bipyramidal structure assigned to IF_5 would, however, suggest that two of the valency electrons of the group 2, $\underline{10}$ are stereochemically inert. The interatomic distances and also the octahedral configurations of the ions $[SeBr_6]^{2-}$ and $[SbBr_6]^{3-}$ indicate that the pairs of 4*s* electrons of the Se and Sb atoms are stereochemically inert. In $[SeBr_6]^{2-}$ the selenium atom has the valency group 2, $\underline{6}$, $\underline{6}$, and yet octahedral bonds are formed. However, in the molecule $Se(C_6H_5)_2Br_2$ the four bonds are



directed towards four of the five apices of a trigonal bipyramid, one equatorial position presumably being occupied by the pair of unshared electrons (valency group (2, $\underline{8}$)). The Se—Br and Se—C distances are 2·52 and 1·91 A. respectively. Whereas in the $[SnCl_6]^{2-}$ and $[PbBr_6]^{2-}$ ions the octahedral (sp^3d^2) radii of Sn^{IV} and Pb^{IV} are only some 3 per cent. greater than the tetrahedral sp^3 radii, the octahedral radius of Se^{IV}

deduced from the $[SeBr_6]^{2-}$ ion is 23 per cent. greater than its tetrahedral radius. Pauling therefore suggests that the bonds are not $4s4p^34d^2$ bonds but $4p^34d^25s$ bonds, the inert pair occupying the 4*s* orbital and the use of the 5*s* orbital accounting for the increased radius of the Se atom. The $[SbBr_6]^{3-}$ ion must be supposed to occur in the salt $(NH_4)_2SbBr_6$, which should be written $(NH_4)_4(SbBr_6)^-(SbBr_6)^{3-}$. In the $(SbBr_6)^-$ ion the bonds would be $5s5p^35d^2$ and in the $(SbBr_6)^{3-}$ ion, $5p^35d^26s$.

In the compounds of these heavy atoms interesting valency groups arise, and it is to be hoped that more attention will be paid to the stereochemistry of these elements. Tellurium is a case in point. In the dihalides Te has the valency group 2, 2+4, two *p* orbitals being used, but an electron diffraction study of $TeCl_2$, $TeBr_2$, and TeI_2 suggests that the interbond angle is at least 150°. The stereochemistry of 4-covalent tellurium also is not entirely satisfactory. The $[TeO_4]^{2-}$ ion is tetrahedral, salts like K_2TeO_4 and K_2SO_4 being isomorphous. In this case there is a group of eight shared electrons, 2, 6. In $TeCl_4$, however, we have 2, 6, 2, $(5s^25p^65d^2)$. The dipole moment of the compound in benzene is 2·54 D., suggesting an unsymmetrical molecule, and electron diffraction results indicate a distorted pyramidal structure which may possibly be regarded as derived from a trigonal bipyramid with one bond position occupied by the pair of unshared electrons. This 2, 6, 2 group is the same as in PbO, which we shall mention later, and it also occurs in a molecule like $Te(CH_3)_2I_2$. This compound was prepared in two forms which were assumed to be the cis and trans isomers of the planar molecule. It was shown later, however, that one of these forms is a salt $[Te(CH_3)_3]^+[Te(CH_3)I_4]^-$, since with alkali the base $Te(CH_3)_3OH$ is formed and KI gives $Te(CH_3)_3I$ and $K[Te(CH_3)I_4]$. It would be of great interest to know the shapes of the $Te(CH_3)_2I_2$ molecule and of the ions $[Te(CH_3)_3]^+$ and $[Te(CH_3)I_4]^-$, in which tellurium has the following sets of valency electrons: 2, 6, 2; 2, 6; and 2, 6, 4. In the latter, ten of the twelve electrons are shared compared with eight in $[ICl_4]^-$ which has the same number of electrons in the fifth shell. We shall conclude this section with some remarks on the stereochemistry of mercury, thallium, tin, and lead.

Mercury

Since comparatively little is known of the structures of mercurous compounds, we shall confine our remarks to divalent mercury. Mercury forms two collinear *sp* bonds with the valency group 2, 2, in molecules like $CH_3—Hg—CH_3$, $C_2H_5S—Hg—SC_2H_5$, and those of the dihalides. The molecules $HgCl_2$, $HgBr_2$, and HgI_2 have been shown by electron diffraction to form linear molecules in the vapour state. In the crystalline state, however, only the chloride exists as simple molecules HgX_2. The fluoride HgF_2 crystallizes with the essentially ionic fluorite structure, and the bromide and iodide have layer structures. In $HgBr_2$ each mercury atom is surrounded by six Br atoms in a very distorted octahedral arrangement, two of these atoms being very much closer to the Hg than the others.

We can therefore regard the Hg as 2-covalent. The iodide has quite a different type of layer structure in which every Hg atom has four equidistant iodine neighbours arranged tetrahedrally. Data on interatomic distances in these halides, and also in some complex halides to be described later, are given in the table below. The similarity in the distances Hg—X in the crystal and in the vapour for the chloride and bromide should be compared with the difference between the corresponding distances for the iodide. For this compound the distances are for *sp* bonds in the vapour molecule and sp^3 bonds in the crystal. In these compounds mercury clearly shows a preference for 2-coordination, the alternative being the formation of four tetrahedral sp^3 bonds, with valency group (2, 6). In this connexion the structures of some complex halides containing

Compound	*Numbers of* X *atoms around* Hg *in crystal*			Hg—X *in vapour molecule*
	2 at	2 at	2 at	
HgF_2		8 at 2·40		
$HgBr_2$	2·48	3·23	3·23	2·40
HgI_2		4 at 2·78		2·55
$HgCl_2$	2·25	3·34	3·63	2·20
NH_4HgCl_3	2·34	2·96	2·96	
$K_2HgCl_4.H_2O$	2·4	2·8	3·15	
$CsHgCl_3$		6 at 2·72		
$(Bu_3As)_2(HgBr_2)_3$	2·25	4 more at 3·1–3·2		

mercury are of interest. According to an early X-ray study $CsHgCl_3$ has the perovskite structure in which Hg would have six equidistant neighbours arranged octahedrally. This structure is characteristic of essentially ionic crystals, and it would be desirable to confirm this symmetrical environment of Hg by six Cl atoms. An entirely different type of structure has been assigned to the corresponding ammonium salt, NH_4HgCl_3. This consists of layers of $HgCl_6$ octahedra linked together in the way shown in Fig. 157 into layers of composition $(HgCl_3)_n^{n-}$. The layers are held together by the NH_4^+ ions. The distances between the Hg atoms and the Cl atoms shared between the octahedra are so large (2·96 A.) that the structure would probably be better described as an aggregate of $HgCl_2$ molecules, Cl^- and NH_4^+ ions, though the environment of the Cl^- ions appears rather unsatisfactory.

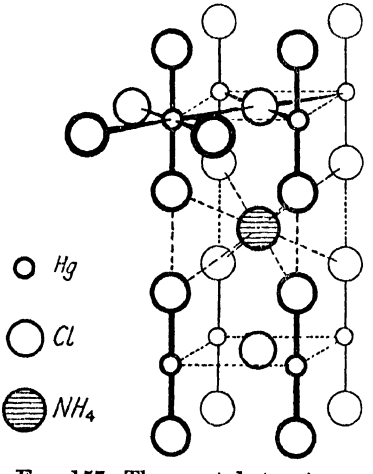
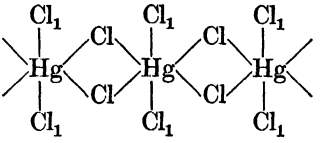


FIG. 157. The crystal structure of NH_4HgCl_3.

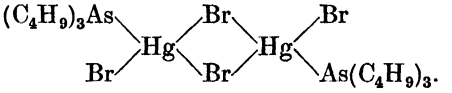
In $K_2HgCl_4.H_2O$ also the Hg atoms have two Cl neighbours much closer

than the others. In crystals of this compound there are chains of $HgCl_6$ octahedra of the type



but the Hg—Cl_1 distances are much shorter than the others. Here again the large values of the latter distances (see above table) are difficult to reconcile with covalent binding in the chains.

Mercuric halides combine with tertiary phosphines and arsines (e.g. $As(C_4H_9)_3$) to form crystalline products $(R_3As)_m(MX_2)_n$. The compound $[(C_4H_9)_3As]_2[HgBr_2]_2$ consists of molecules in which the two Hg atoms are joined by halogen atoms:



This compound is therefore similar in general type to the gold compounds already described (p. 508) and to the bridged palladium compounds mentioned later (p. 527), except that the bonds from the metal atoms are disposed tetrahedrally instead of being coplanar. The product richer in mercuric bromide and having the empirical formula $[(C_4H_9)_3As]_2[HgBr_2]_3$ is found to be a mixed crystal of $[(C_4H_9)_3As]_2Hg_2Br_4$, the above bridged molecule, and $HgBr_2$. In this crystal the environment of a Hg atom of

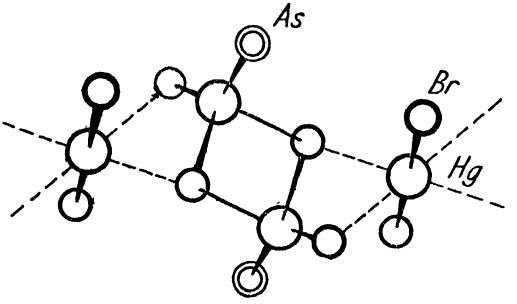
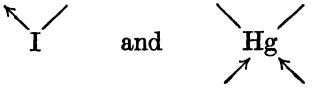


FIG. 158. The environment of a mercury atom of a $HgBr_2$ molecule in $[(C_4H_9)_3As]_2Hg_2Br_4.HgBr_2$.

a $HgBr_2$ molecule is very similar to that in $HgBr_2$ itself. There are two near Br neighbours and four more distant which belong to bridged molecules, as shown in Fig. 158.

In HgI_2 mercury forms four tetrahedral bonds, thereby acquiring the electronic configuration (2, 8, 18, 32, 18) 2, 6. Each iodine atom is attached to two mercury atoms so that we may give the bond picture



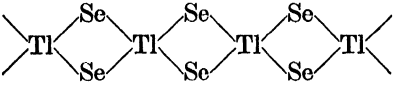
to bring the structure of this crystal into line with our ordinary ideas of the chemistry of these elements. Tetrahedral bonds also occur in one of the forms of HgS. This compound is dimorphous. Metacinnabarite, a rare mineral, crystallizes with the zinc-blende structure, but the more usual form, cinnabar, has a structure unique among those of monosulphides. The Hg atoms have two nearest S neighbours (at 2·52 A., cf. 2·53 A. in metacinnabarite), two more at 2·91 A., and two others at 3·25 A., completing the very distorted octahedron of sulphur atoms around mercury. This type of environment may be compared with that in certain of the halides.

Thallium

We have already discussed some of the evidence for the existence of the thallous ion, Tl^+. The halides show a remarkable resemblance to those of silver in their colours and solubilities. TlF, like AgF, is soluble in water and the others are very insoluble. Their crystal structures, however, which have been described on page 274, are different from those of the silver halides, for TlCl, TlBr, and TlI have the caesium chloride structure at ordinary temperatures. Thallous hydroxide is a strong base soluble in water like the alkali hydroxides, and Tl_2SO_4 is isomorphous with K_2SO_4. There are also complex salts such as $Tl_2LiBi(NO_2)_6$ which is isomorphous with the corresponding K, Rb, and Cs compounds, the latter elements replacing Tl^I in the above formula.

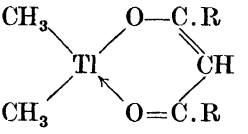
Little is known of the structures of thallic salts, which include the chloride (anhydrous and tetrahydrate, $TlCl_3.4H_2O$) and the sulphate $Tl_2(SO_4)_3.7H_2O$ which forms double salts $NH_4Tl^{III}(SO_4)_2.4H_2O$; compare the alums.

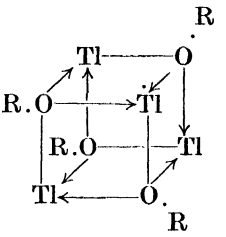
Compounds in which thallium is apparently divalent are probably complex salts containing the element in the uni- and tri-valent states, and the chloride with empirical formula Tl_2Cl_3 may be formulated as thallous thallic chloride, $Tl^I_3(Tl^{III}Cl_6)^{3-}$. (Octahedral $TlCl_6^{3-}$ ions occur in crystals of $K_3TlCl_6.2H_2O$.) Thalloso-thallic sulphate and sulphide may be written $Tl^ITl^{III}(SO_4)_2$ and $Tl^I(Tl^{III}S_2)$ respectively instead of $TlSO_4$ and TlS. The crystal structure of the selenide TlSe has been determined and supports this view of these compounds. In crystals of TlSe the thallium atoms are of two types, one set having four (tetrahedral) and the other eight neighbours. The former are linked by the Se atoms to form chains of tetrahedra sharing opposite edges:



whereas the latter lie between the chains in positions of 8-coordination. The large distance between these latter Tl atoms and their eight Se neighbours (3·42 A.) compared with the Tl—Se distance of only 2·68 A. in the chains suggests the formulation of the compound as an ionic thallous thallic selenide, $Tl^I(Tl^{III}Se_2)$.

In its covalent compounds thallium shows no reluctance to utilizing the two 6*s* electrons for bond formation. Indeed monoalkyl derivatives Tl(Alk) in which the valency group would be (2, 2) are not known, whereas trialkyls (valency group 2, 4) are known and the most stable alkyl derivatives are the dialkyl halides such as $[Tl(CH_3)_2]I$. These are ionic compounds—$[Tl(CH_3)_2]OH$ being a strong base—and in the $[Tl(Alk)_2]^+$ ions the thallium atom has the same outer electronic structure as mercury in $CH_3—Hg—CH_3$, viz. (2, 2). Accordingly the $[CH_3—Tl—CH_3]^+$ ion is linear, as shown by the determination of the crystal structure of $Tl(CH_3)_2I$. In molecules such as $Tl(Alk)_2A$, where A represents a molecule of a β-diketone, the thallium apparently has a completely shared octet (2, 6).

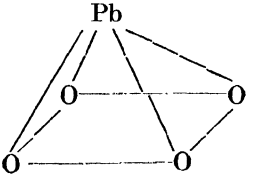


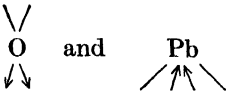


The alkylates (e.g. $TlOC_2H_5$) exist as 4-fold molecules in benzene solution, as shown by molecular weight measurements. A reasonable structure for the complex molecule is that shown diagrammatically above. In this molecule the valency group of the thallium would be (2, 6), but further study of these compounds is required.

Tin and Lead

A comparison of the chemistry of these two elements reveals some interesting resemblances and also some remarkable differences. The atoms of each have the same outer electronic structure, two *s* and two *p* electrons, and each exhibits valencies of 2 and 4. The more metallic nature of lead is shown by the difference between the structures of the elements (see p. 541). We have already compared the relative stabilities of the di- and tetra-valent states of lead. One of the peculiarities of lead is that some compounds which we might expect to form essentially ionic crystals do not appear to do so. Thus in PbO (Fig. 159) a Pb atom has a remarkable arrangement of neighbours, having its four oxygen neighbours lying all to one side. If we formulate PbO as a covalent crystal we find that Pb has the valency group (2, 6, 2), and the only simple explanation of the four pyramidal bonds is that the inert pair of 6*s* electrons occupies the apex of the tetragonal pyramid. Stannous oxide has the same structure.





As in previous cases, we may give the above bond pictures since each

oxygen atom is surrounded tetrahedrally by four Pb atoms. Again, PbS has the rock-salt structure, but the physical properties of galena, e.g. its opacity and brilliant metallic lustre, are not those of simple ionic crystals. Although SnO and PbO have the same crystal structure, SnS has a structure quite different from that of PbS. Instead of a regular octahedral

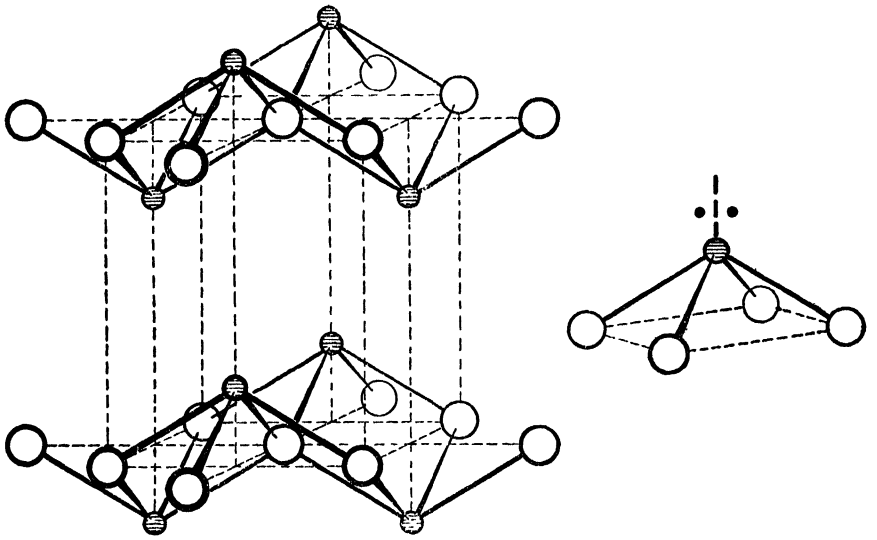
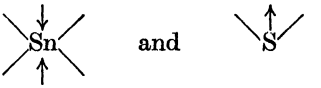


FIG. 159. The crystal structure of PbO (and SnO). The small shaded circles represent metal atoms. The arrangement of bonds from a metal atom is shown at the right, where the two dots represent the 'inert pair' of electrons.

environment the Sn atom has three approximately equidistant S neighbours so that, with the valency group 2, $\underline{6}$ it is forming three pyramidal bonds. Comparison of the dihalides of Sn and Pb is not possible since the structures of the crystalline tin dihalides do not appear to be known. Of the plumbous halides the fluoride has the fluorite structure and the iodide the CdI_2 structure, but the chloride and bromide crystallize with a structure peculiar to these two salts in which a Pb^{2+} ion has nine halogen neighbours. The adoption of this structure is presumably to be attributed to the large size of the metal ion, which makes the 6-coordination layer structures adopted by so many dichlorides and dibromides impossible for the lead salts. In *molecules* of these dihalides we should have the valency group 2, $\underline{4}$, assuming simple electron-pair bonds, and such p^2 bonds would be mutually perpendicular. The structures of the free molecules $PbCl_2$, $PbBr_2$, PbI_2, and $SnCl_2$, $SnBr_2$, and SnI_2 have been studied by the electron diffraction method and the molecules shown to be non-linear. The salt $NH_4Pb_2Br_5$ apparently consists of $PbBr_2$ molecules, NH_4^+ and Br^- ions. It exists, of course, only in the solid state. The nearest neighbours of a lead atom are two Br at 2·89, two Br at 3·16, and four Br at 3·35 A., and the angle between the bonds from the Pb atom to its two nearest Br neighbours is $85\frac{1}{2}\pm2°$.

In the simple molecules $Sn(CH_3)_4$, $Pb(CH_3)_4$, and the tetrahalides such as SnI_4 the metal atoms form four normal tetrahedral sp^3 bonds—valency group 2, 6. The dioxides SnO_2 and PbO_2 both crystallize with the rutile structure and must be regarded as essentially ionic crystals. Lead forms no disulphide, but SnS_2 has the CdI_2 layer structure in which the Sn atoms have six octahedral S neighbours. In this structure the S atoms form three pyramidal bonds, in contrast to the planar arrangement of three Sn^{4+} ions around O^{2-} in SnO_2, and if we regard SnS_2 as a covalent crystal we find that tin has the valency group 2, 6, 4, octahedral sp^3d^2 bonds being formed (see the accompanying bond picture). This same



valency group occurs in the lead atom in the $[PbX_6]^{2-}$ ions in salts such as $(NH_4)_2[PbBr_6]$.

THE STEREOCHEMISTRY OF THE GROUP VIII METALS

The Group VIII metals comprise the three triads

Fe,	Co,	Ni
Ru,	Rh,	Pd
Os,	Ir,	Pt.

All these elements have incomplete penultimate shells and exhibit more than one valency. They do not, however, all exhibit the same valencies, and before considering their stereochemistry we will note some of the differences between the chemical properties of these elements. Iron forms two extensive series of compounds—the ferrous and ferric—in which it shows valencies of 2 and 3 respectively. Ferrous and ferric compounds are readily interconvertible. Ferric salts can be reduced by zinc and acid or by $SnCl_2$, and ferrous salts are oxidized on exposure to air or by oxidizing agents like $KMnO_4$ or $K_2Cr_2O_7$. Both series of salts are stable in the ordinary sense of the word and ferrous and ferric chlorides, for example, may both be recrystallized from water as hydrates. Certain complex ions containing iron are very stable, as, for example, the ferrocyanide ion $[Fe(CN)_6]^{4-}$. Chlorine oxidizes this to the ferricyanide ion, $[Fe(CN)_6]^{3-}$, but $K_3Fe(CN)_6$ is slowly converted into the ferrocyanide when kept. Another complex possessing considerable stability is the nitroprusside ion, $[Fe(CN)_5NO]^{2-}$. In contrast to these cyanide ions the ammines of iron are not at all stable. For example, the $[Fe(NH_3)_6]^{2-}$ ion is decomposed by water, and trivalent iron forms no ammines comparable as regards stability with those of cobalt.

The cobalt salts normally met with are cobaltous (Co^{II}) salts which are not readily oxidized to simple cobaltic salts. The latter have to be prepared by special methods such as electrolytic oxidation, by which means CoF_3 and $Co_2(SO_4)_3.18H_2O$ are made. In coordination complexes, however, cobalt prefers the trivalent state. The $[Co(CN)_6]^{4-}$ ion is readily

oxidized to $[Co(CN)_6]^{3-}$, and many cobaltic complexes possess remarkable stability. In the number and stability of its ammines cobalt is rivalled only by chromium, and we shall consider the cobaltammines shortly. Whereas $Fe(CN)_2$ dissolves in excess KCN to form $K_4Fe(CN)_6$, $Co(CN)_2$ yields in the presence of air $K_3Co(CN)_6$. Similarly, if a cobaltous salt solution is acidified with acetic acid and a solution of KNO_2 is added, the $Co(NO_2)_6^{3-}$ and not the $Co(NO_2)_6^{4-}$ ion is formed. The free acid $H_3Co(CN)_6$ is not attacked by strong nitric acid.

In forming only one series of stable compounds, in which it is divalent, nickel differs from cobalt and still more from iron. In some respects nickel shows a considerable resemblance to copper. Unlike iron and cobalt, nickel forms no stable hexacyano-complex, and $Ni(CN)_2$ dissolves in excess KCN solution to form $K_2Ni(CN)_4$; compare $K_2Zn(CN)_4$, etc. The Ni^{2+} ion is normally 6-coordinated, witness the hexahydrates and hexammines of $NiCl_2$, $NiSO_4$, and $Ni(NO_3)_2$, and nickel forms some 6-covalent complexes, but it prefers to form *four covalent* bonds as in $Ni(CO)_4$, $Ni(CN)_4^{2-}$, and the numerous planar derivatives some of which we shall mention later. Some compounds of univalent nickel have been prepared, e.g. NiCN, $K_2Ni(CN)_3$, and the carbonyl and nitrosyl cyanides of the type $K_2[Ni(CN)_3CO]$. There is also evidence that all the other Group VIII metals except Os and Ir can exhibit univalency, but nothing is known of the structures of these compounds and we shall therefore not discuss them further.

The other six Group VIII metals have many points of resemblance to one another. For example, they are found together in nature and not in large amounts in iron ores. They have no ferromagnetic properties like iron, cobalt, and nickel. Also, they exhibit a valency of four, which is unknown in the first triad. There are, however, noticeable vertical 'family' resemblances. For example, of these six elements only Os and Ru form volatile tetroxides MO_4 and nitroso-compounds of the type $K_2[RuCl_5NO]$ analogous to $K_2[Fe(CN)_5NO]$. Rhodium and iridium resemble cobalt in forming alums, e.g. $KIr(SO_4)_2.12H_2O$, containing the Rh^{3+} and Ir^{3+} ions, many complex ions such as $Ir(CN)_6^{3-}$ and $Ir(NO_2)_6^{3-}$, and ammines. Finally, palladium and platinum are very similar to one another both in the di- and tetra-valent states, in which they are normally 4- and 6 coordinated respectively. Many complex compounds of palladium and platinum are isomorphous with the corresponding nickel compounds, and in the elementary state these three metals are notable for their catalytic activity.

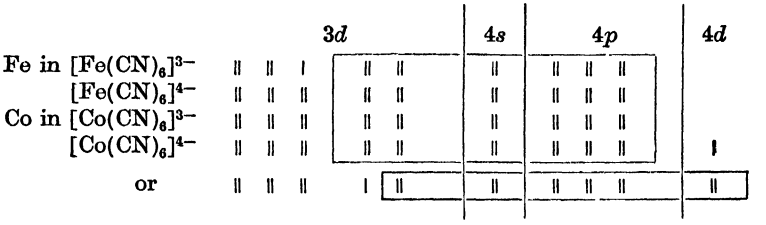
A feature of the chemistry of these Group VIII metals is the extraordinary number and variety of the coordination compounds which they form, and a survey of the formulae and properties of these compounds suggests a number of questions. The original suggestion of Werner that in 'molecular compounds' like $CoCl_3.6NH_3$ the six NH_3 molecules were arranged in the first 'coordination sphere' around the metal atom and the three chlorine atoms in an outer sphere was supported by the chemical

behaviour of such compounds, by the number of ions formed from one 'molecule', and by the numbers of isomers of mixed coordination groups like $[Co(NH_3)_4Cl_2]^-$. The early electronic theory of valency interpreted a structural formula such as $[Co(NH_3)_6]Cl_3$ in the following way. The N atom in NH_3 has a pair of unshared electrons which may be used to form a 'coordinate link' to the cobalt atom, and since none of the valency electrons of that atom are used in forming such bonds, the complex carries the same charge (+3) as the free Co^{3+} ion. The cobalt atom can acquire the same group of twelve shared electrons by forming a complex ion like $[Co(CN)_6]^{3-}$. Although it was possible to relate the formulae of many known compounds to the electronic structures of the component atoms, many questions were left unanswered. Firstly, what determines the number of atoms or groups around the central atom in such complexes? In this group of elements by far the commonest coordination number is six though, as we have seen, 4-coordinated compounds are also formed, particularly by Ni, Pd, and Pt. In $[Co(NH_3)_6]^{3+}$ the effective atomic number (see p. 54) of Co is 36 (that of krypton), and this is also the case for iron in the ferrocyanide ion, but the condition for stability is clearly not, in general, the attainment of a particular total number of orbital electrons—compare, for example, $Fe(CN)_6^{3-}$, E.A.N. = 35, $Ni(CN)_4^{2-}$, E.A.N. = 34, or $AuBr_4^-$, E.A.N. = 84, two short of that of radon (86). Secondly, water is found in many complexes (aquo-complexes), e.g. $[Co(NH_3)_5H_2O](NO_3)_3$, $[Co(NH_3)_3(H_2O)Cl_2]Cl$, but H_2S, in which there are pairs of unshared electrons on the S atom just as on the O atom of H_2O, never enters into such complexes. Similarly there are no $[CoI_6]^{3-}$ or $[Co(PH_3)_6]^{3+}$ ions, i.e. some atoms and groups readily coordinate on to the metal atom whereas others do not. Thirdly, why do the transition metals form so many coordination compounds and some other metals so few, and why in particular do the complexes of trivalent cobalt, and also to a lesser degree those of chromium, possess such remarkable stability compared with those of, say, trivalent iron? The analogous compounds of trivalent nickel are, in fact, unknown. Finally, what determines the spatial arrangement of the four bonds in $Ni(CN)_4^{2-}$ or of the six bonds in $Co(NH_3)_6^{3+}$? Clearly it was necessary to find a way of studying the 'group' properties of a set of eight or twelve shared electrons in order to discover why it is stable in certain atoms and to calculate the strength and disposition of the bonds. Also, as we have found before, it is not sufficient to take into account merely the outer electronic structure of an atom, which is the same for oxygen as for sulphur for example. We must also have regard to the electronegativities of atoms and their sizes. Consider, for example, the halogen complexes $[MX_6]^{n-}$ formed by these Group VIII metals. In the complex fluoride ions (e.g. CoF_6^{3-}, FeF_6^{3-}) the bonds are essentially ionic, as shown by the magnetic data, but CoI_6^{3-}, in which cobalt would have the same electronic structure as in $Co(NH_3)_6^{3+}$, is not formed. The elements of the Pd and Pt triads do, however, form octahedral ions MX_6^{2-} containing chlorine,

bromine, and even iodine, e.g. OsI_6^{2-} and PtI_6^{2-}. Now as we go from fluorine to iodine the electronegativity of the halogen decreases and its size increases and either or both of these changes might account for the above facts. Pauling therefore suggests that the explanation of the facts that certain atoms and groups do not coordinate with any of these metals and that others form coordination complexes only with certain of them lies in the different electronegativities of the metal and coordinating atoms. The metals Fe, Co, and Ni are fairly electropositive and tend to form positive ions. They accordingly form fluoro-complexes with ionic M—F bonds but show little tendency to form complexes with the other halogens. On the other hand, the less electropositive elements of the Pd and Pt triads have far less inclination to form simple ions and readily form covalent complexes with the heavier halogens—compare the similar difference between Cu, which forms the stable Cu^{2+} ion, and Au, the chemistry of which is concerned solely with covalent complexes. In the formulation of complexes such as $Co(NH_3)_6^{3+}$ and $Co(CN)_6^{3-}$ with a set of twelve shared electrons around the metal atom and a total of thirty-six orbital electrons, it is clear that the Co atom (atomic number 27) has effectively acquired a negative 'formal charge' which is inconsistent with the tendency of such a metal to lose electrons and form positive ions. Accordingly, only strongly electronegative atoms are found attached to Co in such complexes, e.g. N (NH_3, NO_2, NO) and O (OH_2, OH^-, O^{2-}). Complex groups such as $C_2O_4^{2-}$, NO_3^-, and SO_4^{2-} are also presumably attached through the oxygen atoms, and these electronegative groups remove part of the excess negative charge on the metal atom. The exceptional stability of complexes containing groups like CN or NO_2 may be due to the possibility of resonance with structures involving double bonds to the central metal atom. Since a characteristic property of transition elements is their ability to utilize electrons of the penultimate shell, this would account for the formation of so many stable ions by these metals. Just as in $Ni(CO)_4$ there is the possibility of resonance between structures involving Ni—C and Ni=C bonds, so in the ferrocyanide ion there could be resonance of the Fe—C bond between the forms $Fe^-{:}C{:}{:}{:}N{:}$ and $Fe{:}{:}C{:}{:}\ddot{N}{:}^-$, and the ionic $Fe^+(CN)^-$ might also be involved. For a group like $—CH_3$ resonance of this kind is not possible. When considering such views it should be remembered that in deducing the octahedral arrangement of six d^2sp^3 bonds we assumed them to be simple electron-pair bonds.

In Chapter III we saw that six octahedral d^2sp^3 bonds can be formed by these elements, the *d* orbitals of the penultimate shell having about the same energy as the *s* and *p* orbitals of the outer shell. The octahedral complexes containing a given coordinating atom or group have, however, very different stabilities for different metal atoms and also for different valency states of the same metal. Thus the $Co(CN)_6^{4-}$ complex is very unstable, being readily oxidized to the $Co(CN)_6^{3-}$ ion, and hexacyano-ions are unknown for any valency of nickel. The arrangement of the electrons

in the metal atoms in the hexacyano-complexes of Fe^{II}, Fe^{III}, Co^{II}, and Co^{III} are set out below.

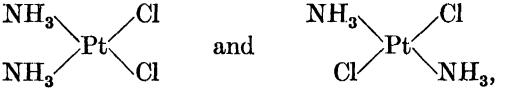


where shared electrons are enclosed by the rectangles. It will be seen that in the first three complexes all the electrons can be accommodated in the 3*d*, 4*s*, and 4*p* shells, whereas in $Co(CN)_6^{4-}$ one 4*d* orbital has to be used in either of the possible arrangements. This presumably accounts for the instability of 6-coordinated complexes of divalent cobalt. Similarly, in the hypothetical $Ni(CN)_6^{3-}$ and $Ni(CN)_6^{4-}$ ions there would be respectively one and two electrons to be placed in the 4*d* shell. If, however, the metal exhibited tetravalency and formed the $Ni(CN)_6^{2-}$ ion, it would have the same stable electronic configuration as Co^{III} in $Co(CN)_6^{3-}$. The metals Pd and Pt do in fact form many hexacovalent ions of the type MX_6^{2-}, in which the metal is tetravalent, but in spite of the similarity in the outer electronic structures of Ni, Pd, and Pt, nickel forms no such complexes.

We shall now give some examples of compounds in which these elements of Group VIII form (*a*) four planar and (*b*) six octahedral bonds.

The Formation of Four Coplanar Bonds by Divalent Ni, Pd, and Pt

As long ago as 1893 Werner suggested that the four atoms or groups attached to divalent Pd or Pt atoms in certain molecules were coplanar with the metal atom, this suggestion being made to account for the existence of compounds like $Pt(NH_3)_2Cl_2$ in two isomeric forms. For coplanar bonds there would be cis- and trans- forms

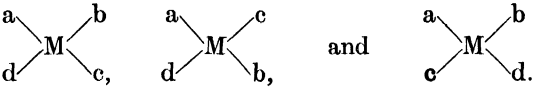


whereas if the bonds were arranged tetrahedrally there would be only one form of such a molecule. There has, however, been much controversy over this question of cis-trans isomerism in compounds Pta_2b_2 and Pda_2b_2. The determination (in 1926) of the molecular weights of the two forms of $Pt(NH_3)_2Cl_2$ showed that the β form was bimolecular in liquid ammonia, but in other cases it was found that both isomers had the same molecular weight corresponding to the simple Pta_2b_2 formula. For example, both forms of $PtCl_2(pyr)_2$ have normal molecular weights in phenol, and the same is true of the isomers of $PtCl_2(Et_2S)_2$ in benzene and of α- and β-$Pt(NH_3)_2(SCN)_2$. We may therefore accept this evidence for the planar arrangement of the four bonds in some at least of these platinum

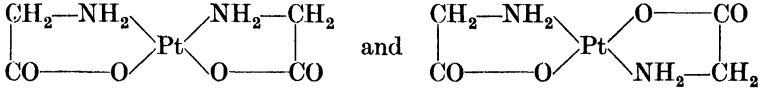
compounds. In 1922 it was shown by X-ray methods that the ions $PdCl_4^{2-}$ and $PtCl_4^{2-}$ are planar in the salts K_2PdCl_4 and K_2PtCl_4. There was no evidence for the planar arrangement of four bonds formed by any element other than Pd or Pt when in 1931 Pauling suggested, as a result of theoretical studies, that a number of other elements (including nickel) should be able to form four planar dsp^2 bonds. (The evidence for the formation of four planar bonds by tellurium was disposed of when it was shown that one of the two alleged isomers of $Te(CH_3)_2I_2$ was actually $[Te(CH_3)_3][Te(CH_3)I_4]$.) We have already dealt with the formation of dsp^2 bonds in Chapter III, and here it is only necessary to remind the reader that in the case of Ni, Pd, and Pt (but not Cu^{II} or Ag^{II}, see p. 215) the magnetic properties of the compounds provide a check on Pauling's theory. It was soon shown that many complexes of divalent nickel exist in two isomeric forms and are diamagnetic. These include nickel dimethyl- and diphenyl-glyoxime, nickel salicylaldoxime, potassium nickel dithio-oxalate, and many others. Although the planar disposition of four dsp^2 bonds formed by Ni, Pd, and Pt is now established beyond any doubt, it is worth while to summarize the experimental evidence under the following heads.

(1) *The Existence of cis-trans Isomers*

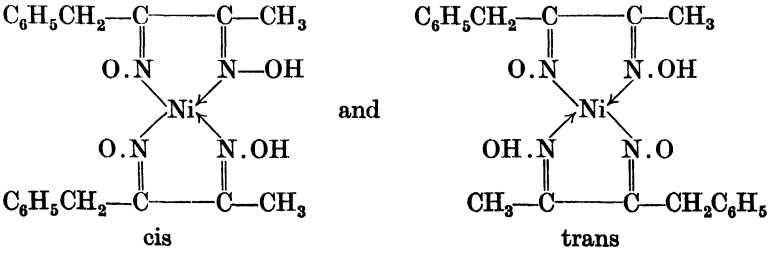
The argument here is as follows. A tetrahedral molecule Ma_2b_2 can exist in only one form but a planar molecule in two isomeric forms. Also, there is only one form of a tetrahedral molecule Mabcd but three isomers of the planar molecule, viz.



Three isomers of $[Pt(NH_3)(NH_2OH)(NO_2)(C_5H_5N)]NO_2$ have been reported. More complex examples of cis-trans isomers include compounds of Ni, Pd, and Pt with glycine,

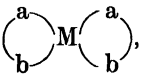


and with unsymmetrical glyoximes such as benzyl-methyl-glyoxime,

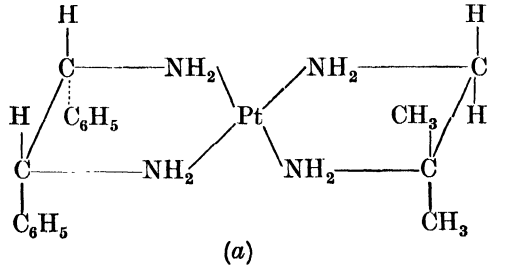


(2) *The Resolution of optically active Compounds*

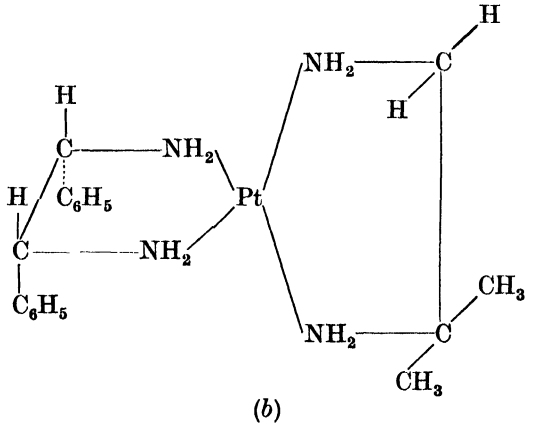
Compounds of the above type containing two unsymmetrical ring systems, which we may represent diagrammatically



would be resolvable into optical antimers if the bonds from M were disposed tetrahedrally, whereas if these bonds are coplanar with M only cis-trans isomerism is possible. Attempts to resolve certain compounds of this type have been made and have been unsuccessful, but the failure to effect a resolution is clearly of doubtful value as evidence for the disposition of the bonds from the metal atom. This difficulty was overcome in an ingenious way by Mills and Quibell (1935), who prepared a compound which would be optically active if the bonds from the central metal atom were coplanar and non-resolvable if these bonds were arranged tetrahedrally. The following sketches show that if the Pt bonds are coplanar, (*a*), the ion possesses neither a plane nor a centre of symmetry, whereas if the Pt bonds are tetrahedral, (*b*), then the planes of the two rings are perpendicular to one another and the ion possesses a plane of symmetry.



(*a*)

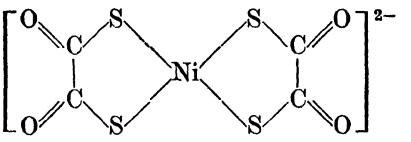


(*b*)

The compound, $[Pt(CH.C_6H_5.NH_2)_2(NH_2.C(CH_3)_2CH_2NH_2)]Cl_2$, was resolved into highly stable optical antimers. The corresponding ion containing Pd was also shown, in the same way, to have coplanar rings.

(3) *The Structures of Crystalline Compounds*

It is convenient to divide into two groups the solids which have been studied by the method of X-ray crystallography. The first comprises crystals consisting of infinite (1-, 2-, or 3-dimensional) complexes, examples of which are PtS and PdO (3-dimensional) and $PdCl_2$ (infinite chains, 1-dimensional complexes). The structures of these compounds have already been described (pp. 391, 315, and 279). We distinguish structures of this type from those of crystals of the second group, which contain finite molecules or complex ions, because in the former case the stereochemistry of the metal atom can be studied *only* in the solid, the structure breaking up when the crystal is dissolved or vaporized. The finite complexes in the crystals of the second group, however, retain their identity and structure in other states of aggregation so that there is always the possibility that the stereochemistry of the metal atom in such complexes might be studied by other methods. Complex ions which have been shown to be planar include $PdCl_4^{2-}$ and $PtCl_4^{2-}$ in their potassium salts, $Pt(NH_3)_4^{2+}$ in $Pt(NH_3)_4Cl_2.H_2O$, and the dithio-oxalate ions



of Ni, Pd, and Pt in their potassium salts. The planar arrangement of four bonds from Ni^{II} may also be inferred from the isomorphism of $K_2Ni(CN)_4.H_2O$ with the corresponding Pd salt and of $BaNi(CN)_4.4H_2O$ with the analogous Pd and Pt compounds, in which planar bonds may safely be assumed. It is interesting to note that $NiCl_2$ is not isomorphous with $PdCl_2$ but has the 6-coordinated layer structure of the halides (other than the fluorides) of divalent iron and cobalt.

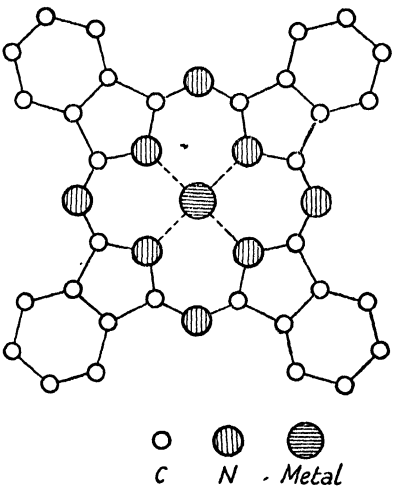
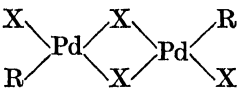


FIG. 160. A molecule of a metallic phthalocyanine, $C_{32}H_{16}N_8M$.

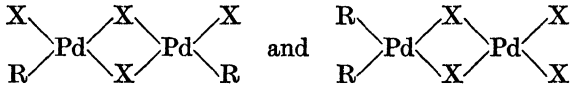
A very elegant demonstration of the planar arrangement of the four bonds formed by a number of metals was provided by the analysis of the crystal structures of the metallic phthalocyanines. The phthalocyanine molecule is planar and there is room at the centre for a divalent metal atom, which replaces the two hydrogen atoms in the formula $C_{32}H_{18}N_8$ and lies in the plane of the molecule. A molecule of a metallic phthalocyanine $C_{32}H_{16}N_8M$ is shown in Fig. 160.

The following metals have been shown to form phthalocyanines: Cu, Ni, Pt, Co^{II}, Fe^{II}, Mn, Mg, and Be. It is surprising to find beryllium in this list, for in all other cases this metal forms four tetrahedral bonds. The formation of planar bonds is presumably to be attributed to the rigidity of the phthalocyanine molecule, and it is noteworthy that this beryllium compound (and also Mg phthalocyanine) hydrates very readily, taking up $2H_2O$ even in moist air. The other anhydrous phthalocyanines show no tendency to hydrate. It should perhaps be mentioned that it is possible to avoid formulating the beryllium compound with four coplanar bonds if it be assumed that the metal atom is attached to only two of the four central nitrogen atoms, but there is no reason for supposing this to be the case.

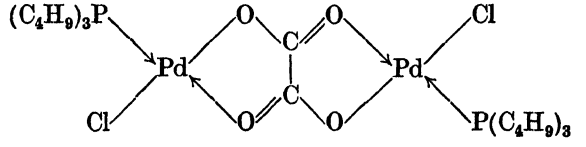
When palladium or platinum is heated with phosphorus pentachloride, products of the type $PdCl_2.PCl_3$ and $PdCl_2.(PCl_3)_2$ (or the corresponding Pt compounds) are obtained, and by the action of alcohol these are converted into $PdCl_2.P(OC_2H_5)_3$ and $PdCl_2.[P(OC_2H_5)_3]_2$ respectively. Other compounds of the same general type $PdCl_2.R$ and $PdCl_2.R_2$ may be prepared in which R is, for example, a tertiary phosphine or arsine. Those with empirical formula $PdCl_2.R_2$ consist of simple planar molecules which can theoretically exist in both cis and trans forms (see below). Those with empirical formula $PdCl_2.R$ have molecular weights corresponding to the double formula $Pd_2Cl_4R_2$. These 'bridged' compounds are of the form



where X represents Cl or Br. An X-ray study of crystalline $[PdBr_2As(CH_3)_3]_2$ showed the molecule to be planar, apart from the methyl groups, with the trans configuration shown above. It is interesting that only one form of this compound is obtainable by crystallizing its solution, but there is evidence that either or both of the other possible forms



may exist in solution together with the trans form. An incomplete study of the oxalato-compound



shows that this also is a planar molecule.

(4) *Evidence from Dipole Moments*

Molecules MX_2Y_2 in which the M—Y bonds are strongly polar would be expected to possess large dipole moments if the Y atoms are in cis

positions and zero moment if they are in the trans positions. If such a molecule had a tetrahedral configuration there would be only one form, which would have a large moment, though rather smaller than that of the cis planar isomer. A survey of the dipole moments of some of these MX_2Y_2 molecules provides results of some interest. It is found that the cis and trans forms of these molecules often differ considerably in stability, depending on the nature of M, X, and Y. For example, the nickel complexes $NiX_2(PR_3)_2$ have the trans configuration when X is Cl, Br, or I and R is C_2H_5, α-C_3H_7, or α-C_4H_9 but the cis configuration when X is NO_3. In the case of palladium compounds PdX_2Y_2 only the trans forms are usually isolable, as is the case with the 'bridged' molecules already mentioned. The dipole moments of a number of platinum compounds $PtX_2(SR_2)_2$ have been measured (X is Cl, Br, I, NO_2, or NO_3 and R is an alkyl group). The α (trans) forms have small moments, around $2{\cdot}4\times10^{-18}$ e.s.u., but the cis forms have moments of $9\text{–}13\times10^{-18}$ e.s.u., according to the nature of X. For an explanation of the small moment of the trans forms, instead of zero moment, see Chapter VI.

We may include the diamagnetism of the planar nickel compounds as confirmation of the use of *d* orbitals in the formation of hybrid dsp^2 bonds, for the diamagnetism of these compounds was predicted by Pauling at the same time as the planar configuration of the bonds.

Group VIII Metals forming Tetrahedral Bonds

Little is yet known of the stereochemistry of 4-covalent tetravalent palladium and platinum. An incomplete crystallographic study of $Pt(CH_3)_3Cl$ indicates that the molecule possesses an axis of 3-fold symmetry and therefore cannot be planar. It is probable that tetrahedral bonds are formed. The methyl derivatives $Pt(CH_3)_4$ and $Pt_2(CH_3)_6$ would then be structurally similar to the corresponding carbon compounds.

For the structures of $Ni(CO)_4$ and Cs_3CoCl_5 see pp. 453 and 290 respectively.

Octahedral Complexes of the Group VIII Metals

We have already remarked on the different stabilities of the octahedral complexes of iron, cobalt, and nickel in the various valency states, and in this section we shall confine our attention largely to complexes containing cobalt. These complexes are in many cases very easily prepared and often possess very great stability towards chemical reagents. Owing to the large number of permutations of atoms and groups which may be attached to cobalt in such complexes they are very numerous, and their variety, their interesting reactions, and possibly also their striking colours have fascinated many chemists. As a result their chemistry has been studied in some detail. The salts $[Co(NH_3)_2(NO_2)_4]NH_4$ and

$[Co(NH_3)_4CO_3]Cl$, for example, are prepared by aerating (to oxidize $Co^{II} \rightarrow Co^{III}$) ammoniacal solutions of cobalt chloride containing sodium nitrite and ammonium carbonate respectively and then simply crystallizing out the cobaltammines. Other related complexes are formed in such reactions as by-products. As regards the stability of certain cobaltammines we may quote the action of concentrated sulphuric acid on $[Co(NH_3)_6]Cl_3$ to form the sulphate of the complex, which is not disrupted in the process. The aquo-pentammine, $[Co(H_2O)(NH_3)_5]Cl_3$, retains its water up to a temperature of 100° C., and even then the complex does not break up, but a rearrangement takes place with the formation of $[Co(NH_3)_5Cl]Cl_2$.

The octahedral configuration of these complexes has long been established beyond any doubt, but nevertheless it had to be proved, just as proof had to be given of the tetrahedral arrangement of carbon bonds. Indeed, when Werner suggested the octahedral arrangement of groups around the metal atom in compounds like $[Co(NH_3)_6]Cl_3$, which had previously been formulated as a 'molecular compound', $CoCl_3.6NH_3$, his views were by no means generally accepted. Moreover, trigonal prism bonds are found in a few cases, so that it is still of interest to review the evidence for the octahedral disposition of the cobalt bonds in these complexes. We may summarize this evidence as follows:

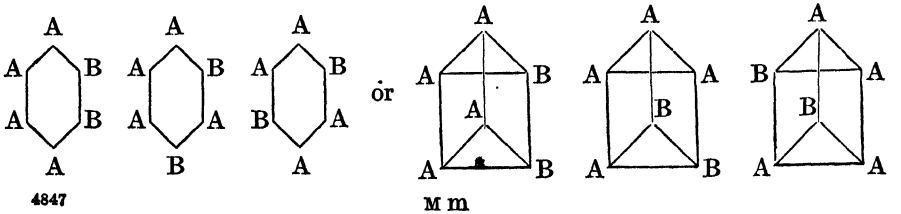
(1) The number of isomers of a given type of complex, e.g. CoA_4B_2, is that to be expected if the atoms A and B are arranged octahedrally around the cobalt atom.

(2) The optical activity of certain complexes is consistent with the octahedral arrangement of bonds.

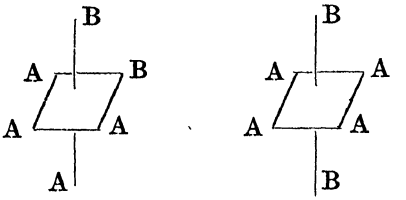
(3) The crystal structures of certain cobaltammines have been determined, and these constitute the most direct proof of Werner's hypothesis.

Let us consider these points briefly in turn.

(1) If we assume that the arrangement of the bonds from the metal atom must be such that the six surrounding atoms or groups may be equidistant from that atom and also that the shortest A—A distances are all equal, as we should expect in a symmetrical complex CoA_6, then the only alternatives to the regular octahedron are the plane hexagon and the trigonal prism. A mono-substituted derivative CoA_5B would exist in only one isomeric form on any model, but the complex CoA_4B_2 would have three isomeric forms on the hexagonal or trigonal prism models, viz.

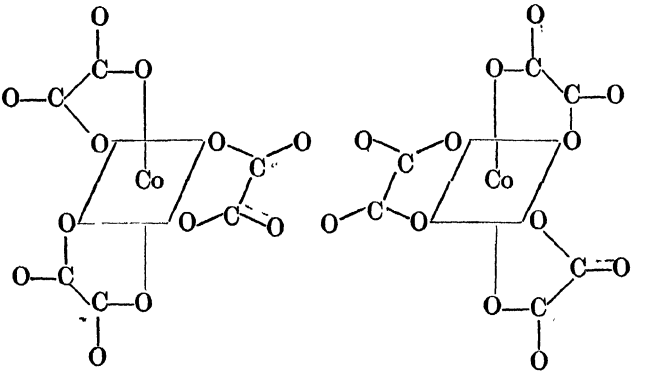


but only two on the octahedral model, viz.



The fact that only two isomers of the numerous complexes of this type which have been prepared have ever been isolated is strong presumptive evidence that the cobalt bonds are arranged octahedrally. It is not, of course, direct proof, for it might happen that the third isomer was much less stable than the other two in every case; compare the stabilities of the cis and trans complexes of divalent palladium.

(2) The demonstration of the optical activity of a compound such as $K_3Co(C_2O_4)_3$ was a striking confirmation of the octahedral arrangement of the bonds from the cobalt atom. A group like $C_2O_4^{2-}$ or N_2H_4 occupies two coordination positions and the resulting complex is enantiomorphous, the two forms (shown below) being related as object and mirror image.



It will be appreciated that the resolution of such a compound appeared surprising, for it was previously formulated as a double salt, $3K_2C_2O_4 \cdot Co_2(C_2O_4)_3$. Nevertheless, it is a curious fact that the resolution of salts like $K_3[Co(C_2O_4)_3]$ and $[Co(N_2H_4)_3]Br_3$ into their optical antimers was not considered by some chemists to prove Werner's hypothesis. There still lingered a belief that the optical activity was in some way dependent on the presence of an organic radical in the complex. It was not until Werner resolved a purely inorganic cobaltammine that the last doubts were removed. The compound in question has the formula

$$\left[Co\begin{Bmatrix}OH\\OH\end{Bmatrix}Co(NH_3)_4\right]_3Cl_6$$

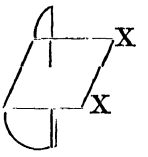
and the probable structure of the complex ion is illustrated in a later section on polynuclear cobaltammines (p. 534). We may mention here

that the following trioxalato and triethylenediamino ions have been resolved into their optical antimers:

$[M^n(C_2O_4)_3]R_{6-n}$, where R is an alkali metal and M is Fe^3, Co^3, Rh^3, Ir^3, Pt^4 (also Al^3 and Cr^3).

$[M^n en_3]X_n$, where X is a halogen or other univalent anion and M is Co^3, Rh^3, Ir^3, Pt^4 (also Zn^2, Cd^2, and Cr^3).

Among other miscellaneous octahedral complexes which have been resolved are tri-dipyridyl ions such as $[Fe^2(dipyr)_3]^{2+}$ and $[Ni^2(dipyr)_3]^{2+}$, various ions of the general type



including $[Co\ en_2Cl_2]^+$, $[Ni\ en_2(H_2O)_2]^{2+}$, and more complex examples like $[Pt\ en,\ NH_3,\ NO_2,\ Cl_2]^+$, $[Pt\ en,\ pyr,\ NO_2,\ Cl_2]^+$, and $[Pt\ en(NH_3)_2Cl_2]^{2+}$.

(3) As we have said, the determination of the crystal structures of compounds containing octahedral complexes provides the most direct proof of the arrangement of the bonds from the metal atom. We give here a few examples of compounds which have been studied by the X-ray method, leading to the complete determination of their structures.

	Isomorphous salts
$K_3[Co(NO_2)_6]$	$K_2Ca[Ni(NO_2)_6]$, $K_2Pb[Cu(NO_2)_6]$
$Ag[Co(NH_3)_2(NO_2)_4]$	
$[Co(NH_3)_5Cl]I_2$	$[Rh(NH_3)_5Cl]Cl_2$, $[Cr(NH_3)_5Cl]Cl_2$

The Empirical Formulae and Constitutions of Cobaltammines

Some idea of the complexity of the chemistry of the cobaltammines may be gathered from the fact that no less than nine compounds with the empirical formula $Co(NH_3)_3(NO_2)_3$ are said to have been prepared. There are many possible types of isomerism and polymerism, as the following examples will show.

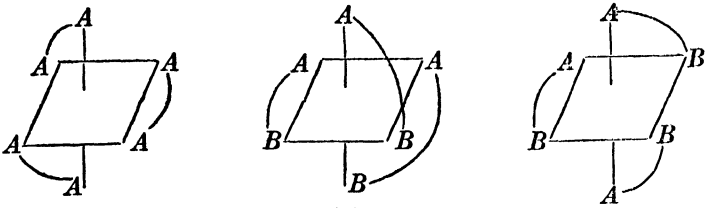
Isomers have the same molecular weight but differ in physical and/or chemical properties. The following kinds of isomerism may be distinguished.

(i) *Stereoisomerism.* The isomers contain exactly the same set of bonds, i.e. the same pairs of atoms are linked together in the isomers.

(*a*) The positions of all the atoms relative to one another are the same. The only difference between the isomers is that they are related as object and mirror image (optical isomerism).

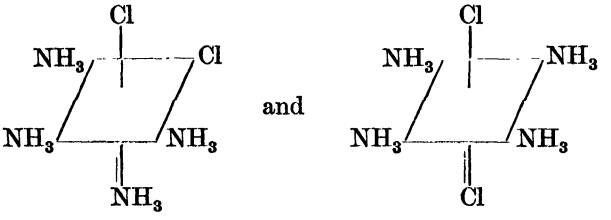
(*b*) The constituent atoms are arranged differently in space relative to one another (geometrical isomerism).

The optical activity of the tri-oxalato compound $K_3[Co(C_2O_4)_3]$ has already been mentioned. An even more interesting case of isomerism can arise when the chelate group is unsymmetrical. For a symmetrical group occupying two coordination positions (e.g. C_2O_4), which we may represent *A–A*, there is only the one stereoisomer (I) which, of course, exists in right- and left-handed modifications. If, however, the group is unsymmetrical there are two possible forms (II and III) exactly analogous to the two stereoisomers of a complex CoA_3B_3, and each form is enantiomorphous. Two such forms of the tri-glycine complex $Co(NH_2CH_2COO)_3$



have been prepared.

Many pairs of geometrical isomers have been made, such as the 'violeo' and 'praseo' series



of which the latter is the much more stable complex. When concentrated hydrochloric acid acts on the carbonato compound $[Co(NH_3)_4CO_3]Cl$ at low temperatures the cis dichloro compound is first formed, but this rapidly changes into the trans isomer. The trans isomer of complexes CoA_4B_2 is often much more stable than the cis, and in the case of $[Co(NH_3)_2(NO_2)_4]^-$ only the trans form is known (see p. 535).

(ii) *Structural Isomerism.* This includes all cases of isomerism where different pairs of atoms are linked together in the various isomers. These may therefore possess very different chemical properties. We may distinguish three simple kinds of structural isomerism.

(*a*) A number of cobaltammines containing groups such as NO_2 or SCN exist in two forms, the isomerism apparently being due to the possibility of linking the group to the metal atom in the two ways, M—NO_2 or M—ONO and M—SCN or M—CNS respectively. When aquo-pentammine cobaltic chloride $[Co(NH_3)_5H_2O]Cl_3$ is treated with nitrous acid under the correct conditions a red compound is formed which evolves nitrous fumes

if treated with dilute mineral acids and which at ordinary temperatures is slowly (and at 60° C. rapidly) converted into a brown isomer. The latter is quite stable towards dilute acids. The isomers are formulated $[Co(NH_3)_5ONO]Cl_2$ and $[Co(NH_3)_5NO_2]Cl_2$. There are also isomers of thiocyanato complexes, such as $[Co(NH_3)_5NCS]SO_4$ and $[Co(NH_3)_5SCN]SO_4$.

(*b*) The term 'ionization isomerism' has been applied to the isomerism of pairs of compounds like $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$. There are also more interesting cases such as $[Co(NH_3)_5SO_3]NO_3$ and $[Co(NH_3)_5NO_2]SO_4$. In these pairs, as in those in (*c*), the isomerism applies only to the solid state, for the actual coordination complexes are of different empirical compositions.

(*c*) Since many of the octahedral complexes are ions and since there are positively and negatively charged complexes, as in the series

$$[Co(NH_3)_4(NO_2)_2]^+, \quad Co(NH_3)_3(NO_2)_3, \quad [Co(NH_3)_2(NO_2)_4]^-,$$

it should obviously be possible to prepare crystalline salts in which both the cation and the anion are octahedral complexes. We could then have pairs of salts with the same composition of which the following are the simplest types: $[M^1A_6][M^2B_6]$ and $[M^1B_6][M^2A_6]$ containing two different metals. The pairs of salts $[Co(NH_3)_6][Cr(CN)_6]$, $[Cr(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_4(H_2O)_2][Cr(CN)_6]$, $[Cr(NH_3)_4(H_2O)_2][Co(CN)_6]$ have been prepared.

(iii) *Polymerism.* Consider a salt of the type $[MA_nB_{6-n}][MA_{6-n}B_n]$ in which the central metal atom is the same in both complexes. Crystals of the compound consist of equal numbers of octahedral complexes of two kinds, so that the simplest structural formula is that given above. The empirical formula is, however, MA_3B_3, which corresponds to an entirely different compound, in which all the structural units are identical. This possibility of the existence of compounds with quite different structures and chemical properties but the same empirical composition adds greatly to the complexity of cobaltammine chemistry. The compounds $[Co(NH_3)_3(NO_2)_3]$ and $[Co(NH_3)_6][Co(NO_2)_6]$ are related in this way, and in the next section we shall see that far more complicated cases are possible.

Polynuclear Cobaltammines

We have seen that in crystalline hydroxides and halides such as $Al(OH)_3$ or $CrCl_3$ the oxygen or chlorine atoms are bonded to two metal atoms, and to three in $Ca(OH)_2$ or CdI_2, and that in finite molecules such as those of the bridged palladium compounds the central halogen atoms are likewise performing the same function of linking together the metal atoms. Accordingly we find more complex cobaltammines in which two or more octahedral groups are linked together to form large finite ions or molecules. Whereas the nitrogen atom in NH_3 can form only one more bond, that in NH_2 can form two, so that the amino group can act as a 'bridge' between two metal atoms. The following examples will suffice to show

the types of polynuclear complexes that can arise in this way. First, we may have two octahedral complexes sharing

(*a*) corners, e.g. $[(NH_3)_5Co{-}NH_2{-}Co(NH_3)_5]Cl_5$

(*b*) one edge, ,, $\left[(NH_3)_4Co\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right]Cl_4$

(*c*) one face, ,, $\left[(NH_3)_3Co\begin{matrix}OH\\OH\\OH\end{matrix}Co(NH_3)_3\right]Cl_3$

These processes can continue further as in

$$\left[(NH_3)_3Co\begin{matrix}OH\\OH\\OH\end{matrix}Co\begin{matrix}OH\\OH\\OH\end{matrix}Co(NH_3)_3\right]Cl_3$$

and in $$\left[Co\left\{\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right\}_3\right]Cl_6$$

which has already been mentioned in connexion with the optical activity of cobaltammines. No structural crystallographic studies have so far been

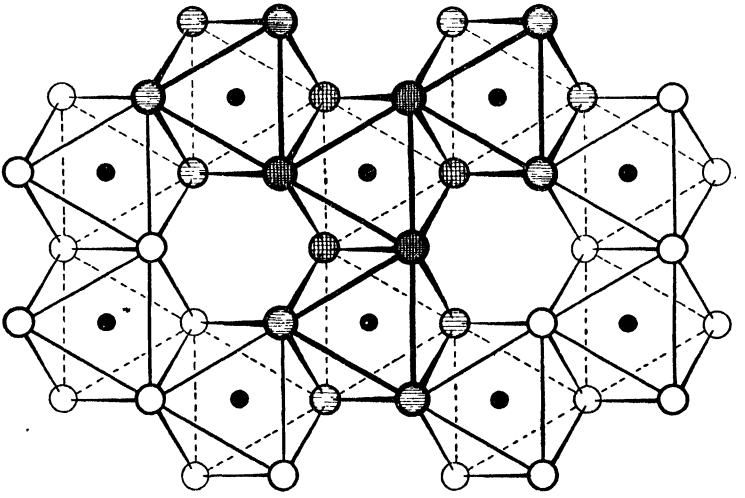
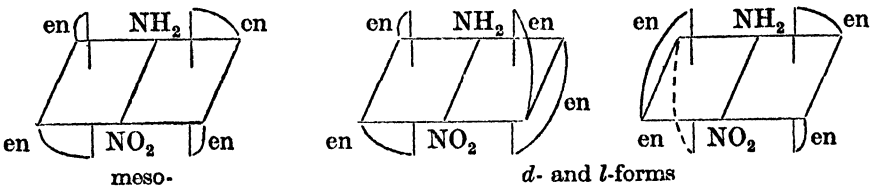


FIG. 161. The complex $\left[Co\left\{\begin{matrix}OH\\OH\end{matrix}Co(NH_3)_4\right\}_3\right]^{6+}$ and its relation to the layer lattice AX_3 of, for example, $Al(OH)_3$. The small black circles represent metal atoms in the plane of the paper and the large circles X atoms above and below that plane forming octahedra around the metal atoms. In the cobalt complex a central octahedron $Co(OH)_6$ shares an edge with each of three other octahedra $Co(NH_3)_4(OH)_2$. The NH_3 groups are shown as heavy circles shaded horizontally and OH shaded horizontally and vertically.

made of any of these polynuclear complexes, but the structure of the last-mentioned complex must be that shown, in idealized form, in Fig. 161. We may note that this salt has the same empirical composition as

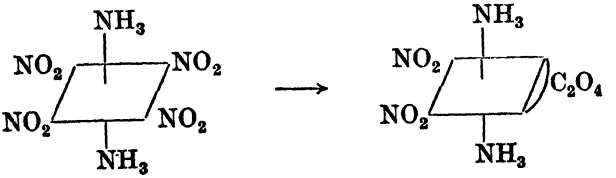
$[(NH_3)_3Co(OH)_3Co(NH_3)_3]Cl_3$. Some of these polynuclear complexes provide very interesting examples of enantiomorphism. For example, $\left[en_2Co\begin{matrix}NH_2\\NO_2\end{matrix}Co\,en_2\right]Br_4$ exists in *d*- and *l*- forms and also in an inactive meso- or 'internally compensated' form:



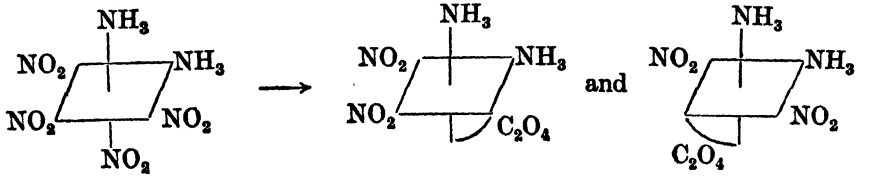
The active forms of this compound were obtained by Werner by resolution with *d*-bromcamphorsulphonic acid.

These binuclear complexes are also of interest in connexion with the constitution of simple cobaltammines. Any complex CoA_4B_2 may theoretically exist in two forms, the cis and trans isomers. Two arguments were used to decide which isomer was which. First, preparation from, or easy conversion into, a complex CoA_4C where C is a group occupying two coordination positions (CO_3, C_2O_4, en, etc.). Actually in many cases both the cis and the trans forms of CoA_4B_2 may be prepared from such a complex—as in the case of the conversion of $[Co(NH_3)_4CO_3]Cl$ into $[Co(NH_3)_4Cl_2]Cl$—the isomer first formed changing into the other on suitable treatment. It was assumed that the isomer first formed had the cis configuration. A more elaborate argument was used to determine the configuration of the $[Co(NH_3)_2(NO_2)_4]^-$ complex in 'Erdmann's salt', $NH_4[Co(NH_3)_2(NO_2)_4]$, and it is worth while setting it out in view of our remarks in Chapter VI on the rearrangement of complexes during reactions.

Only one form of salts of the complex $[Co(NH_3)_2(NO_2)_4]^-$ is known, and the problem is to decide whether the two NH_3 groups are in cis or trans positions relative to one another. The complex reacts with oxalic acid, two NO_2 groups being replaced by C_2O_4. If the original complex has the trans configuration only one oxalato complex is to be expected:

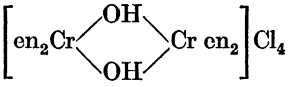


but if the NH_3 groups are adjacent to one another two oxalato derivatives should be possible, and one of them should be enantiomorphous:



Actually, two products were isolated from the action of oxalic acid on Erdmann's salt and one was resolved into optical antimers. This apparently conclusive proof of the cis configuration of the $[Co(NH_3)_2(NO_2)_4]^-$ complex is not, however, in agreement with the results of the X-ray study of the silver salt. The argument is based on the assumption that no change in the configuration of such complexes occurs when coordinated atoms or groups are replaced by others, an assumption which we know now to be untenable. Werner himself discovered many examples of change of configuration during reactions (see Chapter VI, p. 225).

The second argument used to decide the cis or trans configuration of MA_4B_2 complexes rests on the relation of the cis isomer to the binuclear complexes. The isomer which is easily formed from or converted into the bridged complex is taken to be the cis isomer. We may take an example from the chromammines. The salt $[Cr\ en_2(H_2O)OH]Cl_2$ exists in two forms, one of which can be converted into an oxalato compound, $[Cr\ en_2(C_2O_4)]Cl$. On heating, this form may be condensed to the binuclear compound



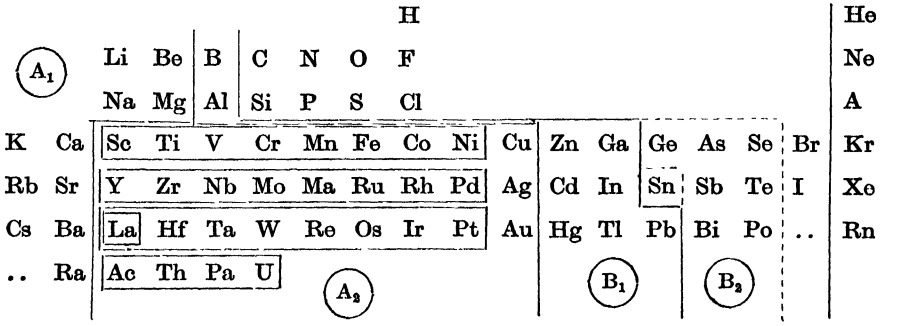
and is accordingly considered to have the cis configuration. It will be seen that these arguments based on chemical reactions lead to mutually consistent conclusions, but since independent studies of the structures of these complexes have not been made, it is not yet possible to verify the configurations assigned to them.

CHAPTER XVII

METALS AND ALLOYS

THE STRUCTURES OF THE ELEMENTS

WE have already mentioned the structures of a number of non-metals in previous chapters. In this concluding chapter we shall be concerned chiefly with the structures of the metallic elements and their alloys. Before proceeding to these, however, we shall review briefly the structures of all the elements in the solid state as far as they are known. For this purpose it is convenient to consider them in groups, and as regards their crystalline structures they fall into a number of groups as indicated below.



The groups are

(1) The inert gases.
(2) Hydrogen, the non-metals of the first two short periods, and the B sub-group elements of Groups IV to VII except Pb. Tin is a borderline case.
(3) Boron, aluminium, the elements of II B and III B and Pb.
(4) The transition elements and those of I B.
(5) The typical and A sub-group elements of Groups I and II.

When we come to the structures of alloys we shall need to consider only the last three groups and certain of the elements of the second group which are included within the dotted lines above. We shall denote these groups by A_1, A_2, B_1, and B_2 (see above). It will be seen that A_1 and A_2 comprise the A sub-group elements together with the Group VIII triads and Cu, Ag, and Au, while B_1 and B_2 include the more metallic B sub-group elements apart from those of I B. The reason for placing these latter elements with the transition elements rather than with the B sub-group elements will be apparent later.

1. The Inert Gases

These elements call for little discussion. They are monatomic in all states of aggregation. Radon has not been studied in the crystalline state,

but the others crystallize with the cubic close-packed structure. We have remarked elsewhere that helium is unique among the elements in that it forms a true solid only under pressure, a minimum of 25 atmospheres being necessary.

2. Non-metals and the Later B Sub-group Elements

Solid hydrogen has a hexagonal close-packed structure in which the rotation of the H_2 molecules probably persists at temperatures down to absolute zero. Apart from nitrogen and oxygen, which crystallize with molecular lattices containing N_2 and O_2 molecules respectively, and one allotropic form of carbon (graphite), all the elements of this group crystallize with structures in which an atom has $8-N$ nearest neighbours, N being the ordinal number of the Periodic Group (i.e. 4 for C, 5 for N, etc.). All the halogens exist as diatomic molecules in the solid, liquid, and vapour states, though dissociation into atoms takes place at high temperatures. For an element in Group VI forming two bonds there are two possibilities, closed rings or infinite chains of atoms. The first possibility is realized in the S_8 molecules in rhombic sulphur which are in the form of puckered 8-membered rings. Chains of atoms occur in plastic sulphur; the structure of the monoclinic form is not known. In selenium and tellurium also there are infinite chains of atoms, the chains being packed together with their axes parallel. According to an electron diffraction study polonium crystallizes with a unique monoclinic structure in which there are three crystallographically different types of atom. The environment in each case is said to be a very distorted octahedron, but according to the published parameters the distances to these nearest neighbours vary over an unusually wide range (2·81–4·13 A.). The determination of the structure of an element obtainable in such minute quantities is very difficult and in this case only 10^{-7} gram of the element, deposited on a collodion film, was used. When selenium and tellurium are vaporized finite molecules are, of course, formed and these are diatomic. Similarly, dissociation of S_8 molecules begins at the boiling-point of sulphur (if not before) and at 900° C. the vapour of sulphur consists entirely of S_2 molecules.

In Group V the $8-N$ rule requires an element to form three bonds. Instead of simple rings and infinite chains we now find polyhedral and infinite layer molecules. Phosphorus forms tetrahedral P_4 molecules in the white form and layers, in which each atom has three nearest neighbours, in the black modification (see p. 399). The P_4 molecules are very stable towards heat. Dissociation into P_2 molecules does not begin until a temperature of 1,000° C. is reached, and for further dissociation into atoms very much higher temperatures are required. The very unstable yellow forms of arsenic and antimony presumably also contain tetrahedral molecules. The metallic modifications and also bismuth crystallize with layer structures. A layer of the arsenic structure is illustrated diagrammatically in Fig. 162. The atoms of a given (double) layer lie in two parallel planes so that each forms three pyramidal bonds to its nearest

neighbours. As already mentioned (p. 399), the next nearest neighbours are three atoms in the adjacent layer, and the difference between the distances to the nearest and the next nearest neighbours decreases in the sequence As, Sb, Bi as the metallic character of the elements increases.

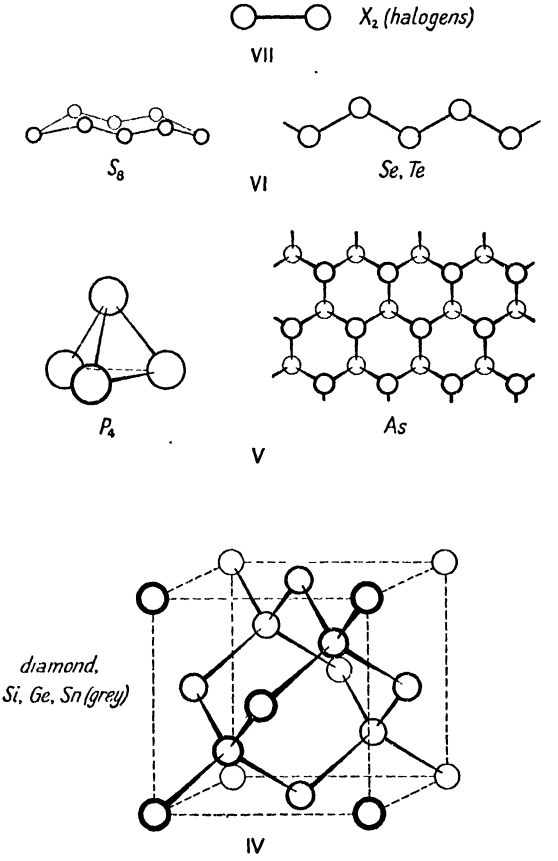


FIG. 162. The $8-N$ rule illustrated for certain elements of the IVth, Vth, VIth, and VIIth Periodic Groups.

In Group IV the formation of four tetrahedral bonds results in a 3-dimensional complex extending throughout the crystal. All the elements C, Si, Ge, and Sn crystallize with the diamond structure, but carbon and tin also form second modifications, graphite (p. 436) and white tin respectively. We shall refer to the structure of white tin shortly.

The obvious interpretation of the $8-N$ rule is that by the formation of $8-N$ single covalent bonds the elements concerned complete their octets of valency electrons. This is satisfactory in the case of the halogens, S_8, P_4, C, and Si, but the remaining elements of this group are semi-metallic and the properties of, for example, selenium or arsenic are not those of a simple molecular crystal in which covalent molecules are held together

by van der Waals bonds. They represent a class of solid intermediate between molecular and metallic crystals.

3. Boron, Aluminium, the Elements of Sub-groups II B and III B, (Sn) and Pb

These elements are grouped together because (1) certain of them have peculiar structures which do not conform with the principles governing those of the elements in the adjacent groups in our classification, and (2) those which have typical metallic structures show certain abnormalities which make it convenient to distinguish them from the 'true' metals of our fourth and fifth groups. Of the II B sub-group elements zinc and cadmium crystallize with a distorted form of hexagonal close-packing, the axial ratio being nearly 1·9 instead of 1·63 as in perfect hexagonal close-packing. The result is that each atom has six nearest neighbours in its own plane, the other six (three above and three below) being at a rather greater distance. In other words, the atoms pack as if they were prolate spheroids instead of spheres. The differences between the distances of these two sets of neighbours are not large (2·659 and 2·906 A. in Zn, 2·973 and 3·286 A. in Cd) and the properties of the elements distinguish them from those of the previous group, the structures of which comply with the $8-N$ rule. Crystalline mercury has a quite different (rhombohedral) structure which may be derived from a simple cubic lattice by distorting it so that the interaxial angle changes from 90° to 70½°. Each atom has six nearest neighbours.

The structures of the typical and B sub-group elements of the third Periodic Group present many problems. The structure of pure boron is not known. Aluminium and thallium have close-packed structures which we shall discuss later. Gallium crystallizes with a rather complex structure in which an atom has the following set of neighbours: 1 at 2·44, 2 at 2·70, 2 at 2·73, and 2 at 2·79 A. Gallium is also notable for its low melting-point (about 30° C.) and the close association of the atoms in pairs may persist in the liquid. (It is reported that the X-ray diffraction pattern of liquid gallium is different from that of a simple close-packed liquid metal like mercury.) Indium crystallizes with a structure which is only a slightly distorted form of cubic close-packing so that each atom has four neighbours at 3·24 and eight more at 3·36 A. Thallium is dimorphous, having cubic (β) and hexagonal (α) modifications, and lead, which we include in this group, has the cubic close-packed structure.

We have said that the elements Al, In, Tl, and Pb, which crystallize with close-packed or approximately close-packed structures, are abnormal in certain respects. In the case of Al there is evidence that the atoms are not completely ionized in the pure metal and that the atomic diameter of the fully ionized Al^{3+} is nearer 2·70 than 2·86 A., the closest distance of approach of atoms in aluminium itself. The melting-point of the metal is only 8° higher than that of Mg, in contrast to the rise

in melting-point with increase in valency in the A sub-group elements:

Li	Be	B	C
178°	1,285°	2,300°	3,500° C.
Na	Mg	Al	Si
97°	650°	658°	1,420°
K	Ca	Sc	Ti
62·5°	803°	1,200°	1,825°

Indium, thallium, and lead form a group of close-packed metals isolated from the rest of the close-packed metals (see table above). As may be seen from the figures below, the interatomic distances in these metals are

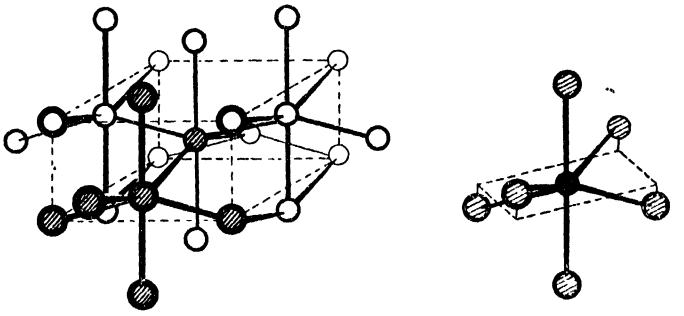


FIG. 163. The crystal structure of white tin, showing the deformed octahedral group of neighbours around each atom.

very large compared with those in the neighbouring elements. This, of course, is to be expected on account of the much higher coordination number, but the distances are much greater than in the close-packed silver and gold, whereas there is very little variation in interatomic distance throughout the whole series of elements from Cu to As or from Ag to Sb, excluding In and white Sn. The figure 2·80 A. given for tin in the table below is the interatomic distance in grey tin (diamond structure). The form of this element normally met with is white tin, which has a less symmetrical structure than the grey variety. In white tin (Fig. 163) each atom has four nearest neighbours at 3·016 A. forming a very flattened tetrahedron around it, and two more neighbours at 3·175 A. It will be noticed that these four nearest neighbours are at a much greater distance than the four nearest in grey tin (at 2·80 A.).

Interatomic distances in the elements (to nearest neighbours)

Cu	Zn	Ga	Ge	As
2·55	2·66	2·70*	2·44	2·51 A.
Ag	Cd	In	Sn	Sb
2·88	2·97	3·24	2·80†	2·90
			3·016‡	
Au	Hg	Tl	Pb	Bi
2·88	3·00	3·40	3·49	3·10

* weighted mean for 7 nearest neighbours. † grey tin. ‡ white tin.

It is considered probable that in Tl and Pb and possibly also in indium and white tin the atoms are only partly ionized, e.g. to the stages Tl^+ and Pb^{2+} in the former elements. The peculiar stability of the pair of *s* electrons in the outer quantum groups of these two elements has already been noted in the previous chapter, and indium and tin also exhibit valencies lower than the group valencies, which are three and four respectively.

4. The Transition Elements and those of Sub-group I B

The characteristic properties of metals which distinguish them from non-metals include high thermal and electrical conductivity, metallic lustre, malleability and ductility, and in some cases great mechanical strength (see, however, later). A few metals and alloys possess remarkable magnetic properties (ferromagnetism), but these are exceptional (see p. 216). The metals are electropositive with respect to the non-metals and replace the hydrogen in acids. All these properties are, of course, exhibited to different degrees by the various metals, and a particular property such as electrical conductivity varies over a wide range. We shall be concerned here only with the geometrical structures of metals, i.e. the relative positions of the centres of the atoms. To account for their physical properties it is also necessary to know what is the electronic state of the atoms, or alternatively what is the nature of the interatomic forces. The view generally accepted is that a metal consists of positive ions embedded in a cloud of electrons. The attractive forces between these ions and electrons are responsible for holding the ions together. The electrons are not permanently associated with particular atoms, as in the structures of other solids we have considered, but are moving rapidly through the metal even at absolute zero. With the application of wave-mechanics to this model it is possible to account for many, though not all, of the properties of metals. From direct measurements of refractive index and absorption coefficients for various wavelengths, calculations have been made of the effective numbers of free electrons per atom. The values found for the alkali metals are

	Li	Na	K	Rb	Cs
Effective number of free electrons per atom	0·55	1·1	0·97	0·94	0·85

and for certain metals in the liquid state

Bi	Pb	Cd	Sn	Hg
5·1	5·1	2·4	4·1	2·1

In contrast to the true metals the elements of the later B sub-groups are generally brittle and some are very hard. Owing to the low coordination numbers in the solid, expansion may occur on solidification (the liquid being much more closely packed)—a property utilized in type metal, an alloy of lead containing antimony and/or tin or bismuth. There may also be marked anisotropy of physical properties such as thermal conductivity, thermal expansion, and diamagnetic susceptibility. Thus arsenic and

antimony show large diamagnetic anisotropy, which disappears on melting, and much larger thermal expansion parallel to than perpendicular to the layers of atoms in their crystals. Zinc and cadmium also exhibit considerable anisotropy of thermal expansion. An indication of the extent of change of structure on melting is provided by the ratio of the electrical resistance of the liquid to that of the solid at the melting-point, as the following values show:

	Ratio $\frac{\text{resistance of liquid}}{\text{resistance of solid}}$ at melting-point
Bi	0·43
Ga	0·58
Sb	0·67
Alkali metals	1·4–1·7
Cu, Ag, Au, Zn, Cd, Sn, Pb, Tl	about 2
Hg	3·2–4·9
	(Crystalline Hg is anisotropic)

That the solids and not the liquids are abnormal in such cases is shown by the following figures for solid and liquid lead and bismuth:

	Resistivity in micro-ohms/cm.	
	Solid	*Liquid*
Pb (325° C.)	50	100
Bi (250° C.)	220	120

We now come to the crystal structures of the elements in this group. Of the forty-five metals in this group the structures of thirty-three are

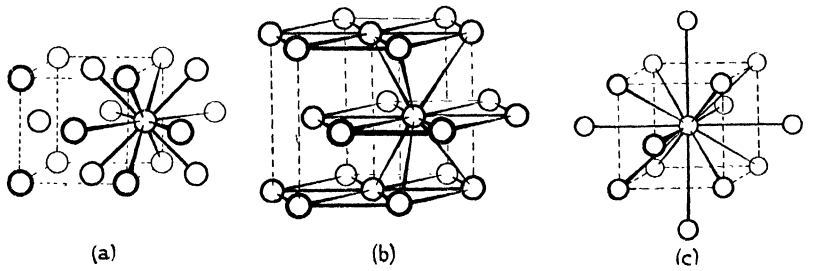
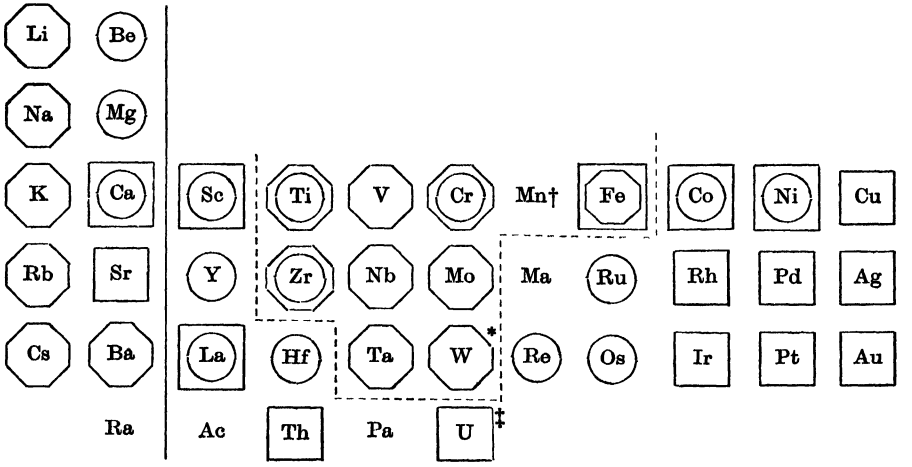


FIG. 164. The three simplest metallic structures: (*a*) cubic close-packing, (*b*) hexagonal close-packing, and (*c*) body-centred cubic.

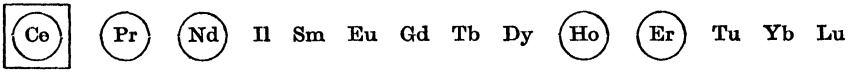
known, and of these all except one crystallize with one or more of three structures. These are the cubic close-packed, hexagonal close-packed, and body-centred cubic structures. The exceptional element is manganese, which crystallizes in three forms, all with complex structures to which we shall refer later. In addition, tungsten and uranium crystallize in less symmetrical forms as well as with close-packed structures. The structures of the elements of this group and also those of the typical and A sub-group elements of the first two Periodic families are indicated in Table 26.

The two simplest forms of closest packing, cubic and hexagonal, have already been described in Chapter III. In Fig. 164 we show these in

TABLE 26



Rare Earths:



represents cubic close-packed

„ hexagonal close-packed

„ body-centred cubic

* Also β-W (see below).
† α-Mn
β-Mn (see below)
γ-Mn.
‡ Also an orthorhombic form.

their conventional orientations together with the body-centred cubic structure. Sufficient atoms of adjacent unit cells are depicted to show the full set of nearest neighbours of one atom. The body-centred cubic structure (C.N. 8) is slightly less closely packed than the others, the effective volume per atom (of radius a) being $6{\cdot}16a^3$ as compared with $5{\cdot}66a^3$ in closest packed structures. In the latter an atom has twelve equidistant nearest neighbours, the next set of neighbours being 41 per cent. farther away. In the body-centred cubic structure an atom has eight equidistant nearest neighbours, but the next set of six neighbours are only 15 per cent. farther away. If this comparatively small difference between the distances to the nearest and the next nearest neighbours be disregarded, the coordination number in the body-centred cubic structure becomes 14 as compared with 12 in the close-packed structures (see the structures of β-W and of Mn below). We may note here an interesting qualitative difference in properties between cubic and hexagonal close-packed metals. The ductility, malleability, and softness of pure metals

depend, at least to some extent, on the ease with which adjacent planes and rows of atoms can glide over one another. (These properties are also very much influenced by the numbers of flaws and crystal boundaries in the material—a single crystal of a metal like cadmium being very soft and easily deformed, whereas the polycrystalline material is quite hard and brittle—and also by the presence of minute amounts of impurity.) Gliding takes place on the most closely packed planes, and the direction of gliding in these planes follows the lines of most closely packed atoms. In a cubic close-packed metal there are four equivalent sets of parallel closest packed planes, perpendicular to the four 3-fold axes which are the characteristic symmetry elements of a cubic crystal, as compared with only one set of such planes in a hexagonal close-packed crystal. Owing to the greater possibility of gliding in a cubic close-packed crystal, such crystals are in general more malleable and ductile than those with hexagonal close-packed structures. Thus Cu, Ag, Au, and γ-Fe are fairly soft, ductile, and malleable in comparison with such metals as Cr, V, and Mo which have hexagonal close-packed and/or body-centred structures. Iron is a particularly important metal which crystallizes with either the cubic close-packed or the body-centred cubic structure, depending on the heat treatment it has received. We shall deal briefly with iron and steel in the section on interstitial compounds.

It will be seen from Table 26 above that polymorphism is very common in this group of metals and less common, at ordinary pressures, in the alkali and alkaline-earth metals. At high pressures caesium adopts a close-packed structure, and this may also be true of others of the last-mentioned metals. There is one feature peculiar to the polymorphism of certain of these transition elements. In the case of other elements a particular polymorphic form is, under a given pressure, stable over one temperature range. (At atmospheric pressure one form may, of course, always be more stable than the other.) Tin, for example, has a transition temperature of 18° C., below which α (grey) tin is the stable form and above which β (white) tin is the stable form. Iron, on the other hand, crystallizes at temperatures below 906° C. with the body-centred cubic structure and from 906° to 1,401° C. with the cubic close-packed structure, but from 1,401° C. to the melting-point (1,530° C.) the body-centred cubic structure again becomes the stable form. We have therefore the face-centred structure stable over a certain temperature range, on both sides of which the body-centred structure is stable. Cobalt exhibits a similar phenomenon, the cubic close-packed form being stable over an intermediate range of temperature above and below which the element crystallizes with the hexagonal close-packed structure. A second point of interest in connexion with the structures of the transition metals is the sequence of structures adopted by the elements preceding the noble metals, Cu, Ag, and Au. The structures of these metals at ordinary temperatures are set out overleaf, where it will be seen that the same sequence of structures occurs in each series.

A.N.	*Structure*	*A.N.*	*Structure*	*A.N.*	*Structure*
Cu 29	cubic c.p.	Ag 47	cubic c.p.	Au 79	cubic c.p.
Ni 28	„	Pd 46	„	Pt 78	„
Co 27	hex. c.p.	Rh 45	„	Ir 77	„
Fe 26	b.c. cubic	Ru 44	hex. c.p.	Os 76	hex. c.p.
Mn 25	cubic (see below)	Ma 43	?	Re 75	„
Cr 24	b.c. cubic	Mo 42	b.c. cubic	W 74	b.c. cubic
V 23	„	Nb 41	„	Ta 73	„

It has been suggested that these changes in structure are associated with the extent to which the *d*-shell is filled. In the I B metals the *d*-shells are full and in these metals the closed *d*-shells are in contact, resulting in intense repulsive forces and hence in close-packed structures. With the decrease in number of electrons in these shells a more open structure becomes more stable. It should, however, be noted that close-packed structures again occur for the elements of the earlier Periodic Groups (see Table 26), so that we may alternatively regard the elements enclosed by the broken lines (which, except for Ti and Zr, are not close-packed at ordinary temperatures) as constituting a group of exceptional elements surrounded by those with close-packed structures.

We have noted that three elements in this group, Mn, W, and U, crystallize with structures other than the close-packed or body-centred cubic structures. All the forms of manganese have complex structures. In the α modification there are four kinds of crystallographically different Mn atoms with the following environments:

Mn^{I}	.	.	12	neighbours	at	distances	from 2·24 to 2·89 A.
Mn^{II}	.	.	13	„	„	„	„ 2·45 „ 2·96 A.
Mn^{III}	.	.	16	„	„	„	„ 2·71 „ 2·82 A.
Mn^{IV}	.	.	13	„	„	„	„ 2·49 „ 2·96 A.

In β-Mn there are two kinds of atoms with different environments, each set having twelve neighbours at distances from 2·36 to 2·67 A. In the third form of Mn which has been reported each atom has eight neighbours at 2·582 A. and four more at 2·669 A. Manganese is remarkable in a number of other respects such as melting-point and compressibility, and it exhibits an anomalous radius in MnS_2, $MnSe_2$, and $MnTe_2$. When introduced to the extent of 0·01–1·0 per cent. into many crystalline compounds of the most diverse chemical types (oxides, sulphides, sulphates, carbonates, silicates, and fluorides) it confers on these compounds the property of fluorescing when exposed either to ultra-violet light or to bombardment by electrons. Some also emit light, of a characteristic colour, when simply rubbed or ground in a mortar (tribo-luminescence). With the possible exception of the rare-earths, manganese possesses this property of acting as a 'phosphorogen' or 'activator' to a greater extent than any other element, and the property is associated with the possibility of electronic transitions within the Mn atom (or ion). In its ordinary chemistry manganese exhibits a variety of valencies, and it is possible

that the complexity of the structures of the element itself is due to the fact that the different sets of atoms are in various states of ionization.

The second (β) form of tungsten has the structure illustrated in Fig. 165. One-quarter of the W atoms have twelve equidistant nearest neighbours at 2·82 A. and the remainder have two at 2·52, four at 2·82, and eight at 3·09 A. This structure, like that of α-Mn, represents a compromise

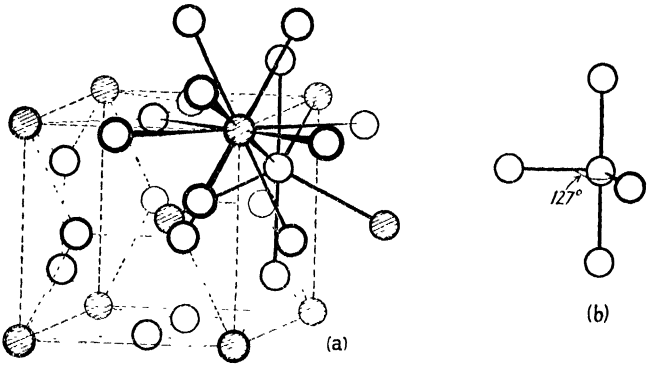


FIG. 165. (*a*) The crystal structure of β-tungsten. As regards environment the atoms are of two types. The twelve equidistant neighbours of an atom of the first type (shaded) and the six nearest neighbours of an atom of the second type (open circles) are shown. (*b*) The arrangement of the four nearest neighbours of an atom in metallic uranium.

between a close-packed structure, with twelve equidistant nearest neighbours, and the body-centred cubic structure with 8+6 neighbours. Finally uranium, which is remarkable for the fluorescence of its compounds containing the uranyl ion, UO_2^{2-}, forms a unique orthorhombic structure which may be regarded as a deformed version of hexagonal close-packing in which each atom has only four nearest neighbours, at 2·80 A. The arrangement of these neighbours is very unusual, for they lie in two perpendicular planes at four of the five apices of a trigonal bipyramid. Pauling has suggested that four of the six valency electrons are used for bond formation, the two 7*s* electrons occupying the remaining equatorial bond position (see Fig. 165 (*b*)). The distances from a uranium atom to its twelve nearest neighbours are as follows: two at 2·76, two at 2·85, four at 3·27, and four at 3·36 A.

5. The Typical and A Sub-group Elements of Groups I and II

The metals of this group call for no separate discussion. As may be seen from Table 26, the alkali metals and barium crystallize with the body-centred cubic structure and the remaining metals with close-packed structures.

INTERATOMIC DISTANCES IN METALS: METALLIC RADII

Apart from the intrinsic interest of the interatomic distances in metals, it is useful to have a set of radii to refer to when discussing the structures of alloys. Since the coordination number 12 is the most common in metals, it is usual to draw up a standard set of radii for this coordination number. For the metals with ideal close-packed structures the radii are simply one-half the distance between an atom and its twelve equidistant nearest neighbours. Many structures, however, deviate slightly from ideal hexagonal close-packing in such a way that six of the neighbours are slightly farther away than the other six, for example,

	Axial ratio	6 *at*	6 *at*	*Mean*
Be . .	1·5848	2·2235	2·2679	2·25 A.
Y . .	1·588	3·595	3·663	3·63 A.
α-Zr . .	1·589	3·166	3·223	3·19 A.

In such cases the mean of the two distances is taken. (We are not here referring to zinc and cadmium which show a very much larger deviation from close-packing, with axial ratios 1·856 and 1·885 respectively.) For metals which crystallize with structures of lower coordination the radii for 12-coordination have to be derived in other ways. From a study of the interatomic distances in many metals and alloys Goldschmidt found that the apparent radius of a metal atom varies with the coordination number in the following way. The relative radii for different coordination numbers are:

C.N. 12 . .	1·00
8 . .	0·97
6 . .	0·96
(4 . .	0·88)

For the alkali metals, for example, the radius for C.N. 12 is derived from half the observed interatomic distance (in the 8-coordinated body-centred cubic structure) by multiplying by 1·03. For some of the B sub-group elements which crystallize with structures of very low coordination (e.g. Ge and white Sn) the problem is more difficult. The use of a ratio such as that given above is difficult to justify for such a large change in coordination number, since the bonds in structures like the diamond structure are probably nearer to covalent than to purely metallic bonds. There are two alternative ways of deriving radii for C.N. 12 for such elements. Many of these elements form alloys with true metals in which both elements exhibit high coordination numbers. The radius of the B sub-group element can thus be found from the interatomic distance in such an alloy, e.g. that of Sb from the Ag—Sb distance in the hexagonal close-packed Ag_3Sb or that of Ge from the Cu—Ge distance in the hexagonal close-packed Cu_3Ge. This method is open to objection since there is probably not true metallic binding in such compounds and it is necessary, of course, to assume that the radius of Ag, for example, in Ag_3Sb is the same as in pure silver. The second method is to derive the radius of the

B sub-group element from the variation in cell dimensions of the solid solution it forms in a true metal. By extrapolation, the cell dimension of the hypothetical form of the B sub-group element with C.N. 12, and hence the interatomic distance therein, may be obtained, assuming a linear relation between cell dimension and concentration of solute atoms. Unfortunately this relation is not always linear, thus necessitating the use of empirical relations. Also, it is not certain that the radius of the solute element is not affected by the nature of the solvent metal, for there may be alterations in the state of ionization of an atom in different alloys. Nevertheless it is possible to derive a set of radii for many elements for C.N. 12 which are valuable when considering the structures of alloys. Such a set of radii is given in Table 27.

TABLE 27

Metallic Radii for 12*-coordination*

Li	Be													
1·58	1·12													
Na	Mg	Al												
1·92	1·60	1·43												
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	
2·38	1·97	1·66	1·47	1·35	1·29	1·37	1·26	1·25	1·25	1·28	1·37	1·53	1·39	
Rb	Sr	Y	Zr	Nb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
2·53	2·15	1·82	1·60	1·47	1·40	1·35	1·34	1·34	1·37	1·44	1·52	1·67	1·58	1·61
		Rare-												
Cs	Ba	earths	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
2·72	2·24	1·82	1·59	1·47	1·41	1·37	1·35	1·36	1·39	1·44	1·55	1·71	1·75	1·82
			Th											
			1·80											

The actual interatomic distances in the elements are plotted against Atomic Number in Fig. 166, which shows a number of points of interest. The general periodic variation is apparent, as also is the fact that there is no general increase in the size of atoms with increasing atomic number. (We could have periodicity combined with an upward trend in all the values.) Thorium, for example, with A.N. 90 is not much larger than lithium (A.N. 3) and actually smaller than sodium (A.N. 11), the explanation lying in the tighter binding of the electrons in the heavier elements owing to the increased nuclear charge. The second point is that although the transition and B sub-group elements of the second long period are larger than those of the first, there is no similar increase in size on going from the second to the third long period. Compare, for example, the atomic diameters of Cu, 2·551, Ag, 2·883, and Au, 2·877 A. We have already referred to the lanthanide contraction and the very close resemblance in chemical properties between such pairs of elements as Zr and Hf or Nb and Ta. The radii of the intervening rare-earths remain constant while the 4*f* sub-shell is being completed. The variation of atomic radii in the long periods, with minima in the neighbourhood of the Group VIII triads, corresponds to maxima or minima in a number of physical properties—compressibility, tensile strength, hardness, and melting-point. Pauling has suggested that if an element such as iron can utilize its 3*d*

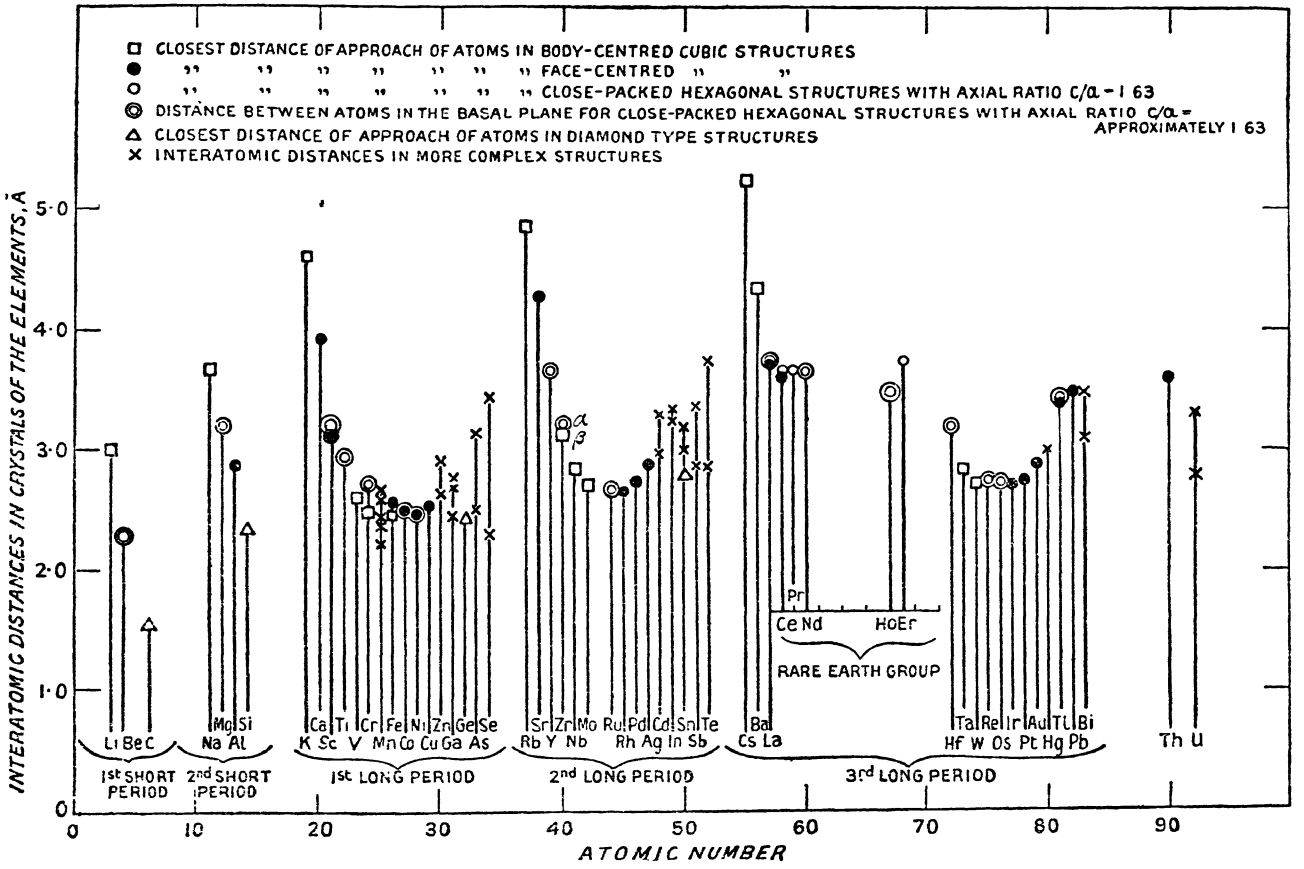


FIG. 166. The variation with atomic number of the interatomic distances in the elements (after Hume-Rothery).

electrons as well as the 4*s* in its carbonyls and in the ferrocyanide and other complex ions, this may also be the case in the metal. Assuming that, for the elements of the first long period, 3*d*, 4*s*, and 4*p* orbitals (nine in number) are available for bond formation, then the maximum number of bonds could be formed when there are nine electrons available per atom. This occurs at Co, Rh, and Ir for the first, second, and third long periods respectively. In the preceding elements there are fewer available electrons and in the later ones more electrons than orbitals available. It cannot be said that this view of the structures of these metals, suggested by the similarity in many cases between metallic and covalent radii, is generally accepted.

THE STRUCTURES OF ALLOYS

Atomic Structure and Physical Properties

In this section, as in the last, we shall be describing the atomic structures of ideal crystals, i.e. the structures which would extend without interruption throughout ideal crystals but which in the normal material, with a mosaic and moreover a polycrystalline structure, persist only over comparatively small volumes. The difference between a normal crystal with mosaic structure and an ideal crystal was pointed out in Chapter V. In the case of metals and alloys the imperfections in the crystals are of the utmost importance in determining the properties of the material, and it is necessary to remember that the properties of the greatest value in metals cannot be explained in terms of the ideal structures we shall be describing. The following points are taken from a report by Bradley, Bragg, and Sykes on researches, chiefly X-ray crystallographic, on the structures of alloys. For the details in the structure of an alloy to be seen under the optical microscope they must be of the order of magnitude of 10^{-4} cm., i.e. the polycrystalline structure or regions of different composition in a non-homogeneous alloy must be on this scale. Atomic arrangement as determined by the X-ray method is on the scale of 10^{-8} cm., interatomic distances lying in most cases between 2 and 3×10^{-8} cm. and cell dimensions between 2 and 12×10^{-8} cm. The structures which are found in the intermediate range, from 10^{-4} to 10^{-8} cm., are probably of as much importance in determining the mechanical properties of a metal as the structures visible under the microscope. Most metals and alloys which have valuable mechanical and physical properties are neither in true equilibrium nor are they structurally homogeneous or perfect crystals. The segregation of atoms leading to one kind of age-hardening probably takes place in a pattern on the scale of 10^{-7} cm., and the incipient precipitation leading to age-hardening in other alloys and to resistance to deformation is probably on a somewhat larger scale, 10^{-6}–10^{-5} cm. Much less is known about the structure of metals and alloys in these intermediate ranges, for it is beyond the resolving power of the optical microscope and produces only complex secondary effects on X-ray photographs which are

difficult to interpret. Only recently has a start been made in this highly important field. As regards the orders of magnitude encountered, this field may be compared with the study of large protein molecules with dimensions of hundreds of Angstrom units, which it is now becoming feasible to study by X-ray methods.

A pure metal such as copper or iron, with a close-packed structure, is extremely soft, being an aggregate of ions held together not by direct bonds between the atoms as in a homopolar or ionic crystal but by the 'atmosphere' of electrons. As far as we know, the elastic limit of a perfect single crystal of a metal, i.e. without impurity atoms or flaws, may tend to zero as perfect purity and regularity of structure are approached. Useful properties arise as the result of the introduction of impurities, often in comparatively small concentration, or after cold-working (rolling or drawing) or age-hardening. The effect of cold-working is to break up the single crystal into an aggregate of small crystals with dimensions of the order of 10^{-4}–10^{-5} cm., and the properties of the resultant material depend on the average size, the state of strain, and the relative orientations of these minute portions of the polycrystalline mass. The physical properties of a large number of commercial alloys are enhanced by heat-treatment processes referred to as age-hardening and precipitation-hardening. In the simple case of a binary alloy the hardening constituent is melted with the solvent metal and the alloy is quenched. Since the solubility of the former metal is lower at lower temperatures the cold solid solution is supersaturated, but the rapid cooling prevents rearrangement of the atoms. The alloy is then subjected to the 'ageing' treatment, which consists in keeping it at a temperature far below its melting-point for a considerable time so that the supersaturated solid solution begins to break down. The Cu-Al alloy mentioned below can be fully hardened at a temperature of 140° C. over a period of 22 hours. The alteration in physical properties takes place during this ageing process, but the alloy may attain maximum hardness before any precipitation visible under the microscope has taken place. Apparently the separation of solute from the supersaturated solution has taken place to different extents in different alloys when maximum hardness is reached. For example, in a silver-copper alloy (7·5 per cent. Cu) of maximum hardness, precipitation is practically complete, i.e. copper has separated out from the silver lattice. On the other hand, in an aluminium-copper alloy containing 4·8 per cent. Cu maximum hardness is reached before such precipitation has taken place, the separation of the solute having proceeded only as far as the segregation of Cu atoms into 'islands' on the Al lattice. As our last example we may take an alloy with the approximate composition $FeCu_4Ni_3$. This is cubic close-packed above 800° C. and if quenched retains this structure as a random substitutional solid solution. If annealed for a week at 650° C. it breaks up into two phases of approximate compositions $FeCu_{13}Ni_8$ and $FeCuNi_2$, both of which are still cubic close-packed but have slightly different cell dimensions. On slow cooling, which is equivalent to a treat-

ment intermediate between quenching and quenching followed by complete annealing, the alloy apparently attempts to remain a single phase but cannot quite achieve this because of the difference in cell dimensions of the two phases mentioned above. The result is apparently a lamellar structure with layers alternately rich in copper and iron, some hundreds of atoms wide and about fifty atoms thick.

Solid Solutions

A characteristic property of metals is that if two (or more) are melted together in suitable proportions a homogeneous solution often results. When cooled this is called a solid solution because, as in the case of a liquid solution, the solute and solvent atoms (applying the term solvent to the metal which is in excess) are arranged at random. Random arrangement of the two kinds of metal atoms is always found if the alloy is cooled rapidly (quenched). In certain solid solutions with particular concentrations of solute a regular atomic arrangement develops on slow cooling or appropriate subsequent heat treatment, and we shall describe shortly some of the features of this 'superlattice' formation. It was necessary to qualify the first statement in this paragraph because (1) solid solutions are not formed by all pairs of metals, and (2) when they are, the range of composition over which solid solutions are formed varies from the one extreme, complete miscibility, to the other, immiscibility, depending on the metals concerned. In what follows we are referring to substitutional solid solutions, i.e. those in which the atoms of the solute replace some of those of the solvent in the lattice of the latter. There is another kind of solid phase, the interstitial solid solution, in which the small atoms of some of the lighter non-metals occupy the interstices between the atoms in metal structures. We deal with these interstitial solid solutions in a later section. It is possible to have a combination of substitutional and interstitial solid solution in ternary or higher systems. For example, an austenitic manganese steel is a substitutional solid solution of manganese in iron and also an interstitial solution of carbon in the (Fe, Mn) lattice.

The conditions determining the formation of solid solutions are as follows:

(1) The tendency to form solid solutions is small if the metals are chemically dissimilar. In general we may say that extended solid solution formation is common between metals of our classes A_1 and A_2, subject to the further restrictions discussed below, and between metals of the same sub-group of the Periodic Table. Thus the following pairs of metals form continuous series of solid solutions: K-Rb, Ag-Au, Cu-Au, As-Sb, Mo-W, and Ni-Pd. For elements of greatly differing electronegativity, e.g. an A sub-group metal and a member of one of the later B sub-groups, not only are the structures of the pure elements quite different but, owing to the difference in electronegativity, compound formation is likely to occur rather than solid solution. For this reason we divided the elements into groups A_1, A_2, B_1, and B_2, and we shall later consider in turn the

types of intermetallic compounds formed between pairs of elements from different groups.

(2) For two elements in the same group in our classification the range of composition over which solid solutions are formed depends on the relative sizes of the two atoms. This is to be expected, since if some of the atoms in a lattice are replaced (at random) by others of a different size, distortion of the lattice must occur and the cell dimensions alter as the concentration of the solute increases. To a first approximation they vary linearly with the atomic percentage of the solute (Vegard's law), though in many cases this law is not exactly obeyed. If the difference between the radii of the metals is greater than about 15 per cent. (of the radius of the solvent atom) there is no extensive formation of solid solutions. There is rather more tolerance at high temperatures, but then precipitation-hardening generally occurs on quenching. For metals crystallizing with very different types of structure the application of this 'relative size' criterion is complicated by the difference in coordination number in the structures of the two metals. We need not, however, go into this point as we shall only be considering solid solutions of metals with typical metallic structures of high coordination.

(3) The mutual solubilities of metals are not reciprocal. Hume-Rothery observed that, other things being equal, a metal of lower valency is likely to dissolve more of one of higher valency than vice versa—the 'relative valency effect'. Though there may be exceptions to this generalization, it is, nevertheless, a useful one. The following figures, taken from the much more extensive data quoted by Hume-Rothery, give some idea of the striking differences in solubilities in cases where the size factor is favourable.

Solubility of:	Zn in Ag . .	37·8% atomic	(Zn)
	Ag Zn . .	6·3% „	(Ag)
	Zn in Cu . .	38·4% „	(Zn)
	Cu Zn . .	2·3% „	(Cu)

We shall now describe some of the changes in structure which take place in certain substitutional solid solutions on cooling slowly or annealing.

Order-disorder Phenomena and Superlattices

Some alloys which are random solid solutions when quenched from the molten state undergo rearrangement when given a suitable heat treatment or in some cases simply when cooled sufficiently slowly. Such a structural change, which begins at a temperature often hundreds of degrees below the melting-point, results in a change from the random arrangement to one in which there is regular alternation of atoms of different kinds throughout the structure. We may illustrate such a change by showing the structure of a portion of the alloy CuAu (*a*) as a random solid solution and (*b*) as the ordered superlattice (Fig. 167).

In this particular case the ordered structure is of lower (crystallographic)

symmetry than the disordered, being a slightly deformed cubic close-packing of the atoms with tetragonal instead of cubic symmetry. In the other examples we give below the symmetry both of the ordered and of the random structures is cubic, the positions of the atoms—disregarding the kind of atom occupying a particular place in the lattice—being the same in both cases. These changes from disordered to ordered structures

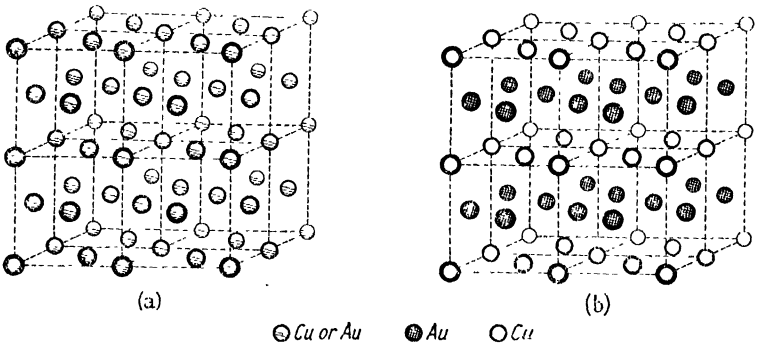


FIG. 167. The crystal stucture of the alloy CuAu in (*a*) the disordered and (*b*) the ordered state.

differ from polymorphic changes in that the positions occupied by the atoms are the same (or practically so) throughout, the atoms merely having changed places. In the case of a polymorphic change the positions of the atoms relative to one another are in general quite different in the two (or more) forms. The possibility of rearrangement to form a superlattice is determined by the thermal energy of the atoms, the difference in potential energies of the ordered and disordered states, and the magnitude of the energy barrier that has to be surmounted before two atoms can change places. The formation of a superlattice is a co-operative phenomenon like the loss of ferromagnetism, which disappears at the Curie point, or the onset of rotation of ions or molecules in crystals. A characteristic of such processes is that the behaviour of a particular atom (or group of atoms in the latter case) is affected by that of its neighbours. Once the process has started it speeds up, giving a curve like that shown in Fig. 47 for the rotation of CH_4 molecules or in Fig. 169 (*a*) for the specific heat of β-brass (see below). The rotation of one methane molecule, for example, in a crystal of that substance loosens the attachments of the others so that not only is the process facilitated for each succeeding molecule but also the thermal energy of the molecules is increasing all the time since the temperature is rising. Although order-disorder transformations may sometimes be loosely compared with melting, since a regular arrangement of atoms gives place to a random one and movement of the atoms relative to one another takes place, it is clear that they differ from the process of melting in certain important respects. There is no general collapse of the whole lattice and the transformation takes place over a wide range of temperature, though in this

latter respect the melting of a glass is similar. In a liquid, however, the arrangement of the atomic centres is less regular than in a solid and, moreover, is constantly changing, whereas in both the disordered and the ordered phases of an alloy the positions of the atomic centres are the same, or the same to within very close limits.

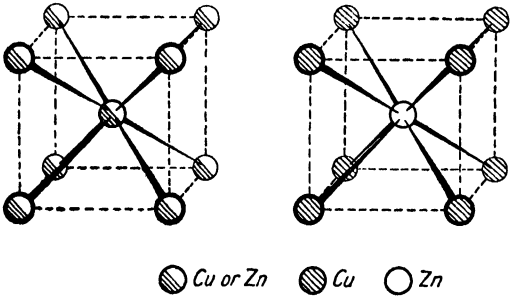


FIG. 168. The structures of the disordered and ordered forms of β-brass.

Starting with an ordered alloy at a low temperature two types of order-disorder transformation may be recognized:

(*a*) Order decreases continuously, passing through all intermediate states, and finally disappears completely at the critical temperature. The specific heat shows an abnormally great increase with rising temperature and at the critical temperature falls suddenly to a value only slightly above the theoretical value.

(*b*) The behaviour is similar to that described in (*a*), except that there is still some order left when the critical temperature is reached so that the last stage of the rearrangement takes place suddenly. In this case there is also a latent heat in addition to the specific heat anomaly.

Order-disorder transformations have been observed in alloys of two types, XY and X_3Y, of which we shall now give some examples.

β-Brass

The structures of the ordered and disordered phases are illustrated in Fig. 168. The atoms are arranged on a body-centred cubic lattice, in one case in a regular way and in the other at random. Instead of drawing a large portion of the structure to show the random arrangement it is more convenient to use a circle with intermediate shading to represent an atom of either kind. The probability of such an atom being either Cu or Zn is one-half. In this alloy the transformation takes place over a temperature range of some 300° C. Below 470° C. it takes place continuously and reversibly, there being no sudden change in the degree of order at the transition point and therefore no latent heat. The specific heat/temperature curve for a change of this sort is shown (for CuZn) in Fig. 169 (*a*). To account for the fact that the specific heat is still abnormal above the transition point it has been suggested that although the long-distance

order has disappeared there is still a tendency for atoms to prefer unlike atoms as nearest neighbours.

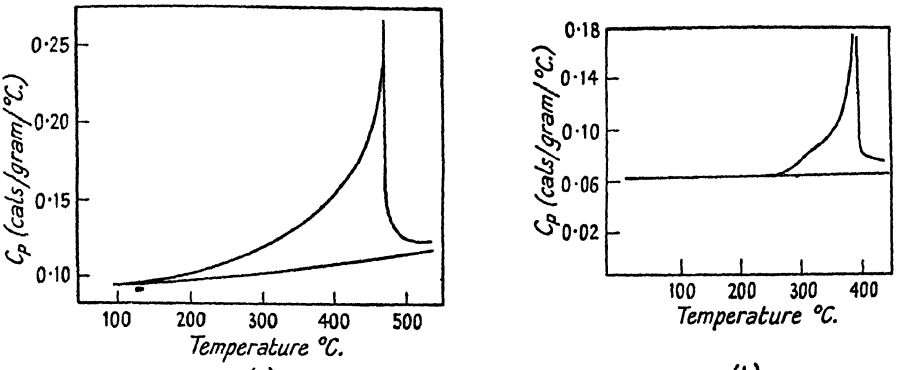


FIG. 169. The variation with temperature, on heating, of the specific heat of (*a*) β-brass and (*b*) Cu_3Au (after cooling at 30° C. per hour). In each case the upper curve is drawn through the experimental values and the lower curve is that to be expected in the absence of a transformation. (After Sykes and Wilkinson and Sykes and Evans.)

Alloys X_3Y

Order-disorder transformations have been observed in the following alloys: Cu_3Au, Cu_3Pd, Cu_3Pt, Ni_3Fe, and Fe_3Al. In the first four cases

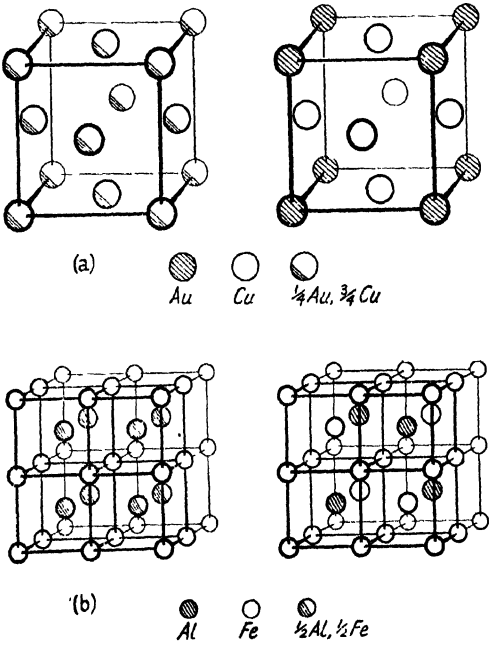


FIG. 170. The crystal structure of (*a*) Cu_3Au and (*b*) Fe_3Al in the disordered and ordered states.

the atoms occupy the positions of a face-centred cubic structure, and the relation of the ordered to the disordered structure is that shown in Fig. 170 (*a*). These transformations are sluggish and inhibited by quenching from high temperatures, and annealing for several months is necessary to produce a high degree of order in Ni_3Fe. The specific heat/temperature curve for Cu_3Au is shown in Fig. 169 (*b*). Investigation of the variation with temperature of the electrical resistance of Cu_3Au shows that a marked degree of order sets in at the critical temperature, for on cooling through this temperature a sudden drop of 20 per cent. occurs. Accordingly there is a latent heat associated with the order-disorder transformation in Cu_3Au. The absence of the expected latent heat in the case of Ni_3Fe is probably due to the extreme slowness of the rearrangement.

The transformation in Fe_3Al is illustrated in Fig. 170 (*b*). The Fe-Al system has been very carefully studied, and the work of Bradley and Jay on this system is one of the most elegant X-ray crystallographic studies in this field.

Intermediate Phases in Alloy Systems

It now remains to describe briefly the types of structure adopted by intermediate phases in alloy systems. We shall limit our survey to binary systems. Adopting the classification of the elements indicated on p. 537, we have to consider three main classes of alloys:

I. Alloys of two 'true' metals, AA

II. „ an A and a B sub-group metal, AB $\begin{cases} A_1B_1 \\ A_2B_1 \\ A_1B_2 \\ A_2B_2 \end{cases}$

III. „ two B sub-group metals, BB.

Of these the second is by far the most interesting as regards the structures of the intermediate phases, and since we subdivide the true metals into two groups A_1 and A_2 and also distinguish the earlier from the later B sub-group elements as B_1 and B_2 respectively, we make further subdivisions in class II as shown. We shall have no more to say of alloys of class I as we have dealt with several systems of this type in our discussion of solid solutions and superlattices, and we shall therefore proceed to alloys containing B sub-group elements. It is not easy to draw a hard-and-fast line between truly metallic alloys and homopolar compounds in some cases, particularly those involving elements of the later B sub-groups (As, Sb, Se, Te), but we shall begin with the more metallic systems containing the earlier B sub-group elements (B_1).

Class II

Systems A_1B_1. Two structures commonly found for phases of composition AB are the caesium chloride and 'sodium thallide' structures. Among the alloys crystallizing with the former structure are LiHg, LiAl, LiTl, MgTl, CaTl, and SrTl. The structure needs no description here, but we shall refer to these alloys in the next section. In the NaTl structure (which

is also that of LiZn, LiCd, LiGa, LiIn, and NaIn) the coordinates of the atoms are the same as in the CsCl structure (i.e. those of a body-centred cubic lattice), but the arrangement of the two kinds of atoms is such as to give each atom four nearest neighbours of the other kind. Owing to the very low coordination number the interatomic distances in alloys with the NaTl structure are very much shorter (some 13 per cent. for NaTl itself) than the sums of the radii derived from the structures of the pure metals.

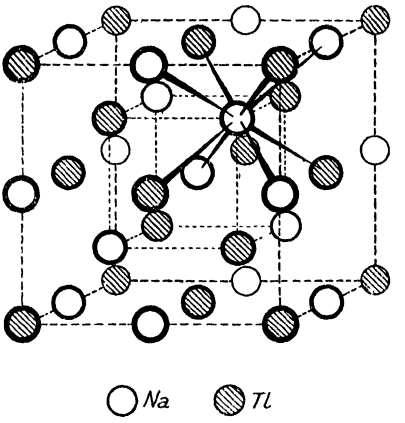


FIG. 171. The crystal structure of NaTl.

Systems A_2B_1. In these systems, containing a transition metal or Cu, Ag, or Au and a metal of one of the earlier B sub-groups, one or more of three characteristic structures are generally found. These are termed the β, γ, and ϵ structures, the solid solution at one end of the phase diagram being designated the α phase. These β, γ, and ϵ phases are not necessarily stable down to room temperature. In the Cu-Al system, for example, part of the phase diagram of which is shown in Fig. 172 (p. 561), the β phase is not stable at temperatures below about 540° C. The structures of these phases are:

β—body-centred cubic,

γ—complex cubic structure containing 52 atoms in the unit cell,

ϵ—hexagonal close-packed.

Although we shall assign formulae to these phases, which are often termed 'electron compounds' for reasons which will be apparent later, they may appear over considerable ranges of composition. Moreover, although we might expect the β (body-centred) structure to contain at least approximately equal numbers of atoms of the two kinds, it sometimes appears with a composition very different from this. Thus, although the coordinates of the positions occupied in these phases are always the same, the distribution of a particular kind of atom over these positions is variable. In the Ag-Cd system the β phase is homogeneous at 50 per cent. Cd and has the CsCl structure, but in the Cu-Sn and Cu-Al systems it

appears with the approximate compositions Cu_5Sn and Cu_3Al respectively. In these cases there is random arrangement of the two types of atom in the body-centred structure. It is interesting that whereas Cu_3Al has the β structure, Ag_3Al and Au_3Al crystallize with the β-Mn structure (p. 546), and the same difference is found between Cu_5Sn (β structure) and Cu_5Si (β-Mn structure). In the case of alloys with the γ structure, the rather complex formulae such as Ag_5Cd_8, Cu_9Al_4, Fe_5Zn_{21}, and $Cu_{31}Sn_8$ are based on the number of atoms (52) in the unit cell. It will be seen that the total numbers of atoms in the formulae quoted are respectively 13, 13, 26, and 39. Thus in the Ag-Cd system the γ phase is stable over the range 57–65 atomic per cent. Cd, allowing a considerable choice of formulae, that chosen (Ag_5Cd_8) being consistent with the crystal structure. A selection of phases with the β, γ, and ϵ structures is given in Table 28.

TABLE 28

Electron : atom ratio 3:2		*Electron : atom ratio* 21:13	*Electron : atom ratio* 7:4
β body-centred	β-Mn cubic structure	'γ-brass' structure	ϵ close-packed hexagonal structure
CuBe	Ag_3Al	Cu_5Zn_8	$CuZn_3$
CuZn	Au_3Al	Cu_9Al_4	Cu_3Sn
Cu_3Al	Cu_5Si	Fe_5Zn_{21}	$AgZn_3$
Cu_5Sn	$CoZn_3$	Ni_5Cd_{21}	Ag_5Al_3
CoAl		$Cu_{31}Sn_8$	Au_3Sn
(for MgTl, etc., see below)		$Na_{31}Pb_8$	

A striking feature of this table is the variety of formulae of alloys with a particular structure. Hume-Rothery first pointed out that these formulae could be accounted for if we assume that the appearance of a particular structure is determined by the ratio of valency electrons to atoms. Thus for all the formulae in the first two columns we have an electron:atom ratio of 3:2, for the third column 21:13, and for the fourth 7:4, if we assume the normal numbers of valency electrons for all the atoms except the triads in Group VIII of the Periodic Table. These fit into the scheme only if we assume that they contribute no valency electrons, as may be seen from the following examples:

CuBe (1+2)/2	Cu_5Zn_8 (5+16)/13	$CuZn_3$ (1+6)/4
Cu_3Al (3+3)/4	Cu_9Al_4 (9+12)/13	Cu_3Sn (3+4)/4
Cu_5Sn (5+4)/6	Fe_5Zn_{21} (0+42)/26	Ag_5Al_3 (5+9)/8
CoAl (0+3)/2	$Na_{31}Pb_8$ (31+32)/39	
$= \frac{3}{2}$	$= \frac{21}{13}$	$= \frac{7}{4}$

Certain other alloys also with the body-centred cubic structure, LiHg, MgTl, etc., which have already been mentioned, have sometimes been regarded as exceptions to the Hume-Rothery rules. They fall into line with the other β structures only if we assume that Hg or Tl provides one valency electron. Since, however, the radii of the metal atoms in these

alloys, as in those with the NaTl structure, are smaller than the normal values, it is probably preferable not to regard these as β electron compounds.

Although the alloys with compositions giving the above comparatively simple electron:atom ratios generally fall within the range of homogeneity of the particular phases, it now appears that the precise values of those

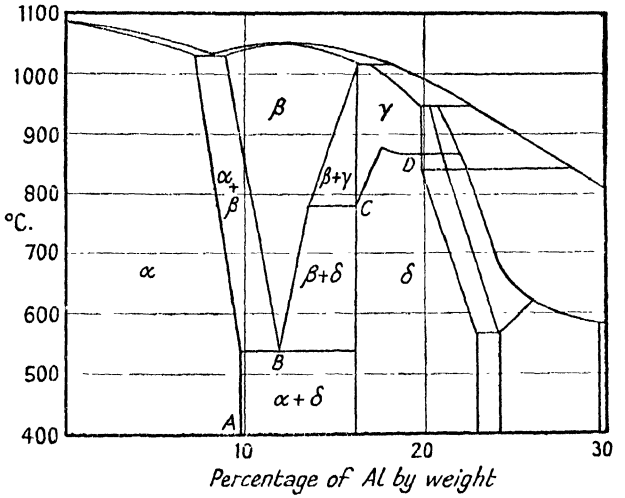


FIG. 172. Part of the phase diagram for the Cu-Al system (after Stockdale).

ratios, 3/2, 21/13, and 7/4, have no special significance. By applying wave-mechanics to determine the possible energy states of electrons in metals it has been found possible to derive theoretical values for the electron:atom ratios at the boundaries of the α, β, and γ phases, the α phase being the solid solution with the close-packed structure of one of the pure metals. In comparing these values with the electron:atom ratios found experimentally we have to remember that phase boundaries may change with temperature, i.e. the tie-lines separating the regions of stability of different phases on the phase diagram are not necessarily parallel to the temperature axis. This is invariably the case with β phases. The range of composition over which the phase is stable decreases at lower temperatures, as may be seen in the phase diagram for the system Cu-Al which we may take as an example. The relevant portion of this diagram is shown in Fig. 172. The boundaries of the β phase meet at the point B. (In some systems these phase boundaries do not meet even when room temperature has been reached, but this may be due, at least in part, to the slow rate at which equilibrium between different phases is attained at such low temperatures.) In Table 29 below are given the experimental values of the electron:atom ratios for four systems in which both β and γ phases occur. The first column gives the electron:atom ratio for maximum solubility in the α phase, i.e. the point A in Fig. 172. The second column gives that ratio for the point corresponding to B and the third for the

boundaries of the γ phase (points C and D in Fig. 172). It will be seen that there is general agreement with the theoretical values, particularly in the first two columns, though all the values for the γ phase boundaries exceed the theoretical electron:atom ratios.

TABLE 29

System	Electron : atom ratios for		
	Maximum solubility in α phase	*β-phase boundary with smallest electron concentration*	*γ-phase boundaries*
Cu-Al	1·408	1·48	1·63–1·77
Cu-Zn	1·384	1·48	1·58–1·66
Cu-Sn	1·270	1·49	1·67–1·67
Ag-Cd	1·425	1·50	1·59–1·63
Theoretical	1·362	1·480	1·538

Systems A_1B_2. The remaining systems, A_1B_2 and A_2B_2, containing elements of the later B sub-groups call for little discussion here since arsenides have been dealt with to some extent in Chapter XII, and sulphides, selenides, and tellurides in Chapter XI. The phase diagrams are generally very simple, showing very restricted solid solution and only one, usually very stable, compound with a formula conforming to the ordinary valencies of the elements (Mg_2Ge, Mg_3As_2, MgSe, etc.). These intermetallic compounds have simple structures which are similar to those of simple salts and they are almost electrical insulators. The structures of some of these compounds are set out below:

Mg_2Si, Mg_2Ge, Mg_2Sn, Mg_2Pb } anti-CaF_2

Mg_3P_2, Mg_3As_2 } anti-Sc_2O_3

Mg_3Sb_2, Mg_3Bi_2 } anti-La_2O_3

MgS, MgSe } NaCl

MgTe wurtzite

The fact that compounds such as Mg_2Si to Mg_2Pb have such high resistances and crystallize with the anti-fluorite structure does not mean that they are ionic crystals. Wave-mechanical calculations show that in these crystals the number of energy states of an electron is equal to the ratio of valency electrons:atoms (8/3) so that, as in other insulators, the electrons cannot become free (i.e. reach the conduction band) and so conduct electricity. That the high resistance is characteristic only of the crystalline material and is not due to ionic bonds between the atoms is confirmed by the fact that the conductivity of molten Mg_2Sn, for example, is about the same as that of molten tin.

Systems A_2B_2. The A_2 metals and the elements of the earlier B sub-groups (B_1 metals) form the electron compounds already discussed. With the metals of the later B sub-groups the A_2 metals, like the A_1, tend to form intermetallic phases more akin to simple homopolar compounds, with structures quite different from those of the pure metals. The nickel arsenide structure, the only one we shall mention in this group, has, like

typical alloys, the property of taking up in solid solution a considerable excess of the transition metal. From Table 30 below it will be seen that many A_2B_2 compounds crystallize with the NiAs structure, an unusual feature of which is the trigonal prism coordination of As by six Ni atoms. The Ni atoms have the same low coordination number, but their neighbours are arranged octahedrally. This structure has been illustrated in Fig. 111 (p. 387).

TABLE 30

Compounds crystallizing with the NiAs *Structure*

	Cu	Au	Cr	Mn	Fe	Co	Ni	Pd	Pt
Sn	CuSn	AuSn			FeSn		NiSn		PtSn
Pb									PtPb
As				MnAs			NiAs		
Sb			CrSb	MnSb	FeSb	CoSb	NiSb	PdSb	PtSb
Bi							NiBi		PtBi
Se			CrSe		FeSe	CoSe	NiSe		
Te			CrTe	MnTe	FeTe	CoTe	NiTe	PdTe	PtTe

Class III

Systems BB. Alloys containing elements of only the earlier B sub-groups have typically metallic properties. Solid solutions are formed to an appreciable extent only by elements of the same sub-group and, of course, the relative size criterion applies as in other systems. Thus Cd and Hg form solid solutions over quite large ranges of composition and Cd and Zn over smaller ranges; compare the radii: Zn, 1·37, Cd, 1·52, and Hg, 1·55 A. Cadmium and tin, on the other hand, are practically immiscible. When both the metals belong to later B sub-groups a 1:1 compound with the NaCl structure occurs in a number of cases, e.g. SnSb, SnTe, PbSe, and PbTe. Finally the zinc-blende or wurtzite structure is found for 1:1 compounds in which the average number of valency electrons per atom is four, i.e. when the atoms belong to the nth and $(8-n)$th sub-groups. Examples of compounds with these structures are the sulphides, selenides, and tellurides of Zn, Cd, and Hg, and GaAs, GaSb, and InSb. Compounds such as BeS and AlP also crystallize with the zinc-blende structure, which is not restricted to elements of the B sub-groups.

The Formulae of Alloys

We have already discussed the question of stoichiometric composition in relation to the Law of Constant Composition in Chapter V. The following points are added to supplement our earlier remarks. Substitutional solid solutions can have any composition within the range of miscibility of the metals concerned, and there is random arrangement of the atoms over the lattice positions of the structure of the solvent metal. At particular ratios of the numbers of atoms superlattices may be formed,

and an alloy with either of the two extreme structures, the ordered and disordered, but with the same composition in each case, can possess markedly different physical properties. Composition therefore does not completely specify such an alloy. Interstitial solid solutions also have compositions variable within certain ranges. The upper limit to the number of interstitial atoms is set by the number of holes of suitable size,

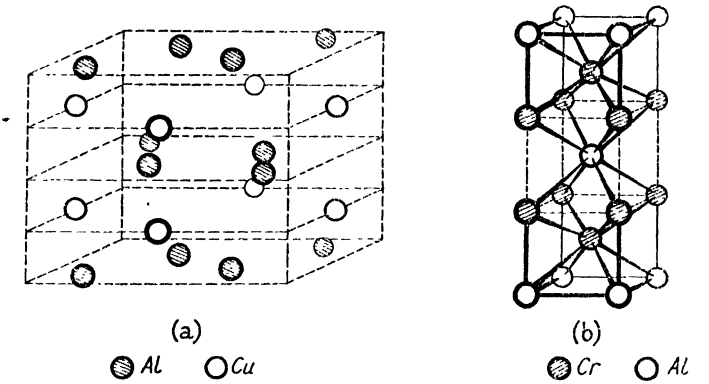


FIG. 173. The crystal structures of (*a*) $CuAl_2$ and (*b*) Cr_2Al.

but this limit is not necessarily reached, as we shall see later. When a symmetrical arrangement is possible for a particular ratio of interstitial to parent lattice atoms this is adopted. In intermediate cases the arrangement of the interstitial atoms is random.

When we come to alloys which are described as intermetallic compounds as opposed to solid solutions, we find that in some cases the ratios of the numbers of atoms of different kinds which we should expect to find after examination of the crystal structure are never attained in practice. When dealing with electron compounds we noted many cases of alloys with quite different types of formulae which crystallize with the same structure (e.g. CuZn, Cu_3Al, and Cu_5Sn all with the β structure). We know that in cases of this kind the compositions are determined by the electron : atom ratios. At an appropriate temperature an elcctron compound, like a solid solution, is stable over a range of composition, and the particular formulae adopted were selected to conform with the numbers of equivalent positions in the crystal structure (e.g. Cu_9Al_4 rather than, say, Cu_9Al_5 which also lies within the range of stability of this phase) and/or Hume-Rothery's simple electron : atom ratios. We have seen that the precise values of these ratios, 3/2, 21/13, and 7/4, have no theoretical significance. An alloy such as Ag_3Al is completely disordered, there being a total of 20 atoms in the unit cell in two sets of 12-fold and 8-fold equivalent positions. There are, however, alloys other than those with the β, γ, and ϵ structures the compositions of which are never those of the ideal structures. In the Cu-Al system, for example, there is a θ phase with ideal formula $CuAl_2$, the structure of which is illustrated in Fig. 173 (*a*). In this (tetragonal)

structure there are, in one unit cell, four Cu and eight Al atoms, the symmetry requiring these numbers of the two kinds of atoms. If, however, an alloy is made up with the composition $CuAl_2$ it is not homogeneous but consists of a mixture of alloys with the $CuAl_2$ and CuAl structures. In other words, the $CuAl_2$ structure is not stable with the Cu:Al ratio equal to 1:2 but prefers a rather greater proportion of aluminium. Thus, although this θ phase is stable over a certain small range of composition, the alloy $CuAl_2$ lies outside this range. The laws applicable to conventional chemical compounds (see, however, FeS, p. 171) do not hold in metal systems, and these facts concerning $CuAl_2$ are not surprising when we remember that the approximate compositions of the phases in this system with the β and ϵ structures are Cu_3Al and Cu_9Al_4 respectively. The β phase in the Cr-Al system provides another example of the same phenomenon. The body-centred solid solution of Al in Cr is stable at high temperatures up to some 30 per cent. Al, i.e. beyond the composition Cr_2Al. If, however, an alloy containing about 25 per cent. Al is cooled slowly the body-centred cubic structure changes to the tetragonal β structure illustrated in Fig. 173 (*b*). As may be seen from the diagram, this structure is closely related to the body-centred cubic structure and its ideal composition is clearly Cr_2Al. Although this β structure is stable over a considerable range of composition, the alloy Cr_2Al lies outside this range. The slow cooling of an alloy with the exact composition Cr_2Al therefore gives an inhomogeneous mixture which actually consists of an Al-rich Cr_2Al component and some body-centred cubic solid solution.

Interstitial Structures

We have already seen that most of the transition metals crystallize with close-packed structures. In a close-packed array of atoms, which we shall regard as rigid spheres, there are holes of two kinds, the centres of which are distinguished in Fig. 174 as small open and black circles. Two close-packed layers are shown, and it is seen that an atom placed in a hole of the first type would have four neighbours arranged tetrahedrally, and in a hole of the second type six neighbours forming an octahedral group around it. For brevity we shall refer to these holes as tetrahedral and octahedral holes respectively. It is clear that there is an upper limit to the size of atoms which can be accommodated in such positions in a close-packed structure. Taking the radius of the close-packed atoms as unity, the maximum radii are: 0·41 for an atom in a tetrahedral hole and 0·59 in an octahedral hole. It is convenient to classify interstitial structures according to the type of hole occupied and the proportion of the total number of such holes which are actually filled. There is no need for all the holes of a given type to be occupied since the lattice is stable in the absence of interstitial atoms. Before proceeding to this classification we may note briefly some characteristics of interstitial structures.

These structures consist of a transition metal containing the small atoms of the non-metals H, B, C, or N in the interstices of the metal lattice

which is, in general, close-packed. The metal atoms are still in contact, their arrangement generally being identical with that in the pure metal, though cementite, Fe_3C, is an exception to this rule. Interstitial structures have many of the characteristic properties of metallic alloys, opacity (contrast the transparent salt-like carbides of Ca, etc.), conductivity, metallic

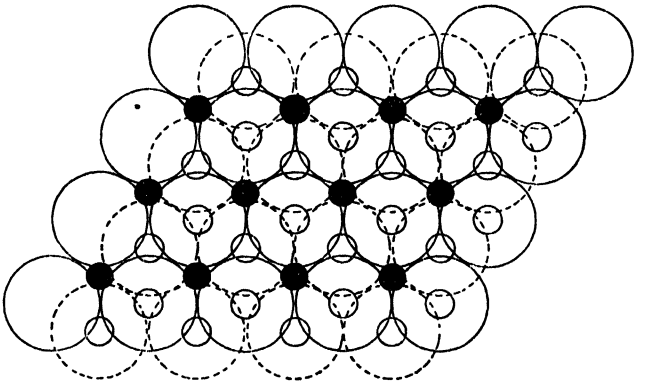


FIG. 174. Two layers of close-packed atoms, showing the tetrahedral holes (small open circles) and octahedral holes (small black circles).

lustre, and variable composition. In contrast to pure metals, however, these compounds are mostly very hard and they melt at very high temperatures. Compounds of the type MX are generally derived from cubic close-packing; those of type M_2X from hexagonal close-packing. The remarks in this section apply more particularly to interstitial compounds other than those of iron. The latter, of supreme importance technically, are described very briefly in the final section. The melting-points and hardnesses of some interstitial compounds are set out below. These compounds may be prepared by heating the finely divided metal with carbon or boron, or in a stream of ammonia, to temperatures of the order of 2,200° C. for carbides, 1,800–2,000° for borides, or 1,100–1,200° for nitrides. Alternatively the metal, in the form of a wire, may be heated in an atmosphere of a hydrocarbon or of nitrogen. The solid solution of the composition 4TaC+ZrC melts at the extraordinarily high temperature 4,215° K. These compounds are very inert chemically except towards oxidizing agents. Their electrical conductivities are high and decrease with rising temperature as in the case of metals, and some exhibit supraconductivity. (The hardness is according to Mohs's scale, on which that of diamond is 10.)

	M.pt. (° K.)	*Hardness*		*M.pt.* (° K.)	*Hardness*
TiC . .	3410	8–9	TiN . .	3220	8–9
HfC . .	4160		ZrN . .	3255	8
W_2C . .	3130	9–10	TaN . .	3360	
NbC . .	3770				
			ZrB . .	3265	9

In a cubic close-packed arrangement of spheres the number of octahedral holes is equal to the number of spheres, and if these holes are all occupied the arrangement of the atoms is that of the NaCl structure. Fewer

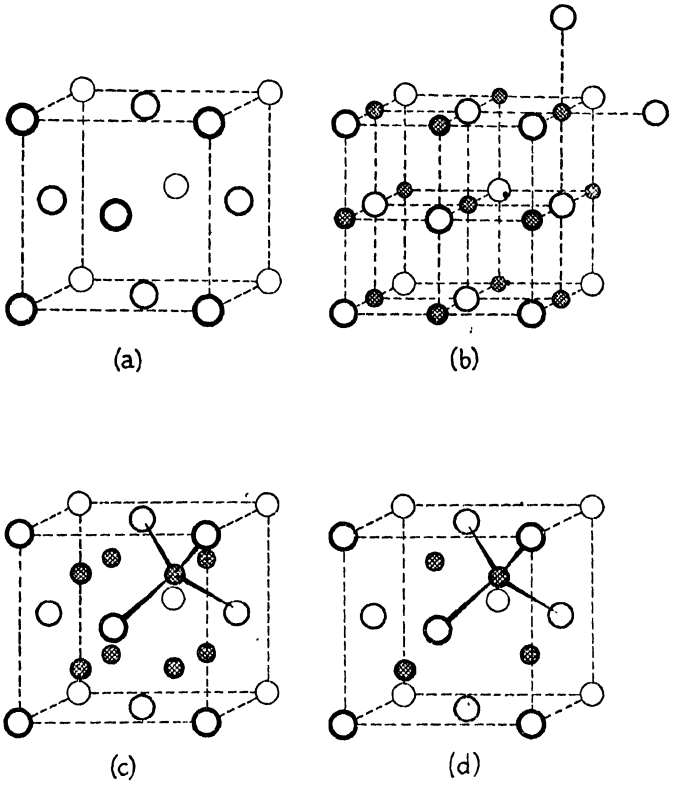


FIG. 175. Cubic close-packing (*a*) and related structures: (*b*) rock-salt, (*c*) fluorite, and (*d*) zinc-blende.

holes than the maximum may be occupied, when compounds approximating to the formulae M_2X and M_4X result. The number of tetrahedral holes is twice that of the spheres, and if all are occupied the CaF_2 structure results. When half the tetrahedral holes are filled in the most symmetrical way the compound has the zinc-blende structure. The relations of these simple structures to cubic close-packing are shown in Fig. 175. The centres of the octahedral holes lie at the mid-points of the sides and body-centre of the face-centred cube, while the centres of the tetrahedral holes lie at points along the body diagonals of the cube with coordinates $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, etc. The structures based on cubic close-packed metal atoms are summarized in the following table, where examples of interstitial compounds are given. A similar scheme could be drawn up for hexagonal close-packing. For example, in V_2C and Mo_2C the carbon atoms occupy half the octahedral holes and in Zr_2H and Ti_2H the hydrogen atoms occupy one-quarter of the tetrahedral holes in lattices of hexagonal close-packed metal atoms.

The structures of carbides of the type MC_2 have been described in Chapter XIII. In the LaC_2 and ThC_2 structures the carbon atoms are in pairs as C_2^{2-} ions. Although these structures may be regarded as derived from cubic close-packed metal lattices with the C_2^{2-} ions in octahedral holes, there is considerable distortion from cubic symmetry owing to the large size and non-spherical shape of the C_2 groups, and these carbides are therefore preferably not classed with the interstitial compounds.

TABLE 31

Interstitial Structures derived from Cubic Close-packing

Non-metal atoms in	*Proportion occupied*	*Structure*	*Examples*
Octahedral holes	all	NaCl	TiC, TiN, ZrC, ZrN, HfC, VC, NbC, TaC
(radius ratio	$\frac{1}{2}$	..	W_2N, Mo_2N
0·41–0·59)	$\frac{1}{4}$	..	Mn_4N, Fe_4N
Tetrahedral holes	all	CaF_2	TiH_2
(radius ratio	$\frac{1}{2}$	Zinc-blende	ZrH, TiH
0·23–0·41)	$\frac{1}{4}$	..	Pd_2H
	$\frac{1}{8}$	..	Zr_4H

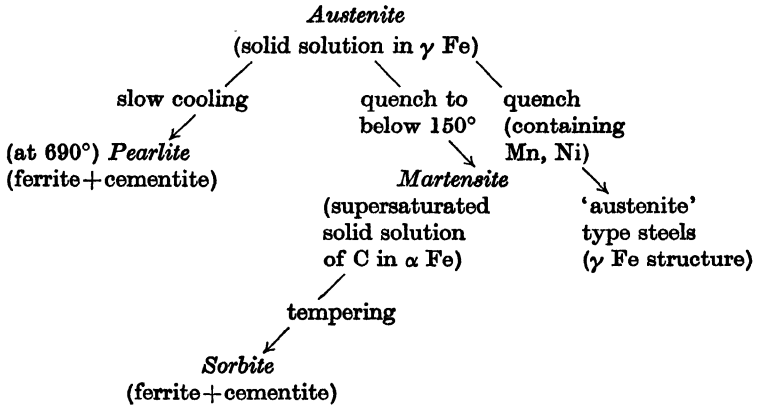
Iron and Steel

A simple steel consists of iron containing a small amount of carbon. Many steels now used for particular purposes also contain one or more of a number of metals (Cr, Mo, W, V, Ni, Mn) which modify the properties of the steel. We shall restrict our remarks to the simple Fe-C system. The properties of the various kinds of 'iron' and of steels which make these materials so valuable are dependent on the amount of carbon and the way in which it is distributed throughout the metal. The Fe-C system is, for two reasons, more complicated than the metal-non-metal systems giving the interstitial compounds just described. Firstly, iron is dimorphous. The form stable at ordinary temperatures is called α iron. It has the body-centred cubic structure and is ferromagnetic. The body-centred structure is stable up to 906° C. and again from 1,401–1,530°, the melting-point. Over the intermediate range of temperature, 906–1,401°, the structure is face-centred cubic (γ iron), in which form the metal is non-magnetic. The Curie point (766° C.) is lower than the α-γ transition point, and the term β iron is applied to iron in the temperature range 766–906° C. Since there is no change in atomic arrangement at the Curie point we shall not refer to β iron in what follows. The second complicating factor is that the C:Fe radius ratio (0·60) lies near the critical limit for the formation of interstitial solid solutions. Accordingly, in addition to the latter a carbide Fe_3C is formed. Thus according to the carbon content and heat treatment the carbon may be present either in the free state as graphite, in solid solution, or as cementite (Fe_3C).

Iron is obtained by smelting oxy-ores with coke, so that in the melt there is an excess of carbon. Molten iron dissolves up to 4·3 per cent. of carbon, the eutectic mixture solidifying at 1,150° C. Pig-iron (cast-iron) contains therefore about 4 per cent. C. There is also up to 2 per cent. Si from the clays associated with the ores. The carbon in cast-iron may be in the form of cementite (white cast-iron) or graphite (grey cast-iron), depending on the silicon content. The presence of silicon favours the decomposition of cementite into graphite, and in general some of the carbon in cast-iron is present in both forms. The material which solidifies at 1,150° containing 4·3 per cent. C is a mixture; the maximum solubility of C in γ Fe at that temperature, i.e. in a homogeneous solid solution, is 1·9 per cent. This solubility falls to 0·9 per cent. at 690°, the lowest temperature at which γ Fe is rendered stable by the presence of carbon. (Iron can be retained in the non-magnetic γ form at ordinary temperatures by adding elements such as Mn and Ni which form solid solutions with γ but not with α iron.) Removal of all but the last traces of impurity from pig-iron gives wrought iron, the purest commercial iron. Steels contain up to 1·5 per cent. C; mild steels from about 0·1 to 0·5 per cent. The production of steels therefore involves either the controlled reduction of the amount of carbon if they are made from pig-iron or the controlled addition of carbon if they are made from wrought iron (the process of cementation). We may summarize the processes which take place in the production of steels as follows.

Above 906° C. the steel is in the form of a (non-magnetic) solid solution of carbon in γ iron (austenite). This is a simple interstitial solid solution in which the carbon atoms are arranged at random since there are not sufficient to form a regular structure. It is fairly certain that in austenite the carbon atoms occupy octahedral holes in the γ Fe lattice. When austenite is cooled slowly, the first process which takes place is the separation of the excess carbon as cementite, since the solubility of carbon falls to 0·9 per cent. at 690°. Below this temperature γ Fe is no longer stable, and the solid solution of C in γ Fe changes at 690° into a eutectoid mixture of ferrite and cementite. Ferrite is nearly pure α Fe; it contains some 0·06 per cent. of C in interstitial solid solution. The remaining carbon goes into the cementite. Pearlite, which is the name given to this eutectoid mixture, has a fine-grained banded structure with a pearly lustre and is very soft. The other extreme form of heat treatment is to quench the austenite to a temperature below 150°, when martensite is formed. This is a supersaturated solid solution of C in α Fe and may contain up to 1·6 per cent. C. It is very hard, extreme hardness being a characteristic of quenched steels. (The original γ solid solution, austenite, can be preserved after quenching only if other metals are present, as mentioned above.) The hard, brittle quenched steels are converted into more useful steels by the process of tempering. This consists in reheating the martensite to temperatures from 200–300°. The object of tempering is the controlled conversion of the quenched solid solution into ferrite and

cementite. The mixture produced by tempering has a coarser texture than pearlite and is termed sorbite. The tempering reduces the hardness but increases the toughness of the steel. Sorbite is thus an intermediate product in the sequence: austenite-martensite-sorbite-pearlite. These forms of heat treatment may be summarized:



It is interesting that the structure of cementite is not related in any simple way to those of α or γ Fe. In the γ structure each Fe atom has twelve equidistant nearest neighbours (at 2·52 A., the value obtained by extrapolation to room temperature), and in the α structure eight, at 2·48 A. In cementite some of the Fe atoms have twelve neighbours at distances ranging from 2·52 to 2·68 A. and the others eleven at distances from 2·49 to 2·68 A. The most interesting feature of the structure is the environment of the carbon atoms. The six nearest neighbours lie at the apices of a distorted trigonal prism, but the range of Fe–C distances is considerable, 1·89–2·15 A., and two further neighbours at 2·31 A. might also be included in the coordination group of the carbon atoms. The reason for this unsymmetrical environment—contrast the octahedral environment in austenite—is unknown.

REFERENCES TO SPECIAL TOPICS

ELECTRONIC THEORY OF VALENCY

L. PAULING, *The Nature of the Chemical Bond*, Cornell U.P. and O.U.P., 2nd edition, 1940.

—— and E. B. WILSON, *Introduction to Quantum Mechanics*, McGraw Hill, 1935.

O. K. RICE, *Electronic Structure and Chemical Binding*, McGraw Hill, 1940.

N. V. SIDGWICK, *The Electronic Theory of Valency*, Clarendon Press, 1927.

—— *The Covalent Link in Chemistry*, Cornell U.P., 1933.

K. FAJANS, *J. Chem. Phys.*, 1941, **9**, 281.

R. HULTGREN, *Phys. Rev.*, 1932, **40**, 891.

G. E. KIMBALL, *J. Chem. Phys.*, 1940, **8**, 188.

L. E. MARCHI, W. C. FERNELIUS, and J. P. MCREYNOLDS, *J.A.C.S.*, 1943, **65**, 329.

R. S. MULLIKEN, *J. Chem. Phys.*, 1933, **1**, 492.

L. PAULING, *J.A.C.S.*, 1931, **53**, 1367.

—— and J. SHERMAN, ibid., 1937, **59**, 1450.

W. G. PENNEY, *Proc. Roy. Soc.*, 1937 A, **156**, 306.

N. V. SIDGWICK and H. M. POWELL, ibid., 1940 A, **176**, 153.

J. H. VAN VLECK, *J. Chem. Phys.*, 1935, **3**, 803.

Covalent Radii

E. C. BAUGHAN, M. G. EVANS, and M. POLANYI, *Trans. Faraday Soc.*, 1941, **37**, 377.

L. PAULING and M. L. HUGGINS, *Z. Krist.*, 1934, **87**, 205.

V. SCHOMAKER and D. P. STEVENSON, *J.A.C.S.*, 1941, **63**, 37.

E. WARHURST, *Trans. Faraday Soc.*, 1944, **40**, 26.

CRYSTAL CHEMISTRY

W. L. BRAGG, *The Crystalline State*, Bell, 1933.

—— *The Atomic Structure of Minerals*, Oxford Univ. Press, 1937.

R. C. EVANS, *Introduction to Crystal Chemistry*, Cambridge Univ. Press, 1939.

O. HASSEL, *Crystal Chemistry*, Heinemann, 1935.

F. SEITZ, *Modern Theory of Solids*, McGraw Hill, 1940.

C. W. STILLWELL, *Crystal Chemistry*, McGraw Hill, 1938.

V. M. GOLDSCHMIDT, 'Geochemie', *Handwörterbuch der Naturwissenschaften*, G. Fischer, Jena, 1933.

—— 'Kristallchemie', ibid., vol. **5**, 1934.

F. LAVES, *Naturwiss.*, 1937, **44**, 705; 1937, **45**, 721.

THE SOLID STATE

Defect Structures

N. F. MOTT and R. W. GURNEY, *Electronic Processes in Ionic Crystals*, Oxford, 1940.

C. FINBAK and O. HASSEL, 'Rotation von Anionpolyedern in kubischen Kristallgittern', *Z. physikal. Chem.*, 1936 B, **32**, 130, 433; 1937 B, **35**, 25.

F. LAVES, 'Übergang zwischen Ordnung und Unordnung in Ionenkristallen', *Z. Elektrochem.*, 1939, **45**, 2.

W. NOWACKI, 'Zur Klassifikation der festen Körper', *Z. Krist.*, 1938, **100**, 77.

— 'Fehlordnungserscheinungen in Festkörpern', *Technik-Industrie und Schweizer Chemiker Zeitung*, **25**, Nr. 5/6, 3 (1942).

L. W. Strock, 'A Classification of Crystal Structures with Defect Lattices', *Z. Krist.*, 1936, **93**, 285.

Polymorphism

M. J. Buerger and M. C. Bloom, 'Crystal Polymorphism', *Z. Krist.*, 1937, **96**, 182.
J. A. Hedvall, 'Changes in Crystal Structure and their influence on the Reactivity and Catalytic Effect of Solids', *Chem. Rev.*, 1934, **15**, 139.
H. Terrey, 'Polymorphism of Elements and Inorganic Compounds at High Pressures', *Rep. Prog. Chem.*, 1937, **34**, 140.

Reactions in the Solid State

Symposium: *Trans. Faraday Soc.*, 1938, **34**, 822.

THE LIQUID STATE

J. T. Randall, *Diffraction of X-rays and Electrons by Amorphous Solids, Liquids and Gases*, Chapman and Hall, 1934.

Symposium on Liquids: *Trans. Faraday Soc.*, 1937, **33**, 1.
Symposium on Electrolytes: *Chem. Rev.*, 1933, **13**, 1.
Symposium on Non-aqueous Solutions: ibid., 1931, **8**, 167.
J. A. V. Butler, 'Intermolecular Forces and the Properties of Liquids', *Rep. Prog. Chem.*, 1937, **34**, 75.
R. W. Gurney, 'Electrolytes and Electrolysis', *Rep. Prog. Physics*, 1937, **4**, 251.
N. F. Mott and R. W. Gurney, 'Recent Theories of the Liquid State', ibid., 1938, **5**, 46.

Fusion

J. G. Kirkwood and E. Monroe, *J. Chem. Phys.*, 1941, **9**, 514.
A. R. Ubbelohde, *Rep. Prog. Chem.*, 1940, **37**, 168 (many references).

Liquid Crystals

Symposium: *Trans. Faraday Soc.*, 1933, **29**, 883.

Glasses

J. Biscoe and B. E. Warren, 'X-ray Study of Soda Boric Oxide Glass', *J. Amer. Ceram. Soc.*, 1938, **21**, 287.
W. Nowacki, 'Die Struktur der Gläser', *Schweizer Archiv*, 1938, **7**, 1.
B. E. Warren, 'X-ray Diffraction Study of the Structure of Glass', *Chem. Rev.*, 1940, **26**, 237.
—— H. Krutter, and O. Morningstar, 'Vitreous SiO_2 and B_2O_3', *J. Amer. Ceramic Soc.*, 1936, **19**, 202.
—— ibid., 1941, **24**, 256.
—— *J. Applied Phys.*, 1942, **13**, 602.
W. H. Zachariasen, *J.A.C.S.*, 1932, **54**, 3841.

METHODS OF STRUCTURAL CHEMISTRY

X-ray Crystallography

J. M. Robertson, 'X-ray Analysis and Application of Fourier Series Methods to Molecular Structures', *Rep. Prog. Phys.*, 1937, **4**, 332.
Symposium: 'Application of X-rays to Industrial Problems', *J. Sci. Inst.*, 1941, **18**, 69, 126.

See also the sections on Crystallography in *Annual Rep. Prog. Chem.*

Electron Diffraction

L. O. BROCKWAY, *Rev. Mod. Physics*, 1936, **8**, 231 (references to 1935).
G. L. CLARK and E. WOLTHIUS, *J. Chem. Educ.*, 1938, **15**, 64.
L. E. SUTTON, *Rep. Prog. Chem.*, 1940, **37**, 36.

Spectroscopy

J. H. HIBBEN, 'Raman Spectra in Inorganic Chemistry', *Chem. Rev.*, 1933, **13**, 345.
—— and E. TELLER, *The Raman Effect and its Chemical Applications*, Chapman and Hall, 1939.
R. A. MORTON, 'Absorption Spectra', *Rep. Prog. Chem.*, 1941, **38**, 7.
G. B. B. M. SUTHERLAND, 'Infra-red and Raman Spectroscopy', ibid., 1938, **35**, 37.
H. W. THOMPSON, 'Molecular Spectra and Thermodynamics', ibid., 1941, **38**, 46.

Thermochemistry

F. D. ROSSINI, 'Modern Thermochemistry', *Chem. Rev.*, 1936, **18**, 233.

Dipole Moments

Symposium on the Dielectric Properties of Matter, *Chem. Rev.*, 1936, **19**, 163.
L. E. SUTTON, 'Electric Dipole Moments', *Rep. Prog. Chem.*, 1940, **37**, 47.
W. H. BESSEY and O. C. SIMPSON, 'Molecular Beams', *Chem. Rev.*, 1942, **30**, 239.
(These articles contain numerous references to the literature.)

Magnetic Measurements

K. N. MATHUR, *Magnetism in relation to Chemical Problems*, Allahabad Law Journal Press, 1940.
E. C. STONER, *Magnetism and Matter*, Methuen, 1934.
J. H. VAN VLECK, *Theory of Electric and Magnetic Susceptibilities*, O.U.P., 1932.

W. R. ANGUS, 'Diamagnetism', *Rep. Prog. Chem.*, 1941, **38**, 27.
K. LONSDALE, 'Diamagnetic and Paramagnetic Anisotropy of Crystals', *Rep. Prog. Physics*, 1937, **4**, 368.
—— 'Magnetism and the Structure of Matter', *Nature*, 1940, **145**, 57.

HYDROGEN (CHAPTER VII)

Acids and Bases

N. BJERRUM, 'Acids, Salts, and Bases', *Chem. Rev.*, 1935, **16**, 287.
N. F. HALL, 'Acid-base Properties of Complex Ions', ibid., 1936, **19**, 89.
W. F. LUDER, 'Electronic Theory of Acids and Bases', ibid., 1940, **27**, 547.

Hydrogen Bond

Symposium on the Hydrogen Bond: *Trans. Faraday Soc.*, 1940, **36**, 871.
J. D. BERNAL and H. D. MEGAW, 'The Function of Hydrogen in Intermolecular Forces', *Proc. Roy. Soc.*, 1935 A, **151**, 384.
E. N. LASSETTRE, 'The Hydrogen Bond and Association', *Chem. Rev.*, 1937, **20**, 259.
J. M. ROBERTSON and A. R. UBBELOHDE, 'Structure and Thermal Properties associated with some Hydrogen Bonds in Crystals', *Proc. Roy. Soc.*, 1939 A, **170**, 222.
W. H. RODEBUSH, 'The Hydrogen Bond and Coordination', *Chem. Rev.*, 1936, **19**, 59.
A. R. UBBELOHDE and I. WOODWARD, 'Isotope Effect in Crystals', *Proc. Roy. Soc.*, 1942 A, **179**, 399.

HALOGENS (CHAPTER VIII)

S. R. CARTER and W. WARDLAW, 'Fluorine and its Compounds', *Rep. Prog. Chem.*, 1936, **33**, 145.
H. TERREY, 'Recent Work on the Oxides of the Halogens', ibid., 1937, **34**, 136.

OXYGEN (CHAPTER XI)

H. B. WEISER and W. O. MILLIGAN, 'Constitution of Colloidal Systems of the Hydrous Oxides', *Chem. Rev.*, 1939, **25**, 1.
T. H. WHITEHEAD, 'The Colloidal Oxides', ibid., 1937, **21**, 113.

NITROGEN AND PHOSPHORUS (CHAPTER XII)

L. F. AUDRIETH, 'Hydrazoic Acid and its Inorganic Derivatives', *Chem. Rev.*, 1934, **15**, 169.
F. W. BERGSTROM and W. C. FERNELIUS, 'Chemistry of Alkali Amides', ibid., 1933, **12**, 43; 1937, **20**, 413.
H. TERREY, 'Metaphosphates and Polyphosphates of Sodium', *Rep. Prog. Chem.*, 1937, **34**, 115.

CARBON (CHAPTER XIII)

A. A. BLANCHARD, 'The Volatile Metallic Carbonyls', *Chem. Rev.*, 1937, **21**, 3.
—— 'Valency Relations among the Metallic Carbonyls', ibid., 1940, **26**, 409.
S. R. CARTER and W. WARDLAW, 'Metallic Carbides', *Rep. Prog. Chem.*, 1936, **33**, 153.
A. J. E. WELCH, 'Metallic Carbonyls and Nitrosyls', ibid., 1941, **38**, 71.

SILICON (CHAPTER XIV)

F. A. BANNISTER, 'Clay Minerals', *Rep. Prog. Chem.*, 1938, **35**, 187.
M. J. BUERGER, 'The Silica Framework Crystals and their Stability Fields', *Z. Krist.*, 1935, **90**, 186.
H. STRUNZ, 'Classification of the Silicates', ibid., 1937, **98**, 60, and see also *Rep. Prog. Chem.*, 1933, **30**, 387; 1937, **34**, 164.

BORON (CHAPTER XV)

Hydrides

S. H. BAUER, *Chem. Rev.*, 1942, **31**, 43.
H. J. EMELÉUS, *Rep. Prog. Chem.*, 1940, **37**, 138.
G. N. LEWIS, *J. Chem. Phys.*, 1933, **1**, 17.
H. C. LONGUET-HIGGINS and R. P. BELL, *J. Chem. Soc.*, 1943, 250.
R. S. MULLIKEN, *J. Chem. Phys.*, 1935, **3**, 635.
L. PAULING, *J.A.C.S.*, 1931, **53**, 3225.
H. I. SCHLESINGER and A. B. BURG, *Chem. Rev.*, 1942, **31**, 1.
A. STOCK, *The Hydrides of Boron and Silicon*, Cornell Univ. Press, 1933.
E. WIBERG, *Ber.*, 1936, **69**, 2816.

STEREOCHEMISTRY OF COORDINATION COMPOUNDS (CHAPTER XVI)

J. C. BAILAR, 'Coordinating Tendency of the Metallic Ions', *Chem. Rev.*, 1938, **23**, 65.
—— 'Stereochemistry of Complex Inorganic Compounds', ibid., 1936, **19**, 67.
F. H. BURSTALL, 'Coordination Compounds', *Rep. Prog. Chem.*, 1938, **35**, 160.
E. G. COX and W. WARDLAW, 'Coordination Compounds', *Science Progress*, 1938, **32**, 463.
H. DIEHL, 'The Chelate Compounds', *Chem. Rev.*, 1937, **21**, 39.
C. S. GIBSON, *Recent Investigations in the Chemistry of Gold*, Brit. Assoc. Report, 1938, 35.
F. G. MANN, 'Polynuclear Metallic Compounds', *Rep. Prog. Chem.*, 1938, **35**, 148.
D. P. MELLOR, 'Stereochemistry of Square Complexes', *Chem. Rev.*, 1943, **33**, 137.
W. WARDLAW, 'Coordination Compounds', *Rep. Prog. Chem.*, 1936, **33**, 157.

METALS AND ALLOYS (CHAPTER XVII)

A. E. VAN ARKEL, *Reine Metalle*, Berlin, 1939.
W. HUME-ROTHERY, *The Metallic State*, Clarendon Press, 1931.
—— *The Structure of Metals and Alloys*, Institute of Metals, 1936.
—— *Research Report of the British Non-ferrous Metals Research Association*, No. 562 (1941).
N. F. MOTT and H. JONES, *The Theory of the Properties of Metals and Alloys*, Clarendon Press, 1936.
A. H. WILSON, *The Theory of Metals*, Cambridge Univ. Press, 1936.

Symposium: Internal Strain in Metals, *Proc. Phys. Soc.*, 1940, **52**, 1.
A. J. BRADLEY, W. L. BRAGG, and C. SYKES, *J. Iron Steel Inst.*, 1940, **141**, 63.
G. HÄGG, 'Interstitial Compounds', *Z. physikal. Chem.*, 1931 B, **12**, 33.
W. HUME-ROTHERY and G. V. RAYNOR, 'Metallic Radii', *Proc. Roy. Soc.*, 1940 A, **177**, 27.
F. LAVES, 'Kristallographie der Legierungen', *Naturwiss.*, 1939, **27**, 65.
H. LIPSON, 'Metal Structures', *Rep. Prog. Chem.*, 1941, **38**, 95.

REFERENCES

1. F. A. Bannister and M. H. Hey, *Min. Mag.*, 1935, **24**, 49.
2. S. H. Bauer, *J.A.C.S.*, 1937, **59**, 1804.
3. —— ibid., 1938, **60**, 524.
4. —— ibid., 1938, **60**, 805.
5. —— and J. Y. Beach, ibid., 1940, **62**, 3440.
6. —— —— ibid., 1941, **63**, 1394.
7. —— —— and J. H. Simons, ibid., 1939, **61**, 19.
8. —— G. R. Finlay, and A. W. Laubengayer, ibid., 1943, **65**, 889.
9. —— and L. Pauling, ibid., 1936, **58**, 2403.
10. J. Beintema, *Rec. trav. chim.*, 1938, **57**, 155.
11. —— ibid., 1937, **56**, 931.
12. J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, 1933, **1**, 515.
13. H. Bommer, *Z. anorg. Chem.*, 1939, **242**, 277.
14. A. J. Bradley and J. W. Illingworth, *Proc. Roy. Soc.*, 1936 A, **157**, 113.
15. —— and S. S. Lu, *Z. Krist.*, 1937, **96**, 20.
16. A. Brager, *Acta Physicochim. U.R.S.S.*, 1939, **10**, 593.
17. H. Brasseur and L. Pauling, *J.A.C.S.*, 1938, **60**, 2886.
18. —— and A. de Rassenfosse, *Nature*, 1939, **143**, 332.
19. —— —— *Z. Krist.*, 1937, **97**, 239.
20. —— —— *Bull. Soc. roy. Sciences*, 1937, 371.
21. —— —— ibid., 1939, 24.
22. —— —— *Bull. Soc. Franc. Min.*, 1938, **61**, 5.
23. —— and J. Toussaint, *Bull. Soc. roy. Sci. Liége*, 1938, 213.
24. H. Braune and P. Pinnow, *Z. physikal. Chem.*, 1937 B, **35**, 239.
25. L. O. Brockway, *J. Phys. Chem.*, 1937, **41**, 747.
26. —— *J.A.C.S.*, 1938, **60**, 1348.
27. —— and J. S Anderson, *Trans. Faraday Soc.*, 1937, **33**, 1233.
28. —— and J. Y. Beach, *J.A.C.S.*, 1938, **60**, 1836.
29. —— and W. M. Bright, ibid., 1943, **65**, 1551.
30. —— and I. E. Coop, *Trans. Faraday Soc.*, 1938, **34**, 1429.
31. —— R. V. G. Ewens, and M. W. Lister, ibid., 1938, **34**, 1350.
32. —— and H. O. Jenkins, *J.A.C.S.*, 1936, **58**, 2036.
33. —— and F. T. Wall, ibid., 1934, **56**, 2373.
34. C. Brosset, *Z. anorg. Chem.*, 1937, **235**, 139.
35. —— ibid., 1938, **238**, 201.
36. —— ibid., 1938, **239**, 301.
37. C. J. Brown and E. G. Cox, *J. Chem. Soc.*, 1940, 1.
38. M. J. Buerger, *Z. Krist.*, 1937, **97**, 504.
39. —— and S. B. Hendricks, *J. Chem. Phys.*, 1937, **5**, 600.
40. —— —— *Z. Krist.*, 1937, **98**, 1.
41. A. Burawoy, C. S. Gibson, G. C. Hampson, and H. M. Powell, *J. Chem. Soc.*, 1937, 1690.
42. V. Cagliotti and G. Giacomello, *Naturwiss.*, 1938, **26**, 317.
43. D. C. Carpenter and L. O. Brockway, *J.A.C.S.*, 1936, **58**, 1270.
44. N. Chatterjee, *Z. Krist.*, 1940, **102**, 245.
45. D. Clark, H. M. Powell, and A. F. Wells, *J. Chem. Soc.*, 1942, 642.
46. R. B. Corey, *J.A.C.S.*, 1938, **60**, 1598.
47. E. G. Cox, F. J. Llewellyn, and T. H. Goodwin, *J. Chem. Soc.*, 1937, 882.
48. —— and K. C. Webster, ibid., 1936, 1635.
49. B. L. Crawford and P. C. Cross, *J. Chem. Phys.*, 1937, **5**, 371.

50. P. C. Cross and L. O. Brockway, ibid., 1935, **3**, 821.
51. H. C. J. de Decker, *Rec. trav. chim.*, 1941, **60**, 413.
52. —— and C. H. MacGillavry, ibid., 1941, **60**, 153.
53. K. Dihlström, *Z. anorg. Chem.*, 1938, **239**, 57.
54. —— and A. Westgren, ibid., 1937, **235**, 153.
55. O. S. Edwards and H. Lipson, *Proc. Roy. Soc.*, 1942 A, **180**, 268.
56. N. Elliott, *J.A.C.S.*, 1937, **59**, 1380.
57. —— and L. Pauling, ibid., 1938, **60**, 1846.
58. R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J. Chem. Soc.*, 1940, 1209.
59. R. V. G. Ewens and W. M. Lister, *Trans. Faraday Soc.*, 1938, **34**, 1358.
60. —— —— ibid., 1939, **35**, 681.
61. F. J. Ewing, *J. Chem. Phys.*, 1935, **3**, 203.
62. —— ibid., 1935, **3**, 420.
63. T. F. Gaskell, *Z. Krist.*, 1937, **96**, 203.
64. W. F. Giauque and J. D. Kemp, *J. Chem. Phys.*, 1938, **6**, 40.
65. —— and C. C. Stephenson, *J.A.C.S.*, 1938, **60**, 1389.
66. P. A. Giguère and V. Schomaker, ibid., 1943, **65**, 2025.
67. N. S. Gingrich, *Phys. Rev.*, 1939, **55**, 236.
68. —— *J. Chem. Phys.*, 1940, **8**, 29.
69. A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, *Trans. Faraday Soc.*, 1937, **33**, 852.
70. P. Günther, K. Holm, and H. Strunz, *Z. physikal. Chem.*, 1939 B, **43**, 229.
71. J. E. Hamilton, *Z. Krist.*, 1938, **100**, 104.
72. G. C. Hampson and L. Pauling, *J.A.C.S.*, 1938, **60**, 2702.
73. —— and A. J. Stosick, ibid., 1938, **60**, 1814.
74. D. Harker, *Z. Krist.*, 1936, **93**, 136.
75. H. Harmsen, ibid., 1939, **100**, 208.
76. O. Hassel and A. Sandbo, *Z. physikal. Chem.*, 1938 B, **41**, 75.
77. —— and L. C. Strömme, ibid., 1938 B, **38**, 466.
78. E. A. Hazlewood, *Z. Krist.*, 1938, **98**, 439.
79. L. Helmholtz, *J.A.C.S.*, 1937, **59**, 2036.
80. —— ibid., 1939, **61**, 1544.
81. —— and M. T. Rogers, ibid., 1939, **61**, 2590.
82. —— —— ibid., 1940, **62**, 1537.
83. A. Helms and W. Klemm, *Z. anorg. Chem.*, 1939, **241**, 97.
84. H. Heritsch, *Z. Krist.*, 1938, **99**, 466.
85. W. L. Hill, G. T. Faust, and S. B. Hendricks, *J.A.C.S.*, 1943, **65**, 794.
86. J. L. Hoard, ibid., 1939, **61**, 1252.
87. —— and W. J. Martin, ibid., 1941, **63**, 11.
88. —— and H. H. Nordsieck, ibid., 1939, **61**, 2853.
89. —— and M. B. Williams, ibid., 1942, **64**, 633.
90. W. Hofmann, *Z. Krist.*, 1935, **92**, 161.
91. E. W. Hughes, *J.A.C.S.*, 1940, **62**, 1258.
92. —— ibid., 1941, **63**, 1737.
93. R. Hultgren and B. E. Warren, *Phys. Rev.*, 1935, **47**, 808.
94. T. Ito and H. Sawada, *Z. Krist.*, 1939, **102**, 13.
95. C. W. Jacob and B. E. Warren, *J.A.C.S.*, 1937, **59**, 2588.
96. R. Juza and H. Hahn, *Z. anorg. Chem.*, 1938, **239**, 282.
97. —— —— *Naturwiss.*, 1939, **27**, 32.
98. J. Karle and L. O. Brockway, *J.A.C.S.*, 1944, **66**, 574.
99. W. Kassatochkin and W. Kotov, *J. Chem. Phys.*, 1936, **4**, 458.
100. J. F. Keggin, *Proc. Roy. Soc.*, 1934 A, **144**, 75.
101. —— and F. D. Miles, *Nature*, 1936, **137**, 577.
102. J. A. A. Ketelaar and K. T. Palmer, *J.A.C.S.*, 1937, **59**, 2629.

103. J. A. A. Ketelaar and T. A. de Vries, *Rec. trav. chim.*, 1939, **58**, 1081.
104. —— and E. Wegerif, ibid., 1938, **57**, 1269, and 1939, **58**, 948.
105. W. Klemm and H. Sodomann, *Z. anorg. Chem.*, 1935, **225**, 273.
106. L. J. Klinkenberg, *Rec. trav. chim.*, 1937, **56**, 749.
107. I. E. Knaggs, *Proc. Roy. Soc.*, 1935 A, **150**, 576.
108. M. L. Kronberg and D. Harker, *J. Chem. Phys.*, 1942, **10**, 309.
109. J. J. de Lange, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc.*, 1939 A, **171**, 398.
110. H. A. Levy and L. O. Brockway, *J.A.C.S.*, 1937, **59**, 2085.
111. G. N. Lewis, ibid., 1924, **46**, 2027.
112. H. Lipson and N. J. Petch, *J. Iron Steel Inst.*, 1940, **142**, 95.
113. —— and A. R. Stokes, *Nature*, 1942, **149**, 328.
114. J. V. Lirmann and H. S. Schdanov, *Acta Physicochim. U.R.S.S.*, 1937, **5**, 306.
115. M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, 1941, **37**, 406.
116. C. S. Lu, E. W. Hughes, and P. A. Giguère, *J.A.C.S.*, 1941, **63**, 1507.
117. D. Lundqvist and A. Westgren, *Z. anorg. Chem.*, 1938, **239**, 85.
118. C. H. MacGillavry and J. M. Bijvoet, *Z. Krist.*, 1936, **94**, 231, 249.
119. —— H. Nijveld, S. Dierdorp, and J. Karsten, *Rec. trav. chim.*, 1939, **58**, 193.
120. —— J. H. De Wilde, and J. M. Bijvoet, *Z. Krist.*, 1938, **100**, 212.
121. F. Machatschki, *Fortschr. Min.*, 1936, **20**, 45.
122. F. G. Mann, A. F. Wells, and D. Purdie, *J. Chem. Soc.*, 1937, 1828.
123. L. R. Maxwell, S. B. Hendricks, and L. S. Deming, *J. Chem. Phys.*, 1937, **5**, 626.
124. —— —— and V. M. Moseley, *Phys. Rev.*, 1937, **52**, 968.
125. —— —— —— *J. Chem. Phys.*, 1935, **3**, 699.
126. —— —— —— *Phys. Rev.*, 1936, **49**, 199.
127. —— and V. M. Moseley, *J. Chem. Phys.*, 1940, **8**, 738.
128. —— —— and S. B. Hendricks, *J. Chem. Phys.*, 1935, **3**, 698.
129. —— —— and L. S. Deming, ibid., 1934, **2**, 331.
130. J. D. McCullough, *J.A.C.S.*, 1937, **59**, 789.
131. —— and G. Hamberger, ibid., 1941, **63**, 803.
132. —— —— ibid., 1942, **64**, 508.
133. R. L. McFarlan, *J. Chem. Phys.*, 1936, **4**, 60.
134. —— ibid., 1936, **4**, 253.
135. K. Meisel, *Naturwiss.*, 1939, **27**, 230.
136. R. C. L. Mooney, *Z. Krist.*, 1938, **98**, 324.
137. —— ibid., 1938, **98**, 377.
138. —— *Z. Krist.*, 1939, **100**, 519.
139. W. J. Moore and L. Pauling, *J.A.C.S.*, 1941, **63**, 1392.
140. J. Morgan and B. E. Warren, *J. Chem. Phys.*, 1938, **6**, 666.
141. St. v. Náray-Szabó, and K. Sasvari, *Z. Krist.*, 1938, **99**, 27.
142. E. W. Neuman, *J. Chem. Phys.*, 1934, **2**, 31.
143. W. Nieuwenkamp, *Z. Krist.*, 1937, **96**, 454.
144. W. Nowacki, ibid., 1938, **100**, 242.
145. K. J. Palmer, *J.A.C.S.*, 1938, **60**, 2360.
146. —— and N. Elliott, ibid., 1938, **60**, 1852.
147. —— —— ibid., 1938, **60**, 1309.
148. L. Pauling, ibid., 1935, **57**, 2680.
149. —— and L. O. Brockway, *Proc. Nat. Acad. Sci.*, 1934, **20**, 340.
150. —— —— *J.A.C.S.*, 1935, **57**, 2684.
151. —— —— ibid., 1937, **59**, 13.
152. —— and D. C. Carpenter, ibid., 1936, **58**, 1274.
153. —— and J. Sherman, *Z. Krist.*, 1937, **96**, 481.
154. W. G. Penney and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, 1934, **30**, 898.

155. W. G. PENNEY and G. B. B. M. SUTHERLAND, *J. Chem. Phys.*, 1934, **2**, 492.
156. R. PEPINSKY, *Z. Krist.*, 1939, **102**, 119.
157. H. M. POWELL and F. M. BREWER, *J. Chem. Soc.*, 1938, 197.
158. —— and D. CLARK, *Nature*, 1940, **145**, 971.
159. —— and R. V. G. EWENS, *J. Chem. Soc.*, 1939, 286.
160. —— and H. S. TASKER, ibid., 1937, 119.
161. R. E. POWELL and H. EYRING, *J.A.C.S.*, 1943, **65**, 648.
162. J. M. ROBERTSON, *Proc. Roy. Soc.*, 1936 A, **157**, 79.
163. —— and A. R. UBBELOHDE, ibid., 1938 A, **167**, 122.
164. —— and I. WOODWARD, *J. Chem. Soc.*, 1937, 219.
165. —— —— ibid., 1940, 36.
166. M. T. ROGERS and L. HELMHOLTZ, *J.A.C.S.*, 1940, **62**, 1533.
167. —— —— ibid., 1941, **63**, 278.
168. —— V. SCHOMAKER, and D. P. STEVENSON, ibid., 1941, **63**, 2610.
169. M. ROUAULT, *Comptes Rendus*, 1938, **207**, 620.
170. W. H. C. RUEGGEBERG, *J.A.C.S.*, 1943, **65**, 602.
171. J. A. SANTOS, *Proc. Roy. Soc.*, 1935 A, **150**, 309.
172. V. SCHOMAKER and R. SPURR, *J.A.C.S.*, 1942, **64**, 1184.
173. —— and D. P. STEVENSON, ibid., 1940, **62**, 1270.
174. N. SCHREWELIUS, *Z. anorg. Chem.*, 1938, **238**, 241.
175. F. SENTI and D. HARKER, *J.A.C.S.*, 1940, **62**, 2008.
176. W. SHAND and R. A. SPURR, ibid., 1943, **65**, 179.
177. P. C. SHARRAH and N. S. GINGRICH, *J. Chem. Phys.*, 1942, **10**, 504.
178. L. G. SILLÉN, *Arkiv för Kemi, Min. och Geol.*, 1937, 12 A, No. 18.
179. H. D. SPRINGALL and L. O. BROCKWAY, *J.A.C.S.*, 1938, **60**, 996.
180. SSU-MIEN FANG, *Z. Krist.*, 1938, **99**, 1.
181. D. P. STEVENSON and J. Y. BEACH, *J.A.C.S.*, 1938, **60**, 2872.
182. —— and H. RUSSELL, ibid., 1939, **61**, 3264.
183. —— and V. SCHOMAKER, ibid., 1940, **62**, 1913.
184. —— —— ibid., 1940, **62**, 1267.
185. G. B. B. M. SUTHERLAND and W. G. PENNEY, *Nature*, 1935, **136**, 146.
186. W. TEICHERT and W. KLEMM, *Z. anorg. Chem.*, 1939, **243**, 138.
187. S. TENGNÉR, ibid., 1938, **239**, 126.
188. W. THEILACKER, *Z. Krist.*, 1935, **90**, 51.
189. —— ibid., 1935, **90**, 256.
190. C. D. THOMAS and N. S. GINGRICH, *J. Chem. Phys.*, 1938, **6**, 659.
191. H. J. VERWEEL and J. M. BIJVOET, *Z. Krist.*, 1931, **77**, 122.
192. —— —— ibid., 1938, **100**, 201.
193. B. E. WARREN and J. T. BURWELL, *J. Chem. Phys.*, 1935, **3**, 6.
194. H. B. WEISER, W. O. MILLIGAN, and J. B. BATES, *J. Phys. Chem.*, 1942, **46**, 99.
195. A. F. WELLS, *Z. Krist.*, 1937, **96**, 435.
196. —— *Proc. Roy. Soc.*, 1938 A, **167**, 169.
197. —— *Z. Krist.*, 1938, **99**, 367.
198. —— ibid., 1938, **100**, 189.
199. C. D. WEST, *Z. Krist.*, 1935, **91**, 480.
200. —— ibid., 1937, **96**, 459.
201. G. W. WHELAND, *Trans. Faraday Soc.*, 1937, **33**, 1499.
202. E. H. WIEBENGA and N. F. MOERMAN, *Z. Krist.*, 1938, **99**, 217.
203. M. B. WILLIAMS and J. L. HOARD, *J.A.C.S.*, 1942, **64**, 1139.
204. A. J. WILSON, *Proc. Roy. Soc.*, 1942 A, **180**, 277.
205. W. A. WOOSTER, *Z. Krist.*, 1936, **94**, 375.
206. O. R. WULF, *Proc. Nat. Acad. Sci.*, 1938, **14**, 609.
207. W. H. ZACHARIASEN, *J. Chem. Phys.*, 1937, **5**, 919.
208. —— *Z. Krist.*, 1937, **98**, 266.
209. —— *J.A.C.S.*, 1940, **62**, 1011.

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