Liversidge Research Lecture

No. 4b
1942

THE IMPERFECT CRYSTAL

J. S. ANDERSON

The Royal Society of New South Wales

John Stuart Anderson

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JOHN STUART ANDERSON 1908-1990

John Stuart Anderson was born on 9 January 1908 at Islington, London (U.K.). At the age of 11 he obtained an L.C.C. Junior Country Scholarship to attend the boy's school section of the Northern Polytechnic (Highbury County School) from 1919 to 1924. He passed the Schools Certificate examination with Distinction or Credits in every subject, and was awarded an Intermediate County Scholarship to enroll for the B.Sc. course at Northern Polytechnic for the period 1924-1926. Then, with a Royal Scholarship (he was top of the list) he entered the Royal College of Science (Imperial College) where, in his second year (1928) he was top of the class, and was awarded the Frank Hutton Prize in Advanced Chemistry. For his third year, involving research, he worked under the supervision of Professor H.B. Baker, and graduated B.Sc. (1st. class Hons.) in 1929. In continuation of research at Imperial College, he worked on nickel carbonyls, and graduated Ph.D in 1931. Then, with a University of London Travelling Scholarship, he went to Heidelberg (Germany) to work for a year with Hieber on iron carbonyls. In 1932 Anderson returned to Imperial College as a Demonstrator, and began research on the X-ray crystallography of organic compounds, and on hydrogen isotope studies of hydrogen exchange in metal ammines. In 1936 he and Emeleus collaborated in the writing of 'Modern Aspects of Inorganic Chemistry', a seminal textbook published in 1938.

In 1938 Anderson obtained a Senior Lectureship at the University of Melbourne, replacing Noel Bayliss (later Sir Noel, FAA) who had accepted the Chair of Chemistry at The University of Western Australia. He turned his attention to searching for a natural source of technecium, an element that had been made artificially in 1937, and also on chemical methods for the separation of zirconium and hafnium. Partly as a result of constraints imposed by the Second World War (1939-1945) the research interests of John Anderson (often referred to as 'JS') moved more to solid-state chemistry, the subject of his Liversidge Lecture in 1942.

In 1946 he was invited to join the newly set up Chemistry Division at the Atomic Research Establishment at Harwell, and in 1947 he moved to Harwell to exercise general oversight of broad-ranging research in inorganic chemistry, and to run, directly, a small and quite uncommitted research group. He continued work on the solid state and non-stoichiometry, including work on oxides and hydrides of uranium. With state-of-the-art X-ray diffraction instruments at Harwell he was able to make important progress in studies of the solid state.

When Professor Hartung retired at the end of 1953, 'JS' was appointed to replace him, and took up the position of Professor and Head of the Chemistry School, University of Melbourne, in 1954. In 1959 he moved back to the U.K. to become Director of the National Chemical Laboratory, and in 1963 he accepted the invitation to take up the Chair of Inorganic Chemistry at Oxford University. He held this position until he retired in 1975. He remained actively interested in chemistry. During 1974-6 he was President of the Dalton division of the Chemical Society, London, and for the period 1975-1982 he was at the University College of Wales, Aberystwyth working in collaboration with J.M. Thomas (now Sir John, FRS); then he came back to Australia as a Visiting Fellow at the Research School of Chemistry, Australian National University. He remained there until 1989 when illness overtook him, and he died on Christmas Day 1990.

Honours and Awards

1942	Liversidge Research Lecture, Royal Society of New South Wales
1944	H.G. Smith Medal, Royal Australian Chemical Institute
1945	Syme Research Prize, University of Melbourne
1953	Tilden Lecture, Chemical Society (London)
1953	FRS
1954	FAA (a Foundation Fellow of the Australian Academy of Science)
1958	Masson Lecture, Australian New Zealand Association for the Advancement of Science (ANZAAS)
1963	Liversidge Lecture, Chemical Society (London)
1964	Fellow of the Imperial College
1966	Matthew Flinders Lecture, Australian Academy of Science
1973	Davy Medal, Royal Society of London
1975	Award for Solid State Chemistry, Chemical Society (London)
1975	Longstaff Medal, Chemical Society (London)
1978	Honorary Fellow, Indian Academy of Science
1979	Hon. D.Sc., University of Bath (U.K.)
1980	Hugo Muller Medal / Lecture, Chemical Society (London)
1984	Liversidge Research Lecture, ANZAAS

Biographical Sources

1.   Hyde, B.G. and Day, P., 'John Stuart Anderson 1908-1990', *Historical Records of Australian Science,* 1992, **9**, 127-149.

2.   Hyde, B.G. and Day, P., 'John Stuart Anderson, 9 January 1908 - 25 December 1990, elected F.R.S. 1953', *Biographical Memoirs of Fellows of the Royal Society*, 1992, **38**, 3-26.

3.   Hyde, B.G., 'John Stuart Anderson 1908-1990', *Chemistry in Australia,* 1991, **58**, 406-407.

Scientific Publications of J.S. Anderson

John Stuart Anderson was the author / co-author of 160 papers and 10 monographs. These are listed as an appendix to the biographical article (1) listed above.

THE IMPERFECT CRYSTAL*

J. S. ANDERSON
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In the formulation of our basic chemical theory, the study of gases and their generalised laws played, as every chemist and physicist recognises, a most significant part. During recent years we have acquired an entirely new insight into the constitution of the solid state of matter, which may well have a comparable effect in moulding our chemical outlook. This is especially true in the domain of inorganic chemistry, and the work of the Braggs and other pioneers in the field of crystal structure must be ranked, with Werner's theory, amongst the most important accessions to general chemical theory.

In any discussion of gases and their properties, we customarily draw a distinction between *ideal* gases and *real* or *imperfect* gases, recognising that the former, which obey the generalised gas laws and conform rigorously to Avogadro's hypothesis, are pure mental abstractions. For most purposes, of course, the conception of the ideal gas is sufficiently close in behaviour to the real gases with which we have to do experimentally. Nevertheless, the thermodynamic properties of real gases differ in certain directions from those of the hypothetical ideal gas, and the imperfections of real gases are responsible for some of their most important properties.

In the same way, our conventional concept of a crystal lattice is equally idealised, and represents also a pure mental abstraction. It is that of a crystal lattice in which every atom is situated on the appropriate lattice position, and every lattice position is occupied by the appropriate atom. It represents a compound of ideally stoichiometric formula, in true thermodynamic equilibrium at 0° K. As such it is, without doubt, quite unattainable in Nature. At any temperature above the absolute zero, all crystals must deviate to some degree from this "perfect" state; *lattice defects* (German "Fehlordnungserscheinungen") appear, and may be considered under two headings:

(*a*) Those that are inherent in the thermodynamics of the solid state, and

(*b*) Those that are intrimsic to the particular crystalline compound under discussion.

As in the case of the imperfect gas, so these lattice imperfections underlie some of the most interesting physical and chemical properties of crystalline solids.

As is well known, we may broadly classify crystal lattices, according to the units of which they are composed and the forces binding them together, under the headings of metallic, homopolar-atomic, ionic and molecular crystals. In the first mentioned, the lattice points are occupied either by identical atoms (as in elementary metals) or by atoms that are electronically similar and usually interchangeable in function. These we shall not discuss, though order-disorder phenomena in alloys are not entirely unrelated to the subject of our

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consideration. Nor shall we deal with molecular crystals, although Ubbelohde and Oldham (1940) have described interesting investigations on the influence of known concentrations of lattice defects on the cohesive properties of molecular crystals. The remaining two lattice types represent limiting cases, towards one or other of which binary compounds tend in greater or lesser degree. The typical "homopolar "or "adamantine" compounds are to some extent heteropolar, being built up from elements of different electron affinity, while, as has been emphasised by Pauling (1939), there is a perceptible contribution of homopolar binding forces to the cohesion of the lattice even in compounds like the alkali halides. Between typical salts and homopolar compounds there is therefore a transition, rather than a sharp demarcation of lattice type.

We shall confine consideration, therefore, to heteropolar binary compounds, and treat the lattice imperfections displayed by them under the two heads already indicated. Firstly, then, we will consider lattice defects involving lattice disorder only, without infringement of the laws of stoichiometry, and secondly we will discuss those which give rise to crystalline phases of variable, non-stoichiometric composition.

Lattice Defects in Thermal equilibrium

If, in a stoichiometric crystal, any lattice site is left unoccupied, or if an atom be moved from its proper site to an interstitial position, a lattice defect is produced. Defects of the former kind - vacant lattice points (Fig. 1*b*) - are usually referred to as *Schottky* defects; they necessarily originate in pairs (i.e., in equal numbers in cation and anion lattices respectively) in order to maintain the stoichiometric balance between anions and cations in the crystal as a whole. The other type, consisting of an interstitial atom together with the lattice site from which it came (Fig. 1*c*) is known as the *Frenkel* defect type. Its occurrence may be (and usually is) effectively limited to either cations or anions in the lattice.
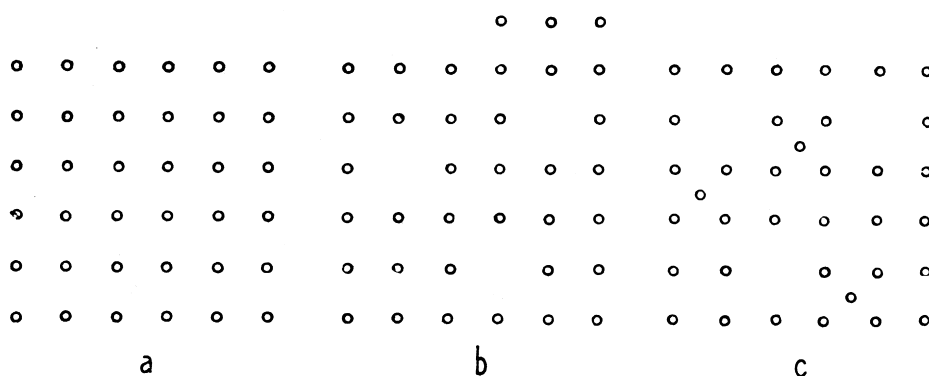

FIGURE 1. - A simple point lattice (*a*), showing the development of Schottky defects (*b*), or Frenkel defects (*c*).

When such defects arise, the free energy of the crystal lattice is increased. The increase may be regarded as representing work done in removing an atom from an interior lattice site and placing it either at the surface of the crystal, to make a Schottky defect, or in an interstitial position within the lattice. Either process may arise from the thermal agitation of the atoms, but will necessarily affect only those atoms possessing not less than some critical energy. If the energy required to create a Schottky or a Frenkel defect be W_S, W_F respectively, the equilibrium concentration of lattice defects at any temperature T may be calculated quite simply, to a first approximation, by the methods of statistical mechanics.

If in a crystal of N lattice points, with N' interstitial positions, there are n lattice defects, then, to a first approximation,

$$n = (N - n)e^{-W_S/kT} \text{ for Schottky defects}$$

$$n = \sqrt{(N.N')}\,e^{-W_F/2kT} \text{ for Frenkel defects}$$

Both types of lattice imperfection are possible, and it is of interest to examine their relative importance in real crystals.   It will be observed at once that the existence of lattice holes is common to both; they differ, and consequently the relative magnitudes of W_S, W_F will also differ, with respect to the disposal of the atoms displaced in creating the hole.

Frenkel defects, from their nature, are likely to be important in crystals where the lattice structure is open enough to accommodate an atom in an interstitial position without much distortion.   This is obviously possible in the zinc blende and wurtzite structures, for example, which are common to ZnO, ZnS, AgCl, AgBr, etc.   Structures of closer packing and higher coordination number have little room for interstitial atoms.   Further, where there is considerable disparity of size between anion and cation, it will clearly be easier to displace the smaller ion (usually the cation) to an inter-lattice position; reference has already been made to the fact that Frenkel defects need affect only one of the lattice components.   This is not necessarily the cation; in the fluorite and related structures (e.g., CaF_2, CeO_2; also $PbCl_2$ structure) only the anion lattice, being of smaller coordination number, is markedly subject to Frenkel defects.

It follows that Schottky defects are intrinsically probable for cases not covered by the foregoing considerations, e.g. for the alkali halides and other compounds with the sodium chloride structure.   As mentioned before, there will then be equal numbers of holes in both cation and anion lattices.

The lattice defects must be distributed statistically throughout the lattice, and so do not influence the symmetry of the crystal.   They may, however, influence the lattice parameter, since they affect the lattice energy; they may also make a perceptible contribution to such properties as the thermal expansion and the compressibility.   Their greatest and most important effect, however, is upon the kinetic phenomena which may occur within the lattice, and which we will next consider.

Diffusion and Electrical Conduction within Crystals

There are three obvious mechanisms whereby diffusion may take place in solids:

(a) Atoms or ions that are small in comparison with the interstices of the lattice may undergo the relatively free zeolitic diffusion.   Apart from openwork lattices of the true zeolite type, capable of permeation by ions of fairly large radius, zeolitic diffusion applies also to the migration of small atoms (H, N, C, B) in metals with which they combine to form interstitial compounds.   The diffusion of hydrogen in palladium, or of nitrogen in iron, is of this type.

(b) One can conceive of the cooperative synchronisation of thermal vibrations in a small zone of the crystal lattice, whereby an interchange of positions is made possible for a pair of adjacent ions in the centre of the zone.   This mechanism has been

discussed by Barrer (1941). It is not easy to assess the probability of such cooperative phenomena, but diffusion of this kind will clearly be relatively more important in the liquid state than in solids.

(c) Probably the most important mechanism in heteropolar crystals is by the migration of Schottky and Frenkel defects. An atom may move from an adjacent lattice site to a lattice hole or an interstitial atom may move from one inter-lattice position to the next (Fig. 2). In either case, the position of the lattice defect moves through the crystal, being associated with the movement of the atoms within the lattice.
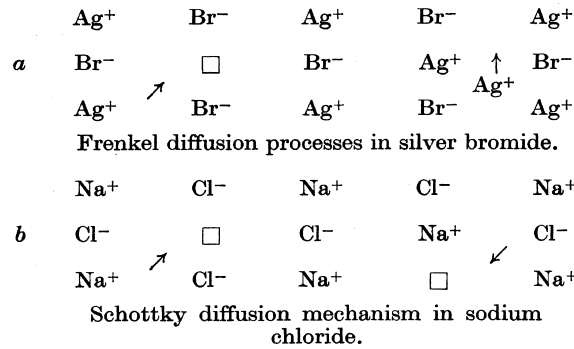
FIGURE 2. - Diffusion of lattice defects.

The movement of an atom from an occupied lattice site to a neighbouring vacant site must involve the surmounting of a certain potential barrier. It is the height of this potential barrier that determines the activation energy for the diffusion process. Graphically, the energy changes during the process may be represented by Fig. 3, where the energy of the atom is represented as a function of its displacement from its equilibrium position in the lattice. Figure 3a represents the activation energy for the migration of a Schottky hole; Figs. 3b and 3c indicate respectively the movement of an atom between lattice site and interstitial position (creation or destruction of Frenkel hole) and the migration of an interstitial atom. It is generally considered that the activation energies for these two alternative Frenkel diffusion processes are likely to be about the same.
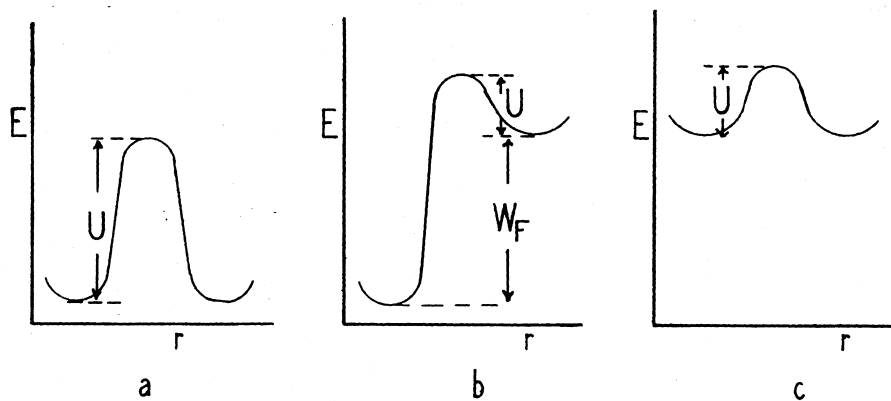
FIGURE 3-Activation energies for diffusion of lattice defects.
(*a*) Diffusion of Schottky defect.
(*b*) Creation or destruction of Frenkel defect.
(*c*) Migration of atom between interstitial positions.

The probability that a given lattice defect will be associated with the energy necessary to surmount the potential barrier U is, of course, proportional to

$e^{-U/kT}$; the mobility is given as a function of temperature by

$$v = v_\mathrm{o}e^{-U/kT}$$

Since the concentration of lattice defects is also an exponential function of the temperature, we have for the actual rate of diffusion

$$r = Ae^{-(E+U)/kT}$$

where A is a factor varying but little with temperature, and E is the energy for the production of a lattice defect (= W_S or 1/2 W_F as defined earlier). From the temperature coefficient of diffusion, the sum $(E + U)$ can be determined.

It is worth noting that in the Schottky mechanism it is, in effect, the hole that moves through the lattice, transporting with it a virtual charge of opposite sign to that of the ion properly occupying the lattice site in question. In sodium chloride, for instance, only the cations are mobile, except near the melting point. Diffusion takes place by the Schottky process (Figs. 2b, 3a), each mobile cation hole transporting a virtual negative charge.

Electrolytic Conduction in Crystals

We have just seen how the existence of lattice defects connotes a certain possibility that they shall be mobile, in virtue of the thermal motion of ions within the crystal lattice. In the absence of any electrical field, the thermal movement of the ions is quite undirected, so that the position of the lattice defects will fluctuate at random. In an electric field, however, the movement of the ions in one or other field direction is favoured, depending on the sign of the mobile ions, so that the lattice defects will migrate along the electric field. By the movement of each defect an electric charge is carried through the lattice, so that the diffusion mechanism provides also a means for the transport of current through heteropolar crystals by an ionic mechanism.
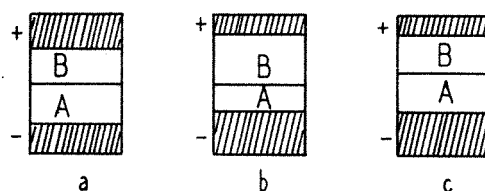

FIGURE 4. Transference experiment with solid electrolyte. (*a*) Initial state. (*b*) Final state, only anions mobile. (*c*) Final state, only cations mobile.

Although very poor conductors at the ordinary temperature, most salts show a marked increase of conductivity at elevated temperatures as is implicit in the expression given for the dependence of diffusion upon temperature. It can be shown that the conduction of solid salts is electrolytic, and the relative mobilities of cations and anions can be determined, by the type of experiment represented diagrammatically in Fig. 4. Here (*a*) represents the initial state of the system, with two pellets of the salt (silver iodide, for example) clamped between electrodes of the appropriate metal (silver, in the instance cited). When a current is passed, the ions migrate through the pellets and are discharged at the electrodes. If the anions alone are mobile, the state after some time has elapsed will be represented by (*b*). Anions pass from pellet I to pellet II; at the cathode silver ions are discharged, at the anode silver is attacked. Hence pellet II increases in weight and pellet I decreases. If, as in (*c*), the cations alone are mobile, they pass right through the pellets from anode to cathode, and only the electrodes change in weight. In either case a complete balance sheet for the transference process may readily be constructed, whence, for salts in

which both ions contribute to the conductivity ("bipolar conduction") the transport number of each ion can be determined, the final state being then intermediate between (*b*) and (*c*).

Measurements involving this kind of technique have been made for many binary salts, especially by Tubandt and his co-workers (Tubandt, 1927, 1931, 1932, 1933; also Jost, 1937; Mott and Gurney, 1940; Seitz, 1940).   The mechanism of conduction in salts has thereby been largely clarified. In the sodium and potassium halides just below the melting point, both ions are mobile.   This, however, is exceptional.   Only the cations are mobile in sodium chloride at lower temperatures, as also in the halides, sulphides, selenides and tellurides of copper and silver.   The halides of barium and lead are pure anion conductors, due - as indicated previously - to the mobility of Frenkel defects in the anion lattices of these salts.

The Concentration of Lattice Defects in Thermal Equilibrium

We have seen that kinetic processes - diffusion or electrical conduction - involve both the concentration of lattice defects and their mobility.   Thus, if x be the concentration, and v the mobility of a Frenkel defect, in a lattice with N lattice points per unit volume, the electrical conductivity is given by

$$\sigma = Nevx$$

or, substituting for v and x the values cited earlier,

$$\sigma = Nev_\mathrm{o}x_\mathrm{o}e^{-(U+1/2W_\mathrm{F})/kT}$$

The temperature coefficient of conductivity, therefore, like that of diffusion, affords a measure of $(U+1/2W_\mathrm{F})$; conductivity measurements are, in practice, the more convenient experimentally.   Neither conductivity measurements nor diffusion measurements provide a means of measuring the actual concentration of lattice defects, however, without supplementary data to separate the two factors that contribute to the overall rate of the kinetic process.

Koch and Wagner (1937) have, by an ingenious device, overcome this difficulty by varying the concentration of lattice defects independently of their mobility, i.e. by varying the concentration of lattice defects at constant temperature.   Silver chloride and bromide form mixed crystals with up to one per cent. of the corresponding cadmium and lead halides.   In these, to preserve the stoichiometric balance between anions and cations, each Cd^{++} or Pb^{++} ion must replace two Ag^+ ions, with the result that one cation site is left vacant for each Cd^{++} or Pb^{++} ion introduced.   The concentration of permanent holes thus created is equal to the concentration of bivalent ions.   At constant temperature, the conductivity is proportional to the total concentration of lattice defects, and since the addition of 1% of $CdCl_2$ to AgCl was found to increase the conductivity more than 100-fold, it is clear that the number of holes created artificially far outweighed the number present in thermal equilibrium.   In such a mixed crystal, therefore, the temperature coefficient of conductivity must have measured only the increase in mobility of the lattice defects, without sensible increase in their concentration. The height of the potential barrier U was thus found directly, and by comparison with measurements on the pure silver halides, the concentration of interstitial silver ions in thermal equilibrium in pure AgCl and AgBr can be calculated. By this means, the following data were obtained.

		AgCl.	AgBr.
Concentration of lattice defects	..	$x = 36e^{-\frac{25000}{2kT}}$	$29e^{-\frac{20000}{2kT}}$
Mobility of lattice defects	.. ..	$v = 0 \cdot 12e^{-\frac{6000}{kT}}$	$0 \cdot 95e^{-\frac{8200}{kT}}$
Activation energy U, for diffusion	..	6,000 cals.	8,200 cals.

From these figures, the concentrations of thermal defects at a few temperatures are as follows:

AgCl	300°C	5.5×10^{-4}
	210°	8.1×10^{-5}
AgBr	426°	2.0×10^{-4}
	300°	4.0×10^{-3}
	210°	7.6×10^{-4}
	20°	8.3×10^{-6}
	-180°	10^{-22}

From the theoretical relationship between conductivity and temperature, it is evident that the logarithm of the conductivity should be a linear function of $1/T$. This is the case experimentally, but it is usually found that a curve with two rectilinear limbs results. At high temperatures the conductivity is a highly reproducible property, and the slope of the curve measures $(U+E)$. At lower temperatures, the conductivity is reproducible neither from one specimen of a salt to another, nor even for the same specimen after varying heat treatment. It is said to be structure sensitive, and reflects the operation of some process of lower activation energy. Whether this is surface diffusion in the surfaces of a Smekal mosaic structure of the crystals, or whether impurities influence the low temperature conduction mechanism (as was deliberately the case in Koch and Wagner's experiments) is a problem still open to debate.

There are a number of substances - Ag_2HgI_4, AgI, Ag_2S - which display a type of allotropy of particular interest to the crystallographer. In the high temperature modification of each of these (Ketelaar, 1938; Strock, 1934, 1936) it is found that the cations are distributed at random over a number of crystallographically equivalent positions. Interstitial positions and ideal positions are indistinguishable, so that the energy W_F is virtually zero, while the potential barrier U is not very high. The result is that such compounds have an astonishingly high conductivity.

It will have been noted that such experiments as those of Tubandt, referred to above, imply that ions may migrate freely across the interface between two samples of solid - whether single crystals or compressed polycrystalline pellets. This is indeed so, even for the interface between salts of different crystal structure and lattice spacing, provided that the mobile ion is common to both lattices. Thus, there is free transport of silver across the interface AgI | AgCl, or AgI | Ag_2S. It does not hold true, generally speaking, for foreign ions, except where ready solid solution occurs. An instance of the latter is provided by the observation that if a pellet of Ag_2S containing 1% of Cu_2S, and a pellet of Ag_2S be superposed, uniformity of composition is very rapidly established at 200-300°, by the migration of copper from one pellet to the other. As a rule, foreign ions are not accepted in appreciable amount by a crystal lattice. Gold may be introduced into sodium chloride crystals at 600° by electrolysis between gold electrodes. On cooling, however, the gold atoms aggregate together into particles of colloid dimensions. Nickel atoms may similarly

be introduced by electrolysis between nickel electrodes, but not by ionic migration across the interface between sodium chloride and nickel salts.

Reactions in Solids

We have, in the foregoing, direct evidence as to both the occurrence and the mechanism of that mobility of ions which is the necessary prerequisite for the occurrence of reactions in the solid phase.

The most fundamental contributions to this subject have probably been made by Wagner and his co-workers (1933, 1934, 1936*a*, 1936*b*; cf. also Jost, 1937, chapter IV, for further extensive bibliography), who have rigorously established the relationship between (*a*) the reaction processes at the interface of a metal and a gaseous or liquid non-metal ("tarnish reactions") and (*b*) the processes of diffusion and electrolytic conduction in the binary compound formed. Thus, in a system of superimposed pellets represented diagrammatically as

$$Ag \mid Ag_2S \; I \mid Ag_2S \; II \mid liquid \; S$$

it is found that only pellet II grows in size, and this is explicable only in terms of the migration of Ag^+ ions through the system, and reaction at the Ag_2S - S interface.   The evidence is complete that it is Ag^+ ions, not neutral Ag atoms that diffuse by the processes already considered, and it follows that there must be an independent compensating flow of electrons in the same direction.   The phase boundary reaction is thus between electrons and sulphur, with formation of sulphide ions.   There are three independent rate processes to be considered; the rate of migration of cations, the rate of migration of electrons, and the velocity of the boundary reaction.   It is the slowest of these (in this instance the migration of electrons) that determines the overall rate of chemical change.

Similar considerations apply to the oxidation of metals that form coherent oxide films (e.g., iron) and also to what may be termed (Wagner, 1936*b*) ionic reactions of higher order.   The latter comprise reactions between binary compounds to form salts, double oxides, etc., as exemplified by the formation of spinels and similar compounds (Fig. 5) and by the reactions of silicates (Fig. 6) (Jander and co-workers, 1931*a*, 1931*b*, 1932, 1934, 1935; Hedvall, 1931; see also Jost, 1937, chapter V, for further bibliography).
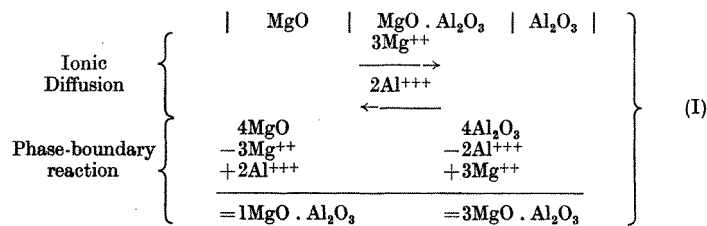
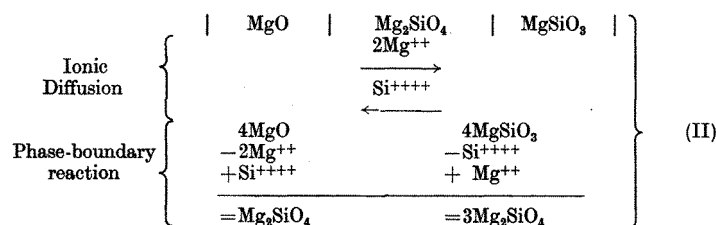Fig. 5.—Solid phase reaction—I. Spinel formation.

Fig. 6.—Solid phase reaction—II. Typical silicate reaction.

It will be noticed that in the ionic reactions of higher order, there is a counter flow of ions rather than the migration of free electrons; also that, in these instances, the anions remain relatively immobile. In the processes of Figs. 5 and 6, the oxygen atoms form a fairly close packed anion lattice both in the reactants and in the product. It is the relatively small and mobile cations that diffuse through the interstices of the anion lattice. Although our knowledge of reactions between solids has been greatly augmented by the work of W. Jander, Hedvall, Hüttig and others, there is still a paucity of data on the kinetics of the process, so that a quantitative comparison with our fairly precise theoretical picture is possible only in a few instances.

Non-Stoichiometric Crystals

In all that has been discussed hitherto, it has been assumed that lattice defects occur in balanced pairs; that is, in Frenkel defects, an interstitial ion and a lattice hole (which represents a virtual charge of opposite sign), or in Schottky defects, equal numbers of holes in both cation and anion lattices. If the defects are not present in such pairs, the stoichiometric balance between the constituents of the compound is destroyed, and its formula is no longer uniquely determined.

A crystalline phase in which this state of affairs obtains is commonly stated to contain an excess of one or other constituent "in solid solution." In the light of our knowledge of the constitution of the solid state we are able to attach to this expression a more precise significance than formerly. There are three possible types to which the "solid solution" of the element B in the compound AB can conform. In *substitutional* solid solutions, atoms of B occupy lattice sites that would normally be occupied by atoms of A. Clearly, this could not occur in ionic compounds, on electrostatic grounds, so that this type of solid solution is practically restricted to alloys and intermetallic compounds, where both elements are present in the lattice in a similar electronic state. *Interstitial* (or additive) solutions are, as the name implies, related to the development of Frenkel defects, atoms of B being present interstitially in the lattice of AB in greater concentration than the vacant B-atom sites. *Subtractive* solid solutions are similarly related to Schottky defects, the numbers of vacant A-atom and B-atom sites being unequal.

Consideration of the thermodynamic stability of such non-stoichiometric compounds will be deferred for the moment. It may, however, be noticed that to preserve electrostatic balance in the crystal, one or other constituent must be present in more than one valence

state. This will be clear from Fig. 7, referred to below. According as the metal or the non-metallic constituent is present in excess, there are four possible ways in which non-stoichiometry may arise.

(*a*) Metal, in excess.
    (i) Anion lattice complete, with metal atoms in interstitial positions.
    (ii) Anion lattice incomplete (i.e., vacant anion lattice sites), with perfect cation lattice.

(*b*) Non-metal in excess.
    (i) Cation lattice complete, with non-metal atoms interstitially.
    (ii) Cation lattice incomplete (vacant cation positions), anion lattice complete.

These possibilities are, of course, subject to ordinary thermal lattice defects, superimposed on the non-stoichiometry. There is general agreement that the types (*a*-i), based on unbalanced Frenkel defects, and (*b*-ii), based on unbalanced Schottky defects, represent the most important cases.

For an example of the application of these principles we may cite cuprous oxide. This, as is well known, has a range of composition on the oxygen-rich side of the formula Cu_2O, and the constitution of the non-stoichiometric phase may be illustrated diagrammatically by Fig. 7. For every O^{2-} ion in excess of the stoichiometric balance, two Cu^+ ions must be replaced by two Cu^{2+} ions, and two Cu^+ lattice sites must be left vacant.

$$Cu^{++} \qquad Cu^+ \qquad \square \qquad Cu^+ \qquad Cu^+ \qquad Cu^+$$
$$O^= \qquad O^= \qquad O^= \qquad O^= \qquad O^=$$
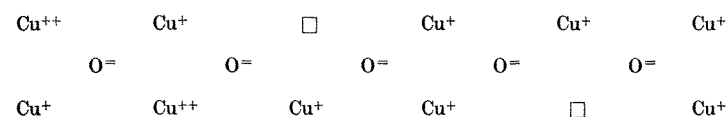$$Cu^+ \qquad Cu^{++} \qquad Cu^+ \qquad Cu^+ \qquad \square \qquad Cu^+$$

Fig. 7.—Lattice defects in cuprous oxide with excess oxygen (=deficit of copper). Vacant cation sites marked by squares.

Electrical Conductivity in Non-Stoichiometric Compounds

As with thermal lattice defects in ionic compounds, so the electrical conductivity of non-stoichiometric compounds provides a phenomenally sensitive and very instructive means of studying their properties. Here, however, electronic (i.e. metallic) conduction, not electrolytic conduction, is involved.

In discussing the electronic constitution of heteropolar compounds, we may use either of two approximations, which correspond respectively to the Heitler-London and the Hund-Mulliken approaches to the problem of molecular structure. Either is permissible, but they are not necessarily equally useful as descriptions of any particular structure. The *discrete ion* picture represents the only interaction between ions as due to the electrostatic attraction or repulsion of their net charge: the electronic levels within any ion are assumed to be unaffected by the proximity of contiguous ions. This model gives a very fair approximation for crystals built up from inert gas-like ions (e.g., NaCl, CaF_2) in their ground state. It implies that the energy of excitation of an electron to the continuum of levels is practically the same as the ionisation energy of the isolated ions. Alternatively, the *collective electron,* or *band* approximation regards the electrons as moving in the

periodic field of all the atoms of the crystal. It affords the most useful description of semi-metallic compounds, in which the polarisation effect of cation and anion is very large. The same compounds tend to display electronic conductivity. Qualitatively, this model is not unfamiliar, for it has long been recognised (Grimm and Sommerfeld, 1926) that certain series of compounds, such as CuBr, ZnSe, GaAs, Ge itself, in which there are, in every case, eight valency electrons between the two atoms, crystallise in a common structural type with almost identical lattice dimensions: all eight valency electrons are utilised in bonding, irrespective of the formal valency of the atoms. In the collective electron model, the discrete electronic energy levels of the isolated atom are replaced by bands of permitted energies. Within any one band, and subject to the Pauli principle, the energy of an electron may change continuously, but the excitation of an electron from one band to the next (corresponding to a quantum jump in an isolated atom) involves the expenditure of energy far in excess of thermal energies. On the model first advanced by Wilson (1931), the essential difference between insulators and electronic semiconductors lies in the possibility of promoting electrons to an unoccupied energy band. In any electronic conductor, there can be a net flow of electrons only in an incompletely filled energy band, so that a crystal is an insulator if every energy band is either completely full or completely empty. The typical inorganic compounds are insulators in this sense, and the excitation of an electron to the lowest conduction band would demand a high energy of excitation. In a Wilson semi-conductor (intrinsic semi-conductor), the spacing between successive energy bands is such that electrons may be promoted to the conduction band by thermal energies. It is probable that no semi-metallic compound owes its conductivity at the ordinary temperature to this simple mechanism.

The formation of non-stoichiometric compounds is directly related to the development of electronic conductivity, however, since it provides a mechanism for the ready transfer of electrons from atom to atom through the lattice. For, consider the possibility of an electron switch from atom to atom along a row of identical cations - e.g., in nickel oxide, NiO, of stoichiometric composition. The process [A] ---> [B] (Fig. 8) is inherently improbable, and must be followed by a reversal of that process, rather than by the propagation of the perturbation along the lattice row. However, in black nickel oxide, of composition $NiO_{1.005}$, for instance (cf. Klemm and Hass, 1934), five Ni atoms in every thousand are presumably present as trivalent ions. If, in a lattice row containing a Ni^{+++} cation, an electron switch takes place (Fig. 8, process [C] ---> [D]), we may see that the resulting state of the system is energetically indistinguishable from the original state.

$$Ni^{++} \quad Ni^{++} \quad Ni^{++} \quad Ni^{++} \longrightarrow Ni^{++} \quad Ni^{+} \quad Ni^{+++} \quad Ni^{++}$$
$$[A] \qquad\qquad\qquad\qquad [B]$$

$$Ni^{++} \quad Ni^{+++} \quad Ni^{++} \quad Ni^{++} \longrightarrow Ni^{++} \quad Ni^{++} \quad Ni^{+++} \quad Ni^{++}$$
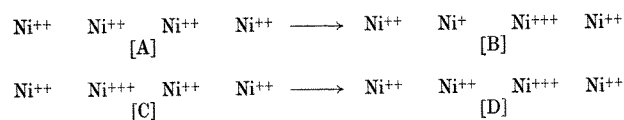$$[C] \qquad\qquad\qquad\qquad [D]$$

FIGURE 8.

It follows from the general principles of quantum mechanics that the migration of electrons along a lattice row in this fashion is readily possible, being governed by the probability of leakage of an electron through the potential barrier between the dissimilar ions. When an electric field is applied, therefore, a mechanism exists for a drift of electrons, the conductivity being determined (*a*) by the magnitude of the potential barriers, and (*b*) by the number of "positive holes" in the conduction band. This latter, as will be noticed, is measured by the degree to which the compound departs from stoichiometric

composition. We do not, for our present purpose, need to go further into the mechanism of conduction (cf. Mott and Gurney, 1940; Seitz, 1940).

As has been stated, intrinsic semi-conductors are almost or quite unknown: the energy gap between the full bands and the conduction band is relatively large in every case, for pure compounds. In every case that has been investigated, however, the electronic conductivity of compounds displaying semimetallic properties is a function of the composition in exactly that manner according with the considerations we have set out.

Amongst the metallic oxides, which constitute the best-investigated group of electronically conducting compounds, two main types of semi-conductor are recognised. In the first, exemplified by Cu_2O, FeO, CoO, NiO, etc., it is found that the conductivity increases as the partial pressure of oxygen in equilibrium with the solid is raised. This implies that these compounds have some range of composition on the oxygen-rich side of the ideal formula. If, at temperatures where reaction can occur, the partial pressure of oxygen is raised, a reaction takes place, which may be symbolised by

$$2M^+ + \tfrac{1}{2}O_2 \longrightarrow O^{--} + 2M^{++} + 2\square.$$
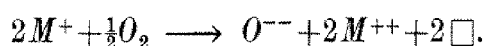
The crystal lattice is thereby extended by the addition of a new anion lattice point, while new vacant cation lattice points, and new positive holes for conduction, are introduced in equivalent amount.

The second type of oxide semi-conductor is that in which the conductivity diminishes as the partial pressure of oxygen in the system is raised. In this case, combination with oxygen obviously destroys the defects upon which conduction depends. Zinc and cadmium oxides are of this type, and the formation of conducting centres by loss of oxygen from the crystal may be symbolised as

$$M^{++} + O^{--} \longrightarrow \tfrac{1}{2}O_2 + M.$$

Anion and cation lattice points disappear in equal numbers, and are replaced by a corresponding number of interstitial metal atoms. Compounds of this kind have, then, a non-stoichiometric range of composition on the metal-rich side of the ideal formula.

The Thermodynamic Stability of Non-Stoichiometric Compounds

A complete theoretical treatment of the relation between the free energy and the composition of a non-stoichiometric compound is lacking as yet. Such a treatment must take account of a number of factors which, by their interplay, must underly the experimental fact that, in certain instances, the permissible range of composition is very considerable. These factors need not be enumerated here.

Schottky and Wagner (1930) have treated the problem from the formal thermodynamic standpoint. While their results cannot be explicitly evaluated, they are interesting as showing firstly, that the activity of each component in a crystalline phase is a continuous function of composition, and secondly, that the range of composition over which a non-stoichiometric phase exists is itself a function of the degree of lattice disorder that obtains. This implies that the composition range of any such compound should be wider at higher temperatures.

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Related to the second point raised by Schottky and Wagner is the correlation that may be drawn between the type of non-stoichiometry exhibited by a compound, and the type of favoured lattice disorder.   Thus, the wurtzite type lattice of zinc oxide is of a type favouring Frenkel defects in thermal equilibrium: in non-stoichiometric zinc oxide, the excess zinc is almost certainly present interstitially, due to the formation of unbalanced Frenkel defects as oxygen evaporates out of the lattice.

It has been pointed out by Mott and Gurney that whenever a polar compound is in contact with an excess of one or other component, the formation of a non-stoichiometric phase must ensue, even though the extent to which deviation from ideality occurs is immeasurably small. An illustration of this thesis where, on classical chemical ideas, it would not be expected, is found in the formation of blue crystals of sodium chloride when the salt is heated in sodium vapour.   With this in mind, we may return to the problem of solid reactions, such as the "tarnish" reactions of Wagner.   In the process of forming silver sulphide, considered previously, we now see that there must be a certain composition gradient through the solid, since one side is in contact with silver and the other side with sulphur.   To the deviation from the ideal formula Ag_2S we may reasonably ascribe the liberation of mobile electrons necessary for the occurrence of the phase boundary reaction.

The range of compositions over which a compound can persist is one of the most interesting problems. In metal-excess systems, the stable range seems usually to be immeasurably narrow, and accessible to investigation only from measurements of the conductivity and the Hall effect (cf. Fritsch, 1935).   When however, compounds are formed with an excess of non-metal, due to the potential variability in valency of the metallic constituent (e.g., Cu_2O, FeS), we may note two factors that can materially widen the range of stable composition.   These are, firstly, that an increase in valency of a metallic cation makes a large contribution to the Madelung energy of the surrounding lattice points; and secondly, that in consequence of the statistical distribution of higher-valent cations and lattice holes, there is a progressive and very marked change in the lattice parameter as the composition changes.   This shrinkage of lattice spacing, as the non-metal excess increases, again reacts upon the cohesive energy of the lattice.   In a qualitative way one can see how these two factors may balance out the endothermicity of lattice hole production over a certain range of composition. In exceptional cases (e.g. FeS, the tungsten bronzes) this range may be very wide, and the experimental evidence leaves no doubt that the maximum of stability may actually differ from the stoichiometric ratio: stoichiometric FeO and FeS do not exist (Hägg, 1933, 1935; Jette and Foote, 1933; Bernal, 1933).

We may, in conclusion, examine how far the matters discussed are relevant to the familiar facts of chemistry.   The formation and properties of metal-excess conductors are known to every student, for the colour change of zinc oxide from white to yellow when heated runs parallel to the development of electronic conductivity.   The marked optical absorption in the visible region in itself marks the diminished energy of excitation of electrons from the ground level to the excited state.   Where similar colour changes occur with other oxides (e.g., with indium oxide, and with more refractory oxides at higher temperatures), we may reasonably infer that the same process is operative, and that we are observing the evaporation of oxygen from the crystal lattice, and the formation of a non-stoichiometric phase.   A wide variety of observations can be brought under the same general heading, including the properties of refractory oxides and ceramic masses at high temperatures.

Attention has already been drawn to the particular interest attaching to the non-metal excess compounds, and the apparent non-existence of the stoichiometric compounds in several familiar instances. The oxide and sulphide of univalent copper likewise extend as uniform phases at least up to the compositions $Cu_{1.995}O$, $Cu_{1.98}S$. It seems as if non-stoichiometric compounds are formed whenever the valence properties of the metal permit it, and as if the range of permissible composition becomes wider as the electronegativity of the nonmetal diminishes.

In this connection, the highly coloured, metallic-looking sulphides of the heavy metals are of especial interest. Their optical properties, so different from those of the true salts of the same metals, suggest that amongst them might be found the intrinsic semi-conductors of Wilson's theory. They have hitherto received but little experimental investigation, however, in comparison with the oxides of the metals. According to recent work carried out in Melbourne, stannous sulphide and lead sulphide belong to the class of non-stoichiometric conductors, with a non-metal excess. Both metals, it will be noted, can potentially exert quadrivalency. The extraordinary sensitiveness of the electrical conductivity towards changes in composition is well illustrated by some of our results. Assuming a reasonable value for the mobility of an electron in stannous sulphide, it appears that "pure" stannous sulphide, as prepared by ourselves and other authors according to a standard procedure, contains about 2×10^{18} conducting centres per gram-molecule. This is due to excess of sulphur, and the upper limit of composition corresponds to the formula $SnS_{1.00001}$. By suitable treatment with hydrogen, the excess of sulphur is partially removed: positive holes are thereby destroyed, and the specific resistance is raised more than one thousandfold, corresponding, perhaps, to a composition $SnS_{1.00000001}$. As this work will be described elsewhere, it will not now be discussed further; the data serve, however, to show how small a departure from the ideal formula is needed to emphasise the semi-metallic properties of such compounds.

The most important aspect of the subject that we have discussed is, however, its implications for chemical philosophy. The Berthollet-Proust controversy is recalled, and the status of the fundamental laws of chemical combination has to be reconsidered in the light of our wider knowledge. It seems that the law of constant proportions, which necessarily holds rigorously for compounds of discrete molecular constitution (e.g., gaseous compounds, and molecular liquids or solids), is a limiting law, to which solid compounds with atomic lattices approximate more or less closely; with a few exceptions, indistinguishably closely. This conclusion, although revolutionary, seems inescapable. We have certain parallels in the development of modern physics - for example, in the classical and quantum theories of radiation, and Bohr's correspondence principle; or in the pragmatic viewpoint that confines the formulation of laws to quantities and properties that are, conceivably at least, experimentally observable. It is the task of the present generation of chemists to work out the implications of these conceptions, for the new outlook has to be built, sooner or later, into the fabric of the general theory and teaching of chemistry.

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