

Finally, the writer's thanks are due to Dr A. E. Green for his continued interest and his valuable assistance.

REFERENCES

- Green, A. E. 1942 *Proc. Roy. Soc. A*, **180**, 173.
 Green, A. E. 1943 *Proc. Roy. Soc. A*, **184**, 231.
 Huber, M. T. 1938 *Contributions to the mechanics of solids dedicated to S. Timoshenko*, p. 89.

The conditions of equilibrium of 'non-stoichiometric' chemical compounds

BY J. S. ANDERSON, *University of Melbourne*

(Communicated by Sir Henry Tizard, *For. Sec. R.S.*—Received 27 September 1944)

The conditions are discussed under which a crystalline binary compound may exist over a relatively wide, but finite, range of chemical composition—e.g. the existence of pyrrhotite, nominally FeS, up to a composition approximately $\text{FeS}_{1.2}$. On the hypothesis that the lattice defects (interstitial atoms or vacant sites), introduced by departure from stoichiometric composition, interact with one another when in adjacent lattice positions, the problem reduces to a form similar to that of Fowler's treatment of regular localized monolayers. It follows that below a certain temperature, determined by the energy of interaction of lattice defects, the phase is stable only when the concentration of defects is less than some limiting value. If this is exceeded, the phase breaks up into a two-phase system. Hence the range of existence of any compound is limited on either side by the compositions at which, for example, the concentration of vacant cation sites and of interstitial atoms reach limiting values. The dependence of these limits on the partial pressure of the volatile component and the degree of lattice disorder in the stoichiometric phase is worked out. The conditions emerge under which (a) the stoichiometric compound may be metastable (e.g. FeS) and (b) the phase is incapable of existence.

Experimental pressure-composition isotherms for the systems Pt-PtS-PtS₂, MS-MS₂ (M = Fe, Co or Ni), and $\text{UO}_3\text{-U}_3\text{O}_8$ are compared with the model. The general form of the equilibrium diagrams is satisfactorily reproduced, and the limitations of the model are shown. The formation of anomalous solid solutions between compounds of different formula type (e.g. YF_3 and CaF_2) is finally discussed and shown to fall within the scope of the theory.

A new conception of the nature of solid compounds was introduced by Schottky & Wagner (1930) in a paper on 'the theory of ordered mixed phases', in which they showed that the composition of any crystalline compound (of atomic lattice type) must be dependent, if only in small degree, on the partial pressures of the components in equilibrium with the crystalline phase. Their discussion was explicitly limited to small departures from the ideal composition; such systems as sodium chloride in equilibrium with sodium vapour, or metallic oxides undergoing incipient decomposition at high temperatures (e.g. the familiar behaviour of zinc oxide), would fall within the scope of their treatment. There are, however, systems of interest to the chemist in which the departure from stoichiometric composition is not small. In this paper an attempt is made to formulate a crude semi-quantitative

theory for the most general case, by extending certain considerations that were found by Lacher (1937) to reproduce very satisfactorily the behaviour of one classical non-stoichiometric system—the combination of hydrogen with palladium. No pretensions are made for the physical completeness of the theory; the purpose of the paper is rather to show that from the acknowledged properties of real crystals there may be derived, without constraint, an interpretation of the chemical facts, and that the resulting model of a binary phase appears good enough to justify detailed comparison with the experimental data.

The principal experimental facts that must be reproduced by any theory of non-stoichiometric compounds may be summed up briefly as follows.

(a) With a number of well-defined, crystalline compounds—notably the oxides, sulphides, selenides, etc., of the transition metals—the composition may vary widely without change of crystal structure. In the light of our present knowledge this cannot lightly be classified as due to solid solubility. Thus, ferrous sulphide (see (c) below) is commonly said to form a wide range of solid solutions with pyrite, FeS_2 , although the lattice types of the two compounds are completely different. Hägg & Sucksdorff (1933) have shown that the variability of composition does not arise from the building in of S_2 groups in place of S atoms, nor from the incorporation of excess sulphur on lattice sites proper to iron, but from the stability of the pyrrhotite lattice when a considerable proportion (up to about 20 %) of the iron lattice sites is vacant. Numerous similar instances could be cited.

(b) In studies of the isothermal or isobaric degradation of many compounds (cf. the long series of papers by W. Biltz and his co-workers on the 'systematic doctrine of affinity', 1908–42) the $(p, X)_T$ or $(T, X)_p$ curves have not infrequently been found to display a bivariant character over a range of compositions, the equilibrium pressure at any temperature, or the equilibrium temperature at any pressure, being dependent upon the composition of the solid phase. Such behaviour necessarily implies that the gas phase is then in equilibrium with a single solid phase of variable composition.

(c) In several well-established instances—e.g. FeS (Hägg & Sucksdorff 1933), FeO (Foote & Jette 1933), NiO (Klemm & Hass 1934)—the crystalline phase of stoichiometric composition is actually unstable, breaking up, in the instances cited, into the free metal and a non-stoichiometric oxide or sulphide of limiting composition.

CASE I. BINARY COMPOUNDS WITH SMALL DEPARTURE FROM IDEAL RATIO

It is convenient to enumerate briefly the equilibrium conditions found originally by Schottky & Wagner (1930), and very clearly treated by Fowler & Guggenheim (1939, pp. 540–53). For simplicity, consider a binary compound AB , in the lattice of which, at all temperatures above the absolute zero, there will exist a certain degree of disorder. It was suggested by Schottky that, in general, deviations from stoichiometric composition are likely to occur in such a manner that they affect, practically,

Equilibrium conditions of non-stoichiometric chemical compounds 71

the disposition of either the A atoms or the B atoms alone. This statement is really valid only for those lattices (e.g. the fluorite and zincblende types) in which Frenkel defects are favoured. It will, however, without incurring any loss of generality, be assumed throughout the paper that a stoichiometric excess of A is accommodated in the form of interstitial A atoms, and that, with excess of B , the B atoms all occupy normal lattice positions, with a surplus of 'holes' on A sites; the B lattice is taken as perfectly ordered.

Let N_A , N_B be the number of atoms of each kind, distributed over N ($= N_B$) lattice sites of each kind:

- N_A^h = number of vacant A sites,
- N_A^i = number of interstitial A atoms, distributed over $2\alpha N$ interlattice positions,
- E_A^h = energy expended to create a lattice hole by transferring an A atom from an interior site to the surface,
- E_A^i = energy expended to shift an A atom from the surface to an interlattice position,
- $-E_X^i$ = energy of each additional A atom (above the stoichiometric number), present on an interlattice position, relative to the energy of an isolated A atom at rest,
- λ_A = activity of atomic A in equilibrium with the crystal phase,
- $q_A(T)$ = contribution of an added A atom to the partition function for the normal vibrational modes of the crystal.

Then the equilibrium concentrations of lattice defects can readily be shown to be:

$$N_A^i = 2\alpha N_B \lambda_A q_A(T) \exp E_X^i/kT, \quad (1A)$$

$$N_A^h = \frac{N_B}{\lambda_A q_A(T)} \exp -(E_A^h + E_A^i + E_X^i)/kT. \quad (2A)$$

In terms of the addition or removal of B atoms, the incorporation of excess B can occur through condensation of a B atom on to a normal lattice site, accompanied by the creation of an additional A hole, or the removal of an interstitial A atom to the A site created. Then each excess B atom on its lattice site has an energy $-E_X^h$ above that of an isolated B atom, and thus, in place of (1A), (2A)

$$N_A^i = \frac{2\alpha N_B}{\lambda_B q_B(T)} \exp -(E_A^h + E_A^i + E_X^h)/kT, \quad (1B)$$

$$N_A^h = N_B \lambda_B q_B(T) \exp E_X^h/kT. \quad (2B)$$

$$\text{From (1) and (2), } N_A^h N_A^i = \bar{N}_0^2 = 2\alpha N_B^2 \exp -(E_A^h + E_A^i)/kT, \quad (3)$$

so that $\bar{N}_0/N_B = \delta$, the degree of disorder in the lattice of the stoichiometric compound is given by

$$\delta = \sqrt{(2\alpha) \exp -(E_A^h + E_A^i)/2kT}. \quad (4)$$

The deviation from stoichiometric composition is $N_B - N_A$, and

$$\begin{aligned} N_B - N_A &= N_A^h - N_A^i \\ &= \frac{2\alpha N_B}{\lambda_B q_B(T)} \exp - (E_A^h + E_A^i + E_X^h)/kT - N_B \lambda_B q_B(T) \exp E_X^h/kT. \end{aligned} \quad (5)$$

Hence the activity of B in equilibrium with the stoichiometric compound is

$$\bar{\lambda}_B = \frac{\sqrt{(2\alpha)}}{q_B(T)} \exp - (E_A^h + E_A^i + 2E_X^h)/2kT = \frac{1}{q_B(T)} \delta \exp - E_X^h/kT. \quad (6)$$

From (3), (5) and (6), writing $N_B - N_A/N_B = n$,

$$\frac{\lambda_B(n)}{\bar{\lambda}_B} = \left\{ \left(\frac{n}{2\delta} \right)^2 + 1 \right\}^{\frac{1}{2}} + \frac{n}{2\delta} = \left(\frac{p(n)}{\bar{p}} \right)^{\frac{1}{2}}, \quad (7)$$

since, for most of the important cases, equilibrium is established between a crystalline phase and a diatomic gas (oxygen, or sulphur vapour at high temperatures) in experimental investigations.

CASE II. GROSS DEVIATION FROM STOICHIOMETRIC COMPOSITION

The relations (1)–(7) are, through the approximations made in their derivation, valid only as long as N_A^h/N_B , N_A^i/N_B are very small. No account is taken of any kind of interaction between the points of defect. The effect of such interactions would become increasingly significant as, with increasing stoichiometric defect, the concentration of defects increased, and must, in fact, be very important. The mutual attraction of atoms in interstitial positions or of cation holes can be regarded, qualitatively, as the driving force behind the segregation of a new phase when the concentration of defects exceeds some critical value. Even where the concentration of defects is small (e.g. zinc oxide with an interstitial excess of zinc) it has been suggested (Miller 1941) that the interstitial atoms form clusters, rather than remaining in random distribution.

Proper allowance for mutual interaction of defects should lead to a relation between the activity of the components A , B and the concentration of lattice defects, which would reproduce satisfactorily the observed $(p, X)_T$ and $(T, X)_p$ relations of typical systems, leading to the explicit prediction of the occurrence of a two-phase univariant region in equilibrium diagrams and describing quantitatively the variation with temperature of the miscibility of two non-stoichiometric phases.

In this paper the consequences of the simplest approximation are considered: that the energy of interaction between defects can be represented as the sum of the contributions of those pairs of defects that occur as nearest neighbours in a completely random distribution. This reduces the problem to a form analogous to that developed by Fowler (1936) for equilibrium in localized monolayers; it is essentially the same as Lacher's treatment (1937) of the palladium-hydrogen system, which

Equilibrium conditions of non-stoichiometric chemical compounds 73

presents many features of analogy to the more general problem here discussed. Although the assumptions are too simple and the approximation undoubtedly too crude, it will be shown that the model does lead to the conclusion that a crystalline phase is stable over a range of composition only, and indicates the factors upon which that stable range depends. In the second part, comparison is made with such experimental data as are available for several systems, and in so far as explicit values can be assigned to the quantities involved, it will be seen that the agreement is as fair as the assumptions would warrant.

N_{HH} , N_{II} may be taken to be the number of pairs of nearest neighbour cation holes and interstitial A atoms respectively, and $2E_{\text{HH}}/z$, $2E_{\text{II}}/z'$ to be the energies of interaction per pair, where z = number of cation sites adjacent to each A site, and z' = number of vacant interlattice positions adjacent to each interstitial A atom. Then (cf. Fowler & Guggenheim 1939, p. 340)

$$N_{\text{HH}} = \frac{1}{2} z N_A^{h^2} / N_B \quad \text{and} \quad N_{\text{II}} = \frac{1}{2} z' N_A^{i^2} / N_B,$$

and the contributions of the energies of interaction to the partition function of the crystal become, respectively,

$$\frac{N_A^h E_{\text{HH}}}{N_B kT} \quad \text{and} \quad \frac{N_A^i E_{\text{II}}}{N_B kT}. \quad (8)$$

As a further simplifying assumption the vibrational partition function of an interstitial A atom, and of the atoms adjacent to a vacant lattice site or to an interstitial atom, is taken to be identical with those of the atoms in a perfectly ordered lattice. Although numerically incorrect, this assumption cannot invalidate any general conclusions. This point has been discussed, though in a different connexion, by Mott & Gurney (1940, pp. 29–33).

For comparison with experiment it is convenient to regard the number of A atoms as fixed, and the number of B (i.e. non-metal) atoms as variable, with all the B atoms occupying proper lattice positions. Then a crystal with N_A^h vacant A sites and N_A^i interstitial A atoms can be regarded as derived from the stoichiometric crystal by the addition of $N_A^h - N_A^i$ atoms of B from the gas phase, a corresponding number of electrons being withdrawn from the full band of the crystal to convert the B atoms to anions. Using the symbols of the previous section, $K(T) \Gamma(T, \lambda_B, N_A)$ may be written for the grand partition function of the crystal, wherein $K(T)$ represents the partition function for the ideal stoichiometric crystal. Then for the partition function for the defects write

$$\begin{aligned} \Gamma(T, \lambda_B, N_A) = & \sum_{N_A^h, N_A^i} \frac{N_B!}{N_A^h! N_B - N_A^h!} \times \frac{2\alpha N_B!}{N_A^i! 2\alpha N_B - N_A^i!} \times [\lambda_B q_B(T)]^{N_A^h - N_A^i} \\ & \times \exp \left[-N_A^i (E_A^h + E_A^i) + (N_A^h - N_A^i) E_X^h - \frac{N_A^h}{N_B} E_{\text{HH}} - \frac{N_A^i}{N_B} E_{\text{II}} \right] / kT. \quad (9) \end{aligned}$$

The equilibrium conditions may, according to the standard procedure, be derived from (9) by partial differentiation of the largest term of $\log \Gamma(T, \lambda_B, N_A)$ with

respect to N_A^h and N_A^i . Writing $N_A^h/N_B = \theta^h$, the fraction of A sites vacant, it is found that

$$\lambda_B = \frac{1}{q_B(T)} \frac{\theta^h}{1 - \theta^h} \exp - (E_X^h - 2\theta^h E_{HH})/kT. \quad (10)$$

Similarly,
$$\frac{1}{\lambda_B} = q_B(T) \frac{\theta^i}{1 - \theta^i} \exp (E_A^h + E_A^i + E_X^h + 2\theta^i E_{II})/kT. \quad (11)$$

In (10) and (11), λ_B represents the absolute activity of B atoms in the gas phase, in equilibrium with the solid. For the case that the solid is in equilibrium with diatomic B_2 molecules, write

$$\lambda_B = (\lambda_{B_2})^{\frac{1}{2}} = \left(\frac{p}{kT} \right)^{\frac{1}{2}} \left(\frac{(2\pi 2m_B kT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 A kT}{h^2} \frac{\rho_B^2}{2} \right)^{-\frac{1}{2}} \exp - D/2kT, \quad (12)$$

in which D = energy of dissociation of the B_2 molecule in its lowest state into two free B atoms, A = moment of inertia of the B_2 molecule, m_B = mass of the B atom, and ρ_B = nuclear spin weight of the B atom (= 1 for O^{16} and S^{32} , the most important cases for comparison with experimental data). Combining (12) with (10) and (11), and substituting the appropriate values for the fundamental constants, the partial pressure of B_2 vapour in equilibrium with a crystal containing a fraction θ^h , θ^i of cation holes and of interstitial A atoms respectively can be found.

As was shown by Fowler (1936), the form of equations (10) and (11) is such that, provided E_{HH} , $E_{II} < 0$ (i.e. if the defect sites exercise attractive forces upon each other, as was suggested, from qualitative considerations, in an earlier paragraph), a two-phase system must be formed under appropriate conditions of temperature and pressure. There is, for a crystal containing significant concentrations of only one type of defect, a critical temperature T_c , defined by $T_c = -E_{HH}/2k$, $T'_c = -E_{II}/2k$, such that for $T > T_c$ there is, over the entire range of θ , only one value of θ corresponding to each value of λ ; for $T < T_c$, λ over a certain range is satisfied by three values of θ .

Thus, in place of (10)

$$\frac{\lambda(\theta)}{\lambda(\frac{1}{2})} = \frac{\theta^h}{1 - \theta^h} \exp - (1 - 2\theta^h) E_{HH}/kT \quad (13)$$

may be written, in which, for $T < T_c$, the condition $\lambda(\theta) = \lambda(\frac{1}{2})$ is satisfied by three values of θ . The value $\theta = \frac{1}{2}$ corresponds to a metastable state of the system (cf. figure 1, which represents the graph of (13) for $T = 0.8T_c$); the other two roots θ_1 , θ_2 , related by the condition $\theta_1 + \theta_2 = 1$, satisfy the rule of equal areas, and correspond to stable states of the system.

The physical significance of this result is clear. Suppose that the metal A (of variable valency) and the non-metal B unite to form two compounds AB and AB_n . A start is made with the stoichiometric phase AB in contact with the gaseous component B or B_2 . As the pressure of B in equilibrium with the crystal is raised, B atoms are built on to the crystal lattice, and an increasing concentration of vacant

Equilibrium conditions of non-stoichiometric chemical compounds 75

A sites (and of A ions of increased valency) is thereby formed. Above a temperature T_c , defined as above by the energy of interaction of cation holes, the compound AB and the compound of higher order AB_n with the same B lattice would be completely miscible. At temperatures below T_c when the concentration of vacant A sites exceeds the 'saturation' value θ_1 , the lattice breaks up into two phases, with the limiting defect concentrations θ_1 and θ_2 respectively. (The presupposition that this occurs

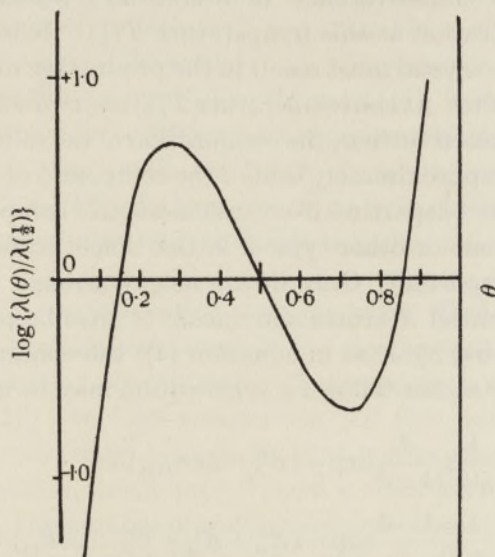


FIGURE 1. Graph of equation (13) for $T = 0.8T_c$.

without change in the B lattice will be discussed shortly.) Hence, for total compositions intermediate between those corresponding to θ_1 and θ_2 , a two-phase system exists in equilibrium with a constant pressure of B . It is this pressure in the univariant region, the 'dissociation pressure of the compound AB_n ', which has ordinarily been measured in studies of chemical equilibria. From (10) and (12) it is seen that

$$\frac{d \log_e p(\frac{1}{2})}{d(1/T)} = -(2E_X^h - 2E_{HH} - D). \quad (14)$$

D is known for the principal diatomic elements; where adequate data are available it should be possible to infer the magnitude of E_{HH} . Hence E_X^h , the energy of addition of a B atom to the AB lattice, should be capable of determination.

Exactly similar considerations apply to the withdrawal of B atoms from the stoichiometric compound. When the concentration of interstitial A atoms exceeds a limiting value, formation of a new phase with the higher, complementary value of θ must occur, and a two-phase system is again formed. The equilibrium of platinum monosulphide, PtS , with sulphur vapour at high temperatures, considered in some little detail in the second part of the paper, provides a concrete instance of the intermediate occurrence of non-stoichiometric phases through both acquisition of sulphur (ultimately forming PtS_2) and degradation (to Pt).

Consider also the isobaric degradation of a compound AB_n under a pressure p . At relatively low temperatures, the pressure p is far in excess of that pressure $p(\frac{1}{2})$ which corresponds to the existence of two solid phases, so that the crystalline phase of nominal formula AB_n is the only solid phase. With rise of temperature, the composition of the solid phase changes gradually as B atoms evaporate from the lattice. A temperature $T(\frac{1}{2})$ is ultimately reached for which $p(\frac{1}{2})$ equals the experimental pressure, p ; the concentration θ^i of interstitial A atoms in the lattice is then the saturation concentration at this temperature $T(\frac{1}{2})$. Hence, abstraction of any more B atoms from the crystal must result in the production of a second solid phase, complementary to the first. At the temperature $T(\frac{1}{2})$ the two solid phases can coexist. If the temperature be raised further, the composition of the solid phase changes, from approximately AB_n to approximately that of the compound of lower order (e.g. AB).

In general, where gross departure from stoichiometric composition is observed, it may be assumed that one or other type of lattice defect so far preponderates that the other type is unimportant. Only in the neighbourhood of the stoichiometric composition can interstitial A atoms and vacant A sites be present in comparable concentrations. Denoting by δ (as in equation (4)) the concentration of defects in the stoichiometric crystal, the following substitution may be made in (10) and (11):

$$\begin{aligned}\bar{\lambda} &= \frac{1}{q_B(T)} \frac{\delta}{1-\delta} \exp - (E_X^h - 2\delta E_{HH})/kT \\ &= \frac{1}{q_B(T)} \frac{1-\delta}{\delta} \exp - (E_A^h + E_A^i + E_X^h + 2\delta E_{HH})/kT.\end{aligned}\quad (15)$$

Hence
$$\frac{\delta^2}{(1-\delta)^2} = \exp - (E_A^h + E_A^i + 2\delta E_{HH} + 2\delta E_{II})/kT. \quad (16)$$

For the case $\delta \rightarrow 0$, this reduces to equation (4), but it must be borne in mind that for the very compounds that display variability of composition, and for the temperatures involved in the experimental studies of equilibria, δ is unlikely to be vanishingly small.

For comparison with (7) write

$$\left. \begin{aligned} \frac{\lambda(\theta)}{\bar{\lambda}} &= \frac{\theta^h}{1-\theta^h} \frac{1-\delta}{\delta} \exp - (2\delta - 2\theta^h) E_{HH}/kT, \\ \text{or, if } \delta \rightarrow 0, \quad \frac{\lambda(\theta)}{\bar{\lambda}} &= \frac{\theta^h}{1-\theta^h} \frac{1}{\delta} \exp 2\theta^h E_{HH}/kT. \end{aligned} \right\} \quad (17)$$

(17) is valid for compositions on the non-metal-rich side of the ideal; for crystals with stoichiometric excess of metal,

$$\left. \begin{aligned} \frac{\bar{\lambda}}{\lambda(\theta)} &= \frac{\theta^i}{1-\theta^i} \frac{1-\delta}{\delta} \exp - (2\delta - 2\theta^i) E_{II}/kT, \\ \text{or, for } \delta \rightarrow 0, \quad \frac{\bar{\lambda}}{\lambda(\theta)} &= \frac{\theta^i}{1-\theta^i} \frac{1}{\delta} \exp 2\theta^i E_{II}/kT. \end{aligned} \right\} \quad (18)$$

Equilibrium conditions of non-stoichiometric chemical compounds 77

It follows from the foregoing considerations that the range of composition accessible to any crystalline phase is determined by (a) the degree of disorder in the stoichiometric crystal (itself a function of the cohesion of the crystal lattice), and (b) the energies of interaction between lattice defects. On either side of the ideal composition is a bivariant range. The limiting concentration of interstitial atoms or of vacant sites which may be present without the crystal breaking up into a two-phase system increases rapidly with rising temperature; hence if this factor alone be considered, the range of existence of a crystal phase should be progressively wider at higher temperatures. The actual range of composition, at any temperature, however, involves also the degree of disorder δ (cf. (4), (5) and (17)), which determines the concentrations of interstitial atoms and of vacant sites that may be present simultaneously. If δ is very small, the range of composition is fixed, essentially, by the ratios E_{HH}/kT , E_{II}/kT ; the pressure of B_2 for equilibrium in the two-phase region is then a correspondingly large multiple of \bar{p} , the pressure in equilibrium with the solid phase.

If δ is not very small, two interesting cases can arise. First, it is possible for δ , the concentration of (e.g.) interstitial atoms in the stoichiometric phase to be greater than the maximum limiting concentration of those defects at any particular temperature (see figure 2). *The ideal composition AB then falls within the two-phase region*, and the ideal compound is metastable or non-existent. As was pointed out in the introductory section, this is exactly what is observed for a number of metallic oxides and sulphides. The number of well-established instances of the non-existence of the ideal compound is rather small, but it is perhaps not without significance that they are all compounds of rather high-melting metals (between interstitial atoms of which the cohesive forces might well be high), and that the compositions lie, in every case, on the non-metal-rich side of ideality.

The second possibility (cf. figure 3) is that the maximum permitted concentration of interstitial atoms is less than would coexist with the maximum concentration of vacant sites permitted by the value of E_{HH}/kT . *The crystal is then incapable of existence*. The limiting condition is readily established and bears a simple, and indeed an obvious, physical interpretation. The boundaries of existence of the phase coincide when

$$\frac{\lambda(\frac{1}{2})}{\lambda} = \frac{1-\delta}{\delta} \exp(1-2\delta) E_{\text{HH}}/kT = \frac{\delta}{1-\delta} \exp-(1-2\delta) E_{\text{II}}/kT. \quad (19)$$

From (19) and (17),

$$\exp(E_{\text{HH}} + E_{\text{II}})/kT = \exp-(E_A^h + E_A^i)/kT.$$

The limiting condition is thus that the expenditure of energy for the creation of a complementary pair of defects shall be at least as great as the energy of interaction of the defects. If

$$-(E_A^h + E_A^i) < (E_{\text{HH}} + E_{\text{II}}), \quad (20)$$

the phase must be unstable, as it would tend to unmix spontaneously into its components, or into one component and a compound of greater lattice energy.

The operation of these several factors may be illustrated by considering a hypothetical case. Suppose the existence of a compound AB such that $E_{II} = 9600$ cal., $E_{HH} = 6400$ cal., corresponding to the critical temperatures 2400 and 1600°K

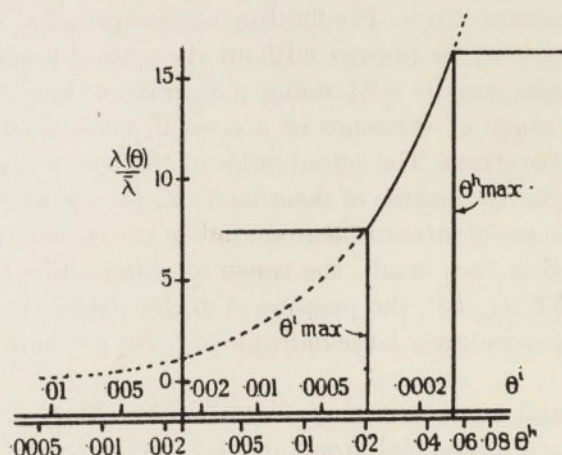


FIGURE 2. Illustrating non-existence of stoichiometric phase AB . Conditions for curve shown: $T_c = 1.6T$; $T'_c = 4T$; $\delta = 0.0025$; stoichiometric defect $= \theta^h - \theta^i$.

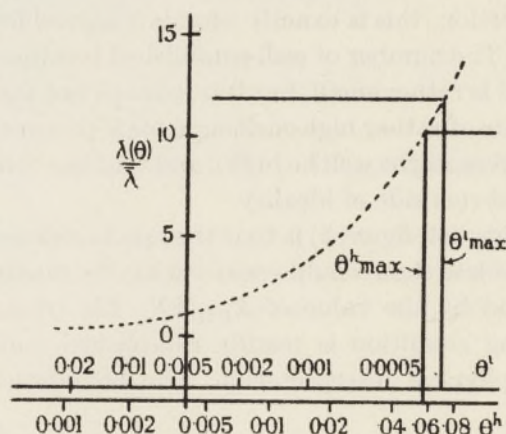


FIGURE 3. Illustrating non-existence of phase AB when intrinsic disorder too great. Conditions $T_c = 1.6T$; $T'_c = 4T$; $\delta = 0.004$.

respectively, and calculate the $(p, X)_T$ curves, and the range of composition of the AB phase, for three assumed values of δ , and at four temperatures. The limits of composition of the AB phase are listed in table 1 for these conditions; figures 4 and 5 show the variation in composition with change in relative pressure of B , $\lambda(\theta)/\bar{\lambda}$, for $\delta = 0.0001$ and 0.001 respectively at 700°K , and figure 6 shows the course of the pressure-composition isotherm for 1200°K , taking $\bar{\lambda} = 20$ mm. From table 1 will be seen the non-existence of the phase AB if δ is too great, i.e. for the case summarized in (20).

Equilibrium conditions of non-stoichiometric chemical compounds 79

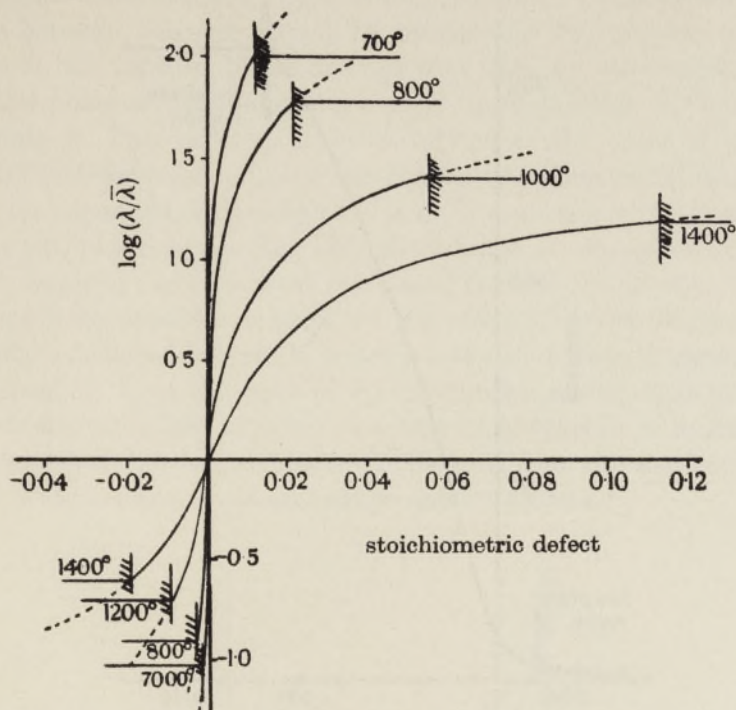


FIGURE 4. Variation of composition of phase AB , with partial pressure of B . Case A of table 1; $\delta = 0.0001$ at 700°K . Hatched lines indicate boundaries of existence of the phase at each temperature.

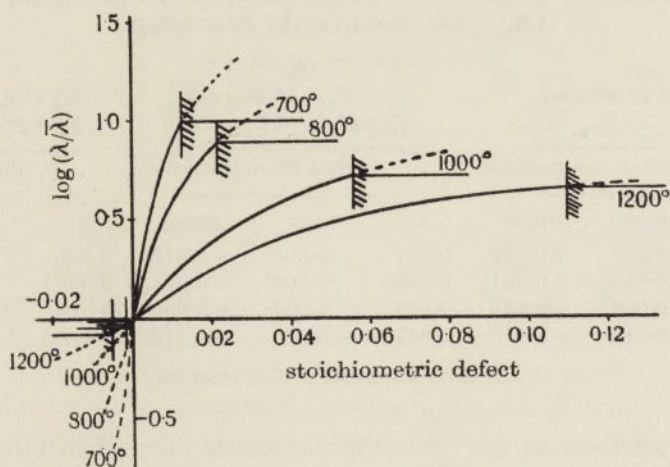


FIGURE 5. Variation of composition of phase AB with partial pressure of B . Case B of table 1; $\delta = 0.001$ at 700°K . Hatched lines indicate boundaries of existence of phase at each temperature.

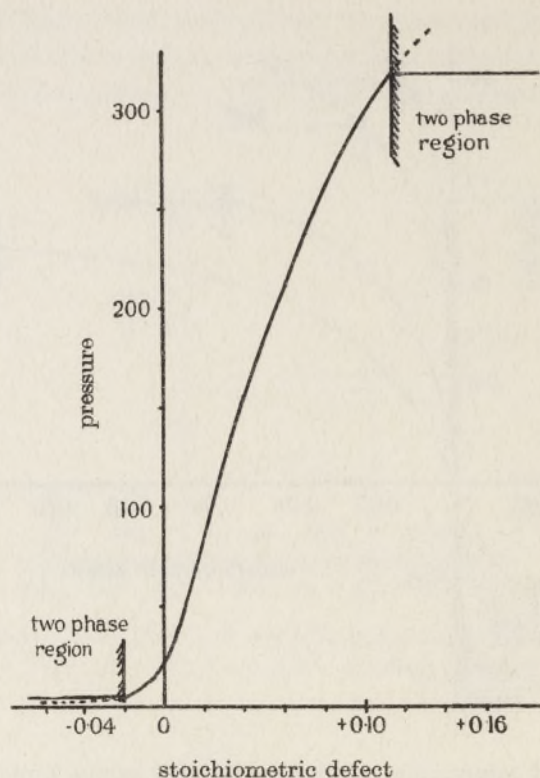


FIGURE 6

TABLE 1. LIMITS OF COMPOSITION OF CRYSTAL PHASE $AB_{1\pm n}$ FOR CONDITIONS SPECIFIED

temp. ° K	(A) $E_A^h + E_A^i = 25,800 \text{ cal.}$ $E_A^h + E_A^i > -(E_{HH} - E_{II})$			(B) $E_A^h + E_A^i = 18,900 \text{ cal.}$ $E_A^h + E_A^i > -(E_{HH} + E_{II})$			(C) $E_A^h + E_A^i = 14,800 \text{ cal.}$ $E_A^h + E_A^i < -(E_{HH} + E_{II})$		
	limits of composition			limits of composition			limits of composition		
	δ	lower	upper	δ	lower	upper	δ	lower	upper
700	0.0001	-0.001	+0.012	0.001	0.000	+0.012	0.005	*+0.028	+0.010
800	0.0003	-0.0025	+0.021	0.0024	0.000	+0.021	0.0097	*+0.054	+0.017
1000	0.0016	-0.009	+0.056	0.008	-0.002	+0.056	0.025	*+0.063	+0.043
1200	0.0046	-0.019	+0.113	0.0176	-0.005	+0.110	0.046	*+0.145	+0.087

* i.e. the compound is non-existent.

It has been assumed in the foregoing discussion that, when formation of the second solid phase takes place, no change occurs in the *B*-atom lattice. Such an assumption is, for most actual cases, obviously incorrect, but the general conclusions are not necessarily invalidated thereby. Consider the case of two compounds AB and AB_n , displaying a measure of mutual solubility in the manner discussed. Commencing with the stoichiometric AB phase, *B* atoms are built on to the lattice

Equilibrium conditions of non-stoichiometric chemical compounds 81

until at P (figure 7) the complementary defect-rich phase Q , based on the AB lattice, appears. In general, however, Q will be metastable with respect to a crystal of composition R , the limiting phase derived from AB_n by abstraction of B atoms. Similarly, the phase S , complementary to R , is metastable with respect to the AB -type phase P . The defect-rich phases formed at the onset of the two-phase system would therefore each undergo subsequent transformation into a more stable crystal lattice; hence the compositions P and R would mark the observable boundaries of the two-phase region. The immediate limits of composition of the AB and AB_n phases, however, remain those calculated from the properties of each phase alone; it should be possible to build up the AB - AB_n phase diagram out of two independently calculated halves. It is noteworthy that there is clear experimental evidence, especially from the work of Hüttig and his school, that in reactions involving the transformations of solids, the product of reaction is formed initially in the crystal lattice of the parent substance, changing from this metastable state into its own stable structure as a subsequent secondary process.

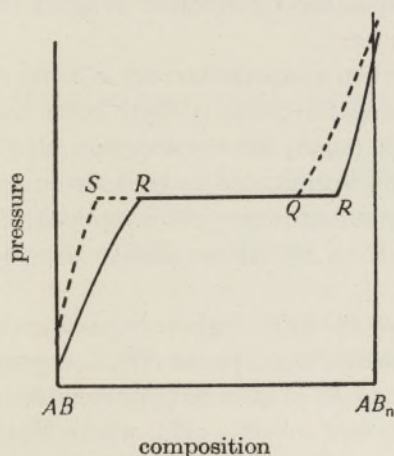


FIGURE 7

In concluding this section, it is worth considering the energy quantities introduced, in relation to the actual occurrence of marked deviations from stoichiometric composition amongst chemical compounds. The energies E_A^h , E_A^i , which determine the intrinsic thermal disorder δ , have been fully discussed by Jost (1933), and by Mott & Littleton (1938), who have shown that both are very much smaller than the lattice energy per ion pair, by an amount depending upon the polarization of the ions surrounding each defect. It has been concluded that for NaCl-type crystals, in which the occurrence of interstitial ions is relatively improbable on steric grounds,*

* In such a case—e.g. Mott's model of an alkali halide crystal with F -centres—withdrawal of B atoms from the lattice will leave the stoichiometric excess of A on proper A lattice points, with a preponderance of holes in the B lattice. Only two types of defect—vacant A sites and vacant B sites respectively—are important over the whole range of composition, and no change in our reasoning is introduced.

the creation of Schottky-type defects involves about 1 eV per pair of holes created. This would give for $\exp - (E_A^h + E_A^i)/kT$ at the ordinary temperature about 10^{-16} , but the actual concentration of defects δ may be two or three powers of ten greater than this, as two factors have been explicitly neglected. These are (a) the effect of defects upon the vibrational frequencies of the neighbouring lattice points, and (b) the variation of E_A^h, E_A^i with the volume of the crystal. This latter factor must be particularly important where gross deviation from stoichiometric composition occurs. It is significant that most of the compounds known to display marked variability of composition are the sulphides, selenides, etc., of transition metals and metals of the *B*-subgroups—i.e. compounds in which both anion and cation are relatively highly polarizable, and in which the binding forces partake of a considerable measure of homopolar character. Hence the energies E_A^h, E_A^i are likely to be very much smaller than in crystals built up from inert-gas-like ions (e.g. NaCl). The degree of intrinsic lattice disorder must be correspondingly greater than in the latter: one may cite the concentration of interstitial silver ions in silver bromide -8.3×10^{-6} at 20° —extrapolated by Koch & Wagner (1937) from their measurements at higher temperatures.

The energy E_X^h , gained when a supernumerary *B* atom condenses on to the lattice, may be either positive or negative; into it there enter factors similar to those considered by Gurney & Mott (1938) for the creation of *F*-centres in alkali halides. Qualitatively, the sign of E_X^h is indicated by the existence or non-existence of higher compounds. Thus, we may consider the following cycle of operations.

(i) Remove an A^+ ion from its lattice site to the gas phase. Work expended = $+W_A$.

(ii) Ionize the A^+ ion to its next higher valence state, A^{++} , and transfer the electron to a *B* atom in the dilute gas phase. Work expended = $+W_A + I_{A^+} - E_B$.

(iii) Condense the A^{++} and B^- ions on to appropriate lattice points on the surface of the crystal. Work expended = $-W_{A'} - W_B$, where $W_{A'} > W_A$ owing to the higher ionic charge now borne by the *A* atom, and W_B is the work of removal of a *B* atom from the lattice.

For the total energy change in the process,

$$E_X^h = I_{A^+} - E_B - (W_{A'} - W_A) - W_B.$$

Without considering in detail the relation of $W_A, W_{A'}, W_B$ to the lattice energy of the crystal (cf. preceding paragraph), it is evident that E_X^h depends upon the difference between the nett expenditure of energy in the ionization process and the nett gain in cohesive energy of the crystal. If I_{A^+} be too great, the higher compound (AB_2 in the case considered) cannot exist, nor (cf. equation (10)) will the compound *AB* display marked variability of composition under accessible conditions of investigation; variability of composition must necessarily run parallel to the display of a multiplicity of valence states and is most markedly displayed by compounds derived from the intermediate valence states of multivalent metals.

The free energy of a solid is a function of the volume, and in the present discussion

Equilibrium conditions of non-stoichiometric chemical compounds 83

it has been tacitly assumed that the degradation or building up of the crystal lattice containing a fixed number N_A of A atoms proceeds at constant volume. This assumption is not true; the volume is actually a function not only of the temperature but also of the stoichiometric excess of B . Hence (cf. Mott & Gurney 1940) the energies of production and of interaction of defects must themselves vary both with temperature and composition. It has been assumed that, in the maintenance of electrostatic balance within the crystal, positions of electron defect or excess have not been localized in the lattice; electrons have been withdrawn from the full band of the crystal (leaving positive holes, where B has been in excess), or placed in the conduction band (where B has been deficient). The mean cationic charge, and therefore the lattice energy, however, varies directly with the composition, and the changes in the cohesion of the lattice are shown by very appreciable alterations of lattice parameter. Thus Hägg & Sucksdorff (1933) found that the volume of the unit cell of ferrous sulphide shrank from 59.8 to 57.3 Å³ as the sulphur content rose from approximately 50 to 55 atoms %. The effect is therefore of considerable magnitude, and must be taken into account in any precise treatment of the problem.

COMPARISON WITH EXPERIMENT

The experimental material, available in the literature, for comparison with the theoretical model is rather sparse. Except for studies of metal hydrides, no published investigations have been made with the express purpose of investigating fully the (p, T, X) relations of systems with non-stoichiometric phases; the interest of chemists has been directed, rather, towards deriving thermochemical data from the univariant equilibria in the two-phase regions. Moreover, in the relevant portions of the $(p, X)_T$ or $(T, X)_p$ figures, the composition of the solid phase is very susceptible to small changes in the independent variable. Where, as in the procedure usually employed, the composition of the solid is inferred from the quantity of the volatile component progressively removed during degradation experiments (cf. Biltz & Juza 1930, and the examples from the Hanover school discussed below), reliance is placed upon diffusion processes in the solid phase (which may well be very slow in such compounds as the sulphides of the bivalent metals) to establish true equilibrium between gaseous component and a solid phase of known gross composition, rather than between vapour and a solid phase of quite unknown composition, possibly relatively few atomic layers thick, on the surface of the solid particles. The peculiar form of the isotherms suggests that some of the careful investigations by Biltz and his co-workers may be affected by such false equilibria.

Most of the systems for which sufficient data are available have been examined from the standpoint of our model; results for a few of them are quoted here. One can proceed by the following semi-empirical method, utilizing the measure equilibrium pressures, $p(\frac{1}{2})$. By inspection of the $(p, X)_T$ isotherms, the critical temperatures T_c, T'_c , which measure the interaction between vacant sites and interstitial atoms, can be estimated. Then, calculating the ratio $p(\theta)/p(\frac{1}{2})$ from equations (10)

and (11), the pressure-composition diagram can be calculated. In the neighbourhood of the stoichiometric compound the intrinsic degree of disorder is of importance; this can be estimated for one particular temperature by fitting one point of the isotherm to an experimental value or, ideally, could be derived without assumptions from the ratio of the two-phase pressures bounding the phase (equations (17), (18) and (16)). The essential point is that these three estimated quantities should suffice to reproduce the (p, T, X) equilibria of the non-stoichiometric phase over its entire range of existence. Having regard to the experimental uncertainties, this test of the model is not very rigorous, but the assumptions made at the outset preclude any possibility of calculating the whole equilibria from first principles.

The system Pt-PtS-PtS₂

This system may be discussed in some detail, as illustrating the application of the model. The experimental material consists of tensimetric measurements by Biltz & Juza (1930) at 616, 651 and 691° C in the range PtS-PtS₂, and at 1060, 1110 and 1186° C in the range Pt-PtS; PtS₂, PtS and metallic platinum were the only solid phases found. In the PtS-PtS₂ region, equilibria were attained only sluggishly, and the recorded pressures show a good deal of random variation; the data do not suffice to show whether, or to what extent, the PtS₂ phase is variable in composition. It is evident, however, that the PtS phase exists over a range of compositions, covering both sides of the ideal formula, but particularly wide on the sulphur-rich side. The platinum phase, at high temperatures, also takes up a considerable proportion of sulphur (i.e. of PtS) in solid solution. Although there is no evidence how extra sulphur is accommodated in the PtS lattice, the most plausible mechanism for the transition of the unique PtS (cooperite) structure (Bannister 1932) into the CdI₂-type layer lattice of PtS₂ (Thomassen 1929) is by the omission of platinum atoms from alternate layers of the structure. The PtS phase may well, therefore, contain as defects, vacant platinum sites and interstitial platinum atoms.

The equilibrium pressures used by Biltz & Juza for thermochemical calculations do not accord well with their recorded data. Accordingly, for the partial pressures of S₂ molecules in the two-phase regions, values are taken agreeing better with their published figures, namely,

PtS + PtS ₂	616° C	$p(\frac{1}{2})$	42 mm.	Pt + PtS	1060° C	$p'(\frac{1}{2})$	36 mm.
	651°		110 mm.		1110°		95 mm.
	691°		323 mm.		1186°		313 mm.

The form of the 691° isotherm shows it to be close to the critical isotherm for the PtS₂-PtS region, and 960° K is taken as T_c . The ratio of the pressures $p(\frac{1}{2})$ and $p'(\frac{1}{2})$ bounding the PtS phase should (from equations (17) and (18)) relate the intrinsic lattice disorder δ directly to T_c and T'_c , which govern the breadth of the composition range. The few temperatures investigated, and the scattering of the data, make the necessary extrapolation of $p(\frac{1}{2})$ and $p'(\frac{1}{2})$ rather uncertain. The measured pressures

in the neighbourhood of the ideal composition PtS are compatible, however, only with a degree of intrinsic lattice disorder considerably greater than that so calculated, using the best values for T_c and T'_c . This is not surprising, and does not necessarily invalidate the model, as the approximations made at the outset lead, as has already been mentioned (cf. Mott & Gurney 1940), to too small apparent concentrations of thermal defects. The data are best fitted by taking $T'_c = 1700^\circ \text{K}$ and $(E_A + E_A')$ for PtS about 12,300 cal. (combination of the values of T_c , T'_c and $p(\frac{1}{2})/p'(\frac{1}{2})$ gives $(E_A + E_A') = \text{about } 20,000 \text{ cal.}$); T_c for interstitial sulphur in the platinum phase = 1600° . These values lead to the equilibrium diagram shown in figure 8, from which the PtS_2 phase is omitted on account of the paucity of data.

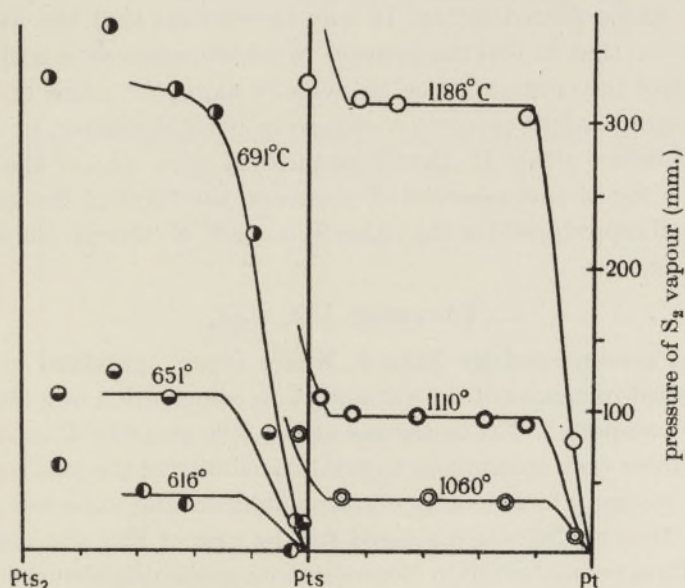


FIGURE 8. System Pt-PtS-PtS₂. Circles show experimental points of Biltz & Juza.

Sulphides of the iron-nickel triad

Iron, cobalt and nickel each form sulphides of the types MS, MS₂. FeS₂, CoS₂ and NiS₂ have the cubic pyrite structure; FeS, CoS and NiS (above 396° , the transition temperature of the trigonal millerite) have the hexagonal nickel arsenide structure. The equilibria in these systems have been investigated by Juza & Biltz (1932, FeS-FeS₂), Hülsmann & Biltz (1935, CoS-CoS₂) and Voigt, Meisel & Biltz (1936, NiS-NiS₂) respectively. The monosulphides display the most gross departure from stoichiometry, both FeS and CoS of ideal formula being apparently non-existent. The equilibria in the neighbourhood of the pyritic phase have been insufficiently studied, but both NiS₂ and CoS₂ take up a considerable excess of sulphur (up to NiS_{3.5} and CoS_{2.8} at least); this is probably achieved by incorporation of S₂ molecules on the lattice positions normally occupied by S₂²⁻ groups, with metal lattice sites left vacant. Similar data for FeS₂ are incomplete, but the observations of Smith (1942)

on the variability in properties of pyrite can be interpreted on a similar basis, and suggest that a relatively high degree of intrinsic lattice disorder obtains in stoichiometric FeS_2 . This is in accord with the apparently small ratio $\bar{p}/p(\frac{1}{2})$ for the pyritic phases, but in each case the data in this range of composition are both scanty and suggestive of hysteresis effects.

The data for nickel sulphide are rather well reproduced on the assumption that $T_c = 990^\circ \text{K}$ (figure 9). The cobalt and iron sulphides, however, show the limitations imposed by the approximations of the model, in that while the non-existence of the stoichiometric phase can be accounted for, the equilibrium pressure of sulphur rises too steeply, and to too high a value in the two-phase region. It is as if the increase in sulphur activity, and in the internal energy of the lattice, were at first offset by some unconsidered factor. It may be relevant that the work of Hägg & Sucksdorff showed that in FeS the increase in sulphur content is accompanied by a large shrinkage of the crystal lattice, principally along the c axis of the hexagonal cell; this anisotropy might point to a change in bond character, or a non-random distribution of defect sites. If, purely empirically, the zero of the θ - p curves is adjusted to the toe of the observed X - p curves, the form of the cobalt-sulphide isotherms is well reproduced for the value $T_c = 1000^\circ \text{K}$, though the agreement has little significance.

The system UO_3 - U_3O_8

This system, investigated by Biltz & Müller (1927), provided one of the first clearly established instances of the variability in composition of a chemically well-defined binary compound. The isotherms at 500, 580 and 610°C show very clearly the transition from very incomplete to total miscibility of the two compounds, the 580° isotherm having a form closely corresponding to that expected at the critical temperature. However, as was discussed for the case of PtS , the degree of lattice disorder in U_3O_8 agreeing best with measurements in the neighbourhood of the ideal composition is greater than that calculated from the ratio of the two-phase pressures bounding the phase. The composition varies so steeply with oxygen pressure close to this composition that some of the experimental points may be regarded as uncertain. The data of Biltz & Müller suggest that UO_3 of ideal composition does not exist, and as in the case of the grossly non-stoichiometric FeS and CoS phases, the model is not adequate to reproduce quantitatively the corresponding portion of the equilibrium diagram (cf. figure 10).*

Anomalous mixed crystals

There is another phenomenon which can be considered within the scope of this discussion, namely, the formation of anomalous mixed crystals between compounds of different formula types. The extent to which this can occur was perhaps first clearly shown when Vogt (1914) showed that the mineral yttrifluorite is a solid solution of yttrium fluoride YF_3 in calcium fluoride CaF_2 . The essential mechanism of such solid solubility, contrary to the Mitscherlich law of isomorphism,

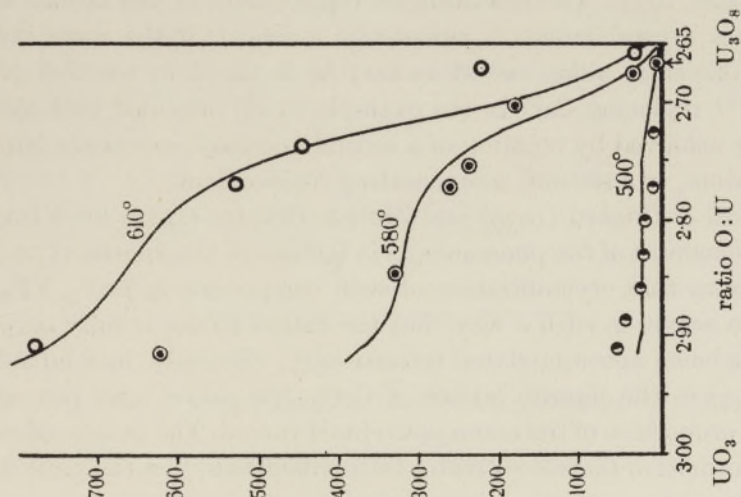


FIGURE 10. System $U_3O_8-2UO_3$. Circles show experimental points of Biltz & Müller.

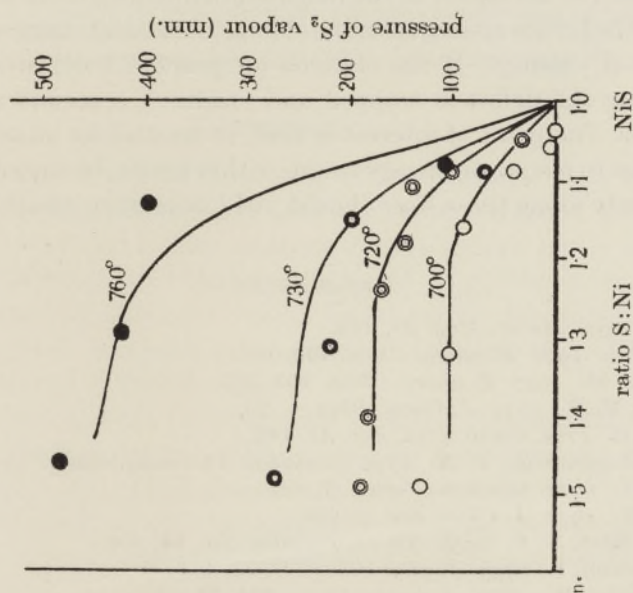


FIGURE 9. Part of system $NiS-Ni_3S_2$. Circles show experimental points of Voigt, Meisel & Biltz.

was perceived by V. M. Goldschmidt, who saw in it a process of great geochemical significance, governing the distribution of the rarer elements in the earth's crust (Goldschmidt 1926, 1937). The condition for replacement of one atomic species by another within a crystal lattice is essentially metrical; if the ionic radii of the elements are sufficiently alike, one atom may be replaced by another of different valency (e.g. Y^{3+} replacing Ca^{2+} in the example cited) provided that electrostatic balance may be achieved by creation of a second anomaly—a vacant lattice point, an interstitial atom, or a second, compensating replacement.

Recently, Zintl & Udgård (1939) and Zintl & Cruatto (1939) have investigated in detail the mechanism of the phenomenon in lattices of the fluorite type, and have conclusively shown that crystallization of such compounds as LaF_3 , YF_3 , ThF_4 in the CaF_2 lattice occurs in such a way that the cation lattice is fully occupied, the excess of anions being accommodated interstitially. Similarly, in solid solutions of La_2O_3 ($= LaO_{1.5}$) in the fluorite lattice of CeO_2 , the cation sites are again fully occupied, but a proportion of the anion positions is vacant. The process of anomalous mixed crystal formation therefore creates lattice defects in just the same manner as does the valency change of one component of a 'pure' compound, in equilibrium with varying partial pressures of the volatile component. The limiting composition of the mixed crystals, and the dependence of miscibility upon temperature, should therefore be governed by the considerations developed in this paper.

Moreover, if one can regard the energy of interaction between defects as arising from strain energy in the lattice, two factors can be distinguished that contribute to it: the distortion of the lattice in the neighbourhood of the defect, and the dimensional change in the lattice arising from the change in size and charge of the ion undergoing a change of valency. If the electron (or positive hole) introduced into the lattice in creating the defect is trapped and localized, a second source of lattice distortion results. The point of interest is that, in anomalous mixed crystals, these two contributions to the strain energy could, within limits, be varied independently. A systematic study along these lines should yield interesting results.

REFERENCES

- Bannister, F. A. 1932 *Miner. Mag.* **23**, 188.
 Biltz, W. & Juza, R. 1930 *Z. anorg. Chem.* **190**, 161.
 Biltz, W. & Müller, H. 1927 *Z. anorg. Chem.* **163**, 257.
 Foote, F. & Jette, E. R. 1933 *J. Chem. Phys.* **1**, 29.
 Fowler, R. H. 1936 *Proc. Camb. Phil. Soc.* **32**, 144.
 Fowler, R. H. & Guggenheim, E. A. 1939 *Statistical Thermodynamics*. Camb. Univ. Press.
 Goldschmidt, V. M. 1926 *Geochem. Verteil.* **7**, 88.
 Goldschmidt, V. M. 1937 *J. Chem. Soc.* p. 655.
 Gurney, R. W. & Mott, N. F. 1938 *Trans. Faraday Soc.* **34**, 506.
 Hägg, G. & Sucksdorff, I. 1933 *Z. phys. Chem. B*, **22**, 444.
 Hülsmann, O. & Biltz, W. 1935 *Z. anorg. Chem.* **224**, 73.
 Jost, W. 1933 *J. Chem. Phys.* **1**, 466.
 Juza, R. & Biltz, W. 1932 *Z. anorg. Chem.* **205**, 273.
 Klemm, W. & Hass, K. 1934 *Z. anorg. Chem.* **219**, 82.
 Koch, E. & Wagner, C. 1937 *Z. phys. Chem. B*, **38**, 295.

- Lacher, J. R. 1937 *Proc. Roy. Soc. A*, **161**, 525.
 Miller, P. H. 1941 *Phys. Rev.* **60**, 890.
 Mott, N. F. & Gurney, R. W. 1940 *Electronic processes in ionic crystals*. Oxford: Clarendon Press.
 Mott, N. F. & Littleton, M. J. 1938 *Trans. Faraday Soc.* **34**, 485.
 Schottky, W. & Wagner, C. 1930 *Z. phys. Chem. B*, **11**, 163.
 Smith, F. G. 1942 *Amer. Min.* **27**, 1.
 Thomassen, L. 1929 *Z. Phys. Chem. B*, **2**, 349.
 Vogt, T. 1914 *N. Jb. Min.* **2**, 9.
 Voigt, A., Meisel, K. & Biltz, W. 1936 *Z. anorg. Chem.* **228**, 275.
 Zintl, E. & Croatto, U. 1939 *Z. anorg. Chem.* **242**, 79.
 Zintl, E. & Udgård, A. 1939 *Z. anorg. Chem.* **240**, 150.

The helium content of atmospheric air*

BY E. GLÜCKAUF AND F. A. PANETH

Chemistry Department, University of Durham

(Communicated by S. Chapman, F.R.S.—Received 2 November 1944)

Figures are given for the helium content of air both on the earth's surface and at heights up to 25 km. No variations exceeding the limits of the analytical error ($\pm 0.2\%$) have been found in air samples from all over the surface of the globe, and no significant changes have been observed in air up to 20 km. height; however, a small and varying surplus of helium averaging about 3% above the normal helium content was present in samples from 20 to 25 km. height. It follows from these results that at least up to 25 km. height, gravitational separation of the constituents has no appreciable effect on the composition of atmospheric air.

1. INTRODUCTION

In 1939, in a discussion at a joint meeting of the Chemical Society, the Physical Society and the Royal Meteorological Society, brief reference was made to new methods for the ozone and helium analysis of atmospheric air; a few results only were given, while it was stated that details would be published elsewhere (Paneth 1939; see also Paneth & Glückauf 1935). As far as the determination of ozone is concerned, this promise has been fulfilled in the meantime (Edgar & Paneth 1941; Glückauf, Heal, Martin & Paneth 1944).

The present paper, and the following one, give the complete information on the helium analyses. The main object of these analyses was to find out whether there is a gravitational separation of the gases of the atmosphere at heights from which air samples can be obtained; as a preliminary step, however, it was necessary to determine whether the helium content of the air at ground level is constant.

In spite of the fact that since the early days of modern chemistry innumerable analyses of atmospheric air have been carried out, not much is known about the

* 'Helium Researches, XVI.' For previous papers of the series see 'Helium Researches, XV' (*Proc. Roy. Soc. A*, **165**, 238, 1938).