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Current Problems in Nonstoichiometry

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Four problems confronting the chemistry of solids are surveyed. From statistical thermodynamics the occurrence of nonstoichiometry can be reasonably correlated with the valence properties of the elements, but theory is obviously too crude to cover grossly nonstoichiometric compounds. Lattice energy calculations can lead to the conclusion that all nonstoichiometric phases should be metastable and numerous ordered intermediate binary phases have recently been discovered. Estimates of the endothermicity of defective structures disagree with reliable equilibrium measurements. Interactions between lattice defects are therefore considered, and attention is directed to lattice relaxation, short range ordering, and the nature of defect clusters or complexes in real systems. On this basis conflicting arguments can probably be reconciled. Attention is finally drawn to the still unresolved question of what factors limit the existence range of a phase in any specific case.

Chemical thought was dominated by the law of constant composition for 120 years, in the sense that a fixed composition and a rational formula were taken as the definitive criteria for a compound. As applied to solid compounds, the law was not a generalization from experimental fact. The controversy between Berthollet and Proust was unsatisfactory; it was settled by a dogmatic, but natural, extrapolation of the conclusions drawn by Dalton from the atomic theory. These are inherently valid for discrete molecules. Until physical scientists were ready to think of crystalline inorganic compounds as infinite three-dimensional assemblics of atoms, the stage was not set for reopening this particular aspect of the recurrent problem of the strictly quantized or the statistical and quasicontinuous description of natural phenomena.

Editor's Note. The symbolism used in this article is that of A. L. G. Rees of the Australian Commonwealth Scientific Research Industrial Organization, while that used by other authors in the symposium is that of F. A. Kroger and H. J. Vink of Phillips Research Laboratories. This was pointed out to the author, who feels that, of the accepted symbolisms for defect solids, that of Rees is best suited to convey the chemical and structural information required.

Since about 1930, but especially in the last few years, the concept of nonstoichiometric compounds has been a stimulating influence in inorganic chemistry. It has opened up new ideas; it has led to much new work on the constitution and the valence problems of inorganic compounds; it has shed light on the mechanism of reactions taking place in the solid state. Indeed, it goes to the roots of our ideas about the definition of a chemical compound.

It has become clear, however, that some serious problems remain unsolved. A real divergence has arisen between the essentially structural and the essentially thermodynamic ideas, and the attractive clarity of our theoretical outlook has been blurred. This introductory symposium paper seeks to formulate some questions that need to be answered.

We note certain key stages in the development of the subject, which point ahead to the still unresolved problems. Kurnakov's work (1910–14) really reopened the dormant issue. Systematic studies of heterogeneous equilibria had revealed solid solutions and intermediate phases in many (especially in intermetallic) systems. By studying a range of quantitative properties across equilibrium diagrams, Kurnakov showed that singularities or turning points of values of physical properties—maxima of melting points, maxima or minima of electrical conductivity or of thermoelectric power, etc.—did not necessarily coincide with the compositions assigned to intermediate phases of rational formula. He recognized that this implied a certain indeterminacy in defining intermetallic or quasimetallic compounds, and described them as berthollides [Kurnakov, 1914 (25)]. Because he was chiefly concerned with intermetallic systems—to which it is still generally considered that one must extend a good deal of chemical license—his work did not immediately have much impact on theory.

The palladium-hydrogen system presented another long-standing anomaly. The relation of hydrogen to the metals can be given a formal thermodynamic description in terms of solid solutions, but the uniquely high sorption of hydrogen in palladium evinced evidence of highly specific—i.e., chemical—forces of interaction. This was probably the first nonstoichiometric system for which equilibrium measurements were made (Hoitsema, 1895; Gillespie, 1926), revealing two nonstoichiometric ranges which merged into a single phase above 568° C. at 20 atm. The stoichiometry of the β phase constituted a puzzle, for although Procrustean reasoning assigned to it the formula Pd_2H, its formula was irrational and dependent on the equilibrium hydrogen pressure, with isotherms rising very steeply for hydrogen contents exceeding $PdH_{0.6}$. It was early recognized that hydrogen must be present as H atoms, not H_2 molecules. With the additional evidence furnished by x-ray diffraction and, more especially, by neutron diffraction studies, it has since become clear that the palladium-hydrogen system is not peculiar, but exemplifies features—e.g., partial occupancy of crystallographic sites, the problems of composition limits and of the succession of phases of related structure—which must find a natural place in any successful theory of nonstoichiometric compounds.

Because intermetallic systems undoubtedly display certain special features that follow from their metallic binding forces, considerable importance attached to the growing evidence that the chalcogenides, the essentially ionic oxides, the nitrides, and other representative binary compounds of the transition metals were, not infrequently, both variable and irrational in composition. Schenck and Dingmann's equilibrium study of the iron-oxygen system (39) was notable in this connection: They showed that stoichiometric ferrous oxide, $FeO_{1.000}$, the oxide of an important and typical valence state, did not exist. It lay outside the broad existence field of a nonstoichiometric phase. It is, perhaps, still not certain whether the wüstite phase extends just to the stoichiometric composition at the lowest extreme of the limited range over which it is stable, but in general much accurate work on this most important system has confirmed the first conclusions. A great deal more evidence of the same kind, extending over much of the periodic system, came from the lengthy series of papers by Biltz and his coworkers on the systematic doctrine of affinity, which added an immense fund of reliable information on the dissociation equilibria and the succession of phases in the oxides, sulfides, selenides, arsenides, etc., of the metals, together with x-ray diffraction data, densities, and magnetic and other properties bearing on the existence and constitution of compounds of variable composition.

Yet more important was the publication by Schottky and Wagner (1930) of their classical paper on the statistical thermodynamics of real crystals (*41*). This clarified the role of intrinsic lattice disorder as the equilibrium state of the stoichiometric crystal above 0° K. and led logically to the deduction that equilibrium between the crystal of an ordered mixed phase–i.e., a binary compound of ionic, covalent, or metallic type–and its components was statistical, not unique and determinate as is that of a molecular compound. As the consequence of a statistical thermodynamic theorem this proposition should be generally valid. The stoichiometrically ideal crystal has no special status, but the extent to which different substances may display a detectable variability of composition must depend on the energetics of each case–in particular, on the energetics of lattice disorder and of valence change. This point is taken up below, for it is fundamental to the problems that have to be considered.

The Schottky-Wagner papers gave a background against which to view the experimental facts. Ferrous oxide and palladium hydride appeared as striking instances of a more general phenomenon; nonstoichiometry could be given an exact structural meaning. Thus the FeO_{1+x} and FeS_{1+x} phases were recognized, from their cell dimensions and densities, as iron-deficient, with an excess of cation vacancies [Jette and Foote, 1932 (*23*)] and (as far as the evidence then went) a sensibly perfect oxygen or sulfur sublattice. The work of Ehrlich (1939, 1949) (*16*) on titanium oxides and chalcogenides, and of Haraldsen (1937) (*21*) and Tengner (1938) (*44*) and others on transition metal sulfides and selenides, revealed how remarkably incomplete the occupancy of lattice sites could be.

At the other end of the composition scale, the predicted widespread occurrence of slight nonstoichiometry linked up with the mechanisms of solid state reactions and with the properties of semiconductors. To preserve electrostatic neutrality, with the creation of cation vacancies or of interstitial cations in an ionic crystal there must go a corresponding number of positive holes and electrons. To the chemist, these excess charges, localized, must correspond to some chemically and energetically reasonable species. Wagner and his pupils (1933, 1936) formulated a quantitative theory (*47*) of the kinetics of solid state reactions, and especially of the oxidation of metals, in terms of the mobility of point defects and of positive holes or electrons. As semiconductor physics has developed, it has been found that measurements of the concentrations of current carriers provide by far the most sensitive means of detecting and measuring very small deviations from stoichiometry, and of studying the dissociation equilibria of nearly stoichiometric compounds.

Problem 1. The Occurrence of Nonstoichiometry

The observed facts fall into two groups:

1. For certain compounds, stoichiometric deviations are detectable but, in general, are very small: within the range only of special analytical experiments or of methods based on direct determination of carrier concentrations. Examples are PbS_{1+x}, Cu_2O_{1+x}, ZnO_{1-x}, alkali halides containing *F*-centers, etc. It is reasonable to assume that the stoichiometric deviation is small enough for the lattice defects to be isolated and randomly distributed, so that the Schottky-Wagner theoretical treatment properly applies (possibly with some correction for activities in place of concentrations).

2. At the other extreme—and it is with these that this paper and this symposium must be chiefly concerned—are the crystals which show gross departure from ideal stoichiometry—e.g., $Fe_{0.84}O$, $Ti_{0.96}O_{0.96}O_{0.69}$ to $Ti_{0.74}O_{0.98}$, $NiTe_{1.0}$ to $NiTe_{2.0}$, etc. Even a zeroth order treatment, in which the lattice defects are regarded as randomly distributed, shows that a high proportion of atoms have an incomplete coordination environment, and a high proportion of vacant lattice sites or of interstitials must be adjacent to one another. The stability of such defective crystals, as compared with alternative structures, is a serious question.

In view of the very wide differences indeed between different substances it is pertinent to inquire whether all ionic, covalent, and metallic binary phases are variable in composition, and what factors determine the quantitative differences actually observed.

Knowledge on the first point is incomplete, largely because interest has been so concentrated on a few classes of compounds—notably the oxides, hydrides, sulfides, nitrides, etc., of the transition metals—but partly for a deeper reason. Ormont (1959) (*32*) has pointed out that the question is not meaningful beyond a certain limit, set by the inherent properties of the stoichiometric material and by the attainable purity of experimental samples. If the vacancies or interstitials produced by nonstoichiometry are outweighed by those present as a result of intrinsic lattice disorder, or if the charged carriers created by nonstoichiometry are fewer than those conferring intrinsic conductivity, there is no means of detecting them. It appears from the available evidence that, above their Tammann temperatures—i.e., when inner equilibrium is attainable—many typical ionic compounds contain more than 10^{16} to 10^{17} defect pairs per cubic centimeter. Only methods based on counting electrons (or positive holes) would give evidence of nonstoichiometry below a mole fraction of 10^{-4} to 10^{-5}. Such compounds as the silicides, arsenides, etc., of transition metals frequently have high intrinsic electronic conductivity; stoichiometric deviations below the direct analytical limit may well be inaccessible to observation. In any case, intrinsic properties may be swamped by the effects of impurities, and especially by the variable-valence impurities such as iron. There are very few materials, outside the small range that have been intensively studied as semiconductors, for which the total impurity concentrations have been reduced to 10^{-6}. There is thus a limit beyond which fixity or variability of composition has no operational meaning.

As an example, it appears still uncertain whether the high temperature conductivity of very pure magnesium oxide, and the way it varies with the ambient oxygen pressure, involves any measure of nonstoichiometry, or whether it is wholly attributable to residual impurities [Mitoff, 1959 (29)]. At very high temperatures the conductivity of refractory oxides may be intrinsic, and may mask any displacement of stoichiometric equilibrium.

To explore the factors that determine how far nonstoichiometry may be observed in practice, we may consider the straightforward case of an oxide, MO, in which the intrinsic lattice disorder is of Frenkel type. It will be involved in simultaneous internal and external equilibria which [using the symbolism of Rees (1954) (33)] may be represented by the equations:

$$\mathrm{M^{2+}}|\square + \Delta \rightleftharpoons \square_{+} + \mathrm{M^{2+}}|\Delta \tag{1}$$

$$\mathrm{M\ gas} + \Delta + 2\,\mathrm{M^{2+}}|\square_{+} \rightleftharpoons \mathrm{M^{2+}}|\Delta + 2\,\mathrm{M^{+}}|\square_{+} \tag{2}$$

$${}^{1}/_{2}\,\mathrm{O_2} + 2\,\mathrm{M^{2+}}|\square_{+} \rightleftharpoons 2\,\mathrm{M^{3+}}|\square_{+} + \square_{+} + \mathrm{O^{-2}}|\square_{-} \tag{3}$$

$$2\,\mathrm{M^{2+}}|\square_{+} \rightleftharpoons \mathrm{M^{3+}}|\square_{+} + \mathrm{M^{+}}|\square_{+} \tag{4}$$

For convenience, Equations 2 and 3, which represent alternative ways of writing the nonstoichiometry reaction, show the positive holes or electrons as trapped at cation positions. Equilibria 2 and 3 are linked through the intrinsic disorder process (Equation 1), the intrinsic conduction equilibrium (Equation 4), and the Gibbs-Duhem relation ($n_1\delta\mu_1, + n_2\delta\mu_2 = 0$) between the thermodynamic potentials of the components in equilibrium with the crystal. Reaction 3 is usually the more convenient to translate into experimental terms.

Examination of the equilibrium conditions shows that the equilibrium constant for intrinsic disorder (Equation 1) involves only the (endothermic) energy needed to create a complementary pair of defects in the ordered, stoichiometric crystal lattice. Writing $\overline{N}^h$, $\overline{N}^i$ as the number of cation vacancies and of interstitial cations, respectively, in a stoichiometric crystal with N lattice sites in all, at an expenditure of energy denoted by E^h, E^i, respectively, then the intrinsic disorder, ζ, is given by Equation 5.

$$\zeta = \frac{\overline{N}^h}{N} = \frac{\overline{N}^i}{N} = \text{const. exp. } -(E^h + E^i)/2kT \tag{5}$$

The energy changes in the processes represented by Equations 2 and 3 involve not only the creation or elimination of lattice defects but the essentially chemical factors:

1. The ionization energy of M, or the dissociation energy and electron affinity of the nonmetal, for the incorporation of either component in the crystal lattice.
2. A valence change on the part of cations proper to the crystal lattice—and it is here that the energetic accessibility of other valence states enters the argument and the frequent occurrence of nonstoichiometry among transition metal compounds falls into place.
3. The change in local Madelung energy resulting from changes in ionic charge, partially offsetting the energy change (2).
4. The energy of relaxation of the crystal lattice immediately around the lattice defects and, more particularly, around the altervalent ions.

In the subsequent discussion it is argued that this last merits more attention than it has, on the whole, received.

The net ΔE or ΔH for incorporation of excess of either component in the stoichiometric phase can be either negative or positive. Whether the equilibrium constants of Reactions 2 and 3 permit of significant deviations from stoichiometry therefore depends largely on the term $T\Delta S$, in which the configurational entropy of random distribution of defects is the dominant factor. Even if ΔH is large and positive, nonstoichiometry might become significant at high enough temperatures.

What determines whether nonstoichiometric behavior can readily be observed is largely the form of the dissociation pressure–composition isotherms in the equilibrium diagram. If the free energy rises too steeply with excess of either component, it may not be practicable to detect stoichiometric changes which, in principle, are taking place. The explicit relation between the stoichiometric defect ($= x$ for the composition MO_{1+x}) and the free energy is complicated and awkward to work out, but the relative pressure $p(x)$ / $p(0)$[where $p(x)$ is the equilibrium pressure over MO_{1+x}, and $p(0)$ is the equilibrium pressure of the stoichiometric phase, $MO_{1.000}$] is rather simple, and depends only on the intrinsic properties of the stoichiometric crystal: the equilibrium constants for Reactions 1 and 4. Bloem and Kröger (1956) (9) and Brouwer (1954) (*14*, *15*) have refined the treatment of the defect equilibria to take account of the ionization of defects. Figure 1, based on their treatment, shows the $(p(x)/p(0), X)_T$ relations for some hypothetical, but representative, cases: (i) intrinsic lattice disorder, ζ, very small, intrinsic electronic conductivity ($\bar{n} = \bar{p}$ electrons or positive holes per cc.) very small; (ii) ζ in the range typical of ionic compounds at the Tammann point, $\bar{n}$ very small; (iii) ζ large as in ii but $\bar{n}$ of comparable magnitude; (iv) ζ as in ii, $\bar{n}$ large; and (v) ζ large and n large.

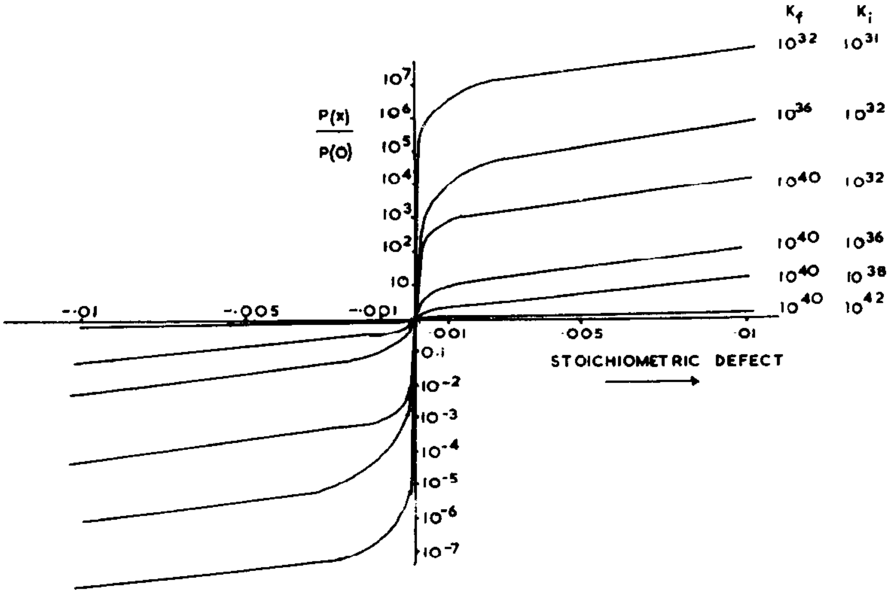

Figure 1. Reduced pressure, p(x)/p(0) for phase AB_{1+x} *as dependent on stoichiometric defect*

K_f. *Equilibrium constant for intrinsic lattice disorder (Equation 1)*
K_i. *Equilibrium constant for intrinsic current carriers (Equation 4)*

It is clear that for most typically electrovalent compounds, built up from inert-gas type cations of low electron affinity and inert-gas type anions of high ionization potential—e.g., compounds of the A subgroup metals, and the halides of the metals in general—the free energy curve must rise very steeply for small departures from ideal composition. Nevertheless, because the creation of lattice defects in such crystals is highly endothermic, the intrinsic disorder, ζ, must increase steeply with temperature and nonstoichiometry can be expected to be observable at high enough temperatures: "High" is to be defined here in terms of the properties of the substance considered. Thus many of the oxides of stable valence states of the metals show *n*-type conductivity at moderately high temperatures, without analytically detectable changes of composition. Thorn and Ackermann (1961) (*45*) have shown that some of the most stable oxides lose oxygen and vaporize incongruently at 2400° to 2800° K.—e.g., $ZrO_{1.96}$, $ThO_{1.95}$. Sawyer (1960) (*38*) has shown that, in contrast to its existence limits at lower temperatures, uranium dioxide in equilibrium with the metal becomes oxygen-deficient at 2500° to 3000° K. The composition ranges which thus become appreciable at the highest temperatures are as compatible with the straightforward Schottky-Wagner conception as is, for example, the behavior of zinc oxide at 1200° K., or potassium chloride in equilibrium with potassium vapor at 800° K.

Intrinsic lattice disorder may well be higher in crystals where the binding forces are largely covalent than in purely ionic crystals. Although the creation of a vacancy involves the severance of bonds and a change in hybridization of the atoms adjacent to the vacant site, the bonds in many structures are inherently electron-deficient because of the high coordination number of each atom. Cohesive energy lost in breaking bonds may be partly compensated by an increase in the bond order of the other bonds formed by atoms adjacent to the vacancy. Thus in the NiAs structure, the bonds must be largely covalent-metallic; each metal atom forms six fractional-order metal-metal bonds to its nearest neighbors in the same sheet and six bonds to the octahedrally disposed nonmetal atoms. The same factors that diminish the endothermicity of lattice defects lead also to a small energy gap, or even an overlap between valence band and conduction band. Although there is a regrettable lack of thermodynamic data and of studies of the electronic properties of these quasimetallic substances, their extreme tolerance for stoichiometric deviations can be qualitatively understood; both ζ and $\bar{n}$ are very large. Thus Ehrlich (1939, 1949) (*16*) has interpreted the densities and cell dimensions of the titanium chalcogenides as indicating that at least 5% of metal and nonmetal sites are vacant in the stoichiometric compounds TiS, TiSe, and TiTe. It is noteworthy that, outside the NiAs and similar structures favoring the formation of metal-metal bonds, grossly nonstoichiometric compounds (especially oxides) arise mostly from atoms or ions in oxidation states that confer the d^1, or d^2, or d^3 configuration, such as Ti(II) and V(II)—i.e., at the beginning of the transition series proper. Ternary compounds of the valence-controlled framework-structure type—e.g., tungsten bronzes—are also formed by the elements at the beginning of the transition series, but from higher oxidation states—e.g., Ti(IV − III), W(VI − V), Mn(IV − III). This correlation of nonstoichiometric behavior with electron configuration of the metals will fall into place when the constitution of nonstoichiometric compounds is better established.

Problem 2. Are Grossly Nonstoichiometric Compounds Thermodynamically Stable?

This question must be asked on two grounds. First, because the high concentrations of lattice defects found in some cases (the TiO phase is an extreme example) must raise doubt about the relation of the nonstoichiometric phase to the type structure in terms of which it is described. Secondly, successions of ordered intermediate phases have been discovered during the last few years, in phase diagrams where, previously, nonstoichiometric compounds of broad range had been reported.

Theoretically, the discussion must turn on the relative energies of complex ordered structures and of defective, random structures. Bertaut (5) (1953) attempted to compute the electrostatic lattice energy of the pyrrhotite phase $FeS_{1.14}$ $(Fe^{+2}_{0.625}, Fe^{+3}_{0.250}|\square^{+})(S^{-2}|\square_{-})$ or $(Fe^{+2}_{5}, Fe^{+3}_{2}, \square)(S^{-2}_{8})$, for several alternative cases: a completely disordered structure with higher-valent cations and vacancies randomly distributed over all cation sites; and structures with the vacancies ordered into alternate cation sheets, with various hypotheses about the disposition of the higher valent cations. It emerged that while additional stabilization energy comes from the optimum ordered arrangement of the Fe^{+3} ions, the energy liberated by ordering the vacancies alone is very large. Bertaut's calculation gave around 320 kcal. per mole, or 500 to 1000 times the energy of the usual order-disorder transformation—so large that the entropy contribution to the free energy would be negligible and the equilibrium constant for vacancy disorder physically meaningless. If this is so, it can plausibly be argued that a nonstoichiometric phase, with irrational composition and inherently random distribution of vacancies or interstitials, should be highly endothermic with respect to ordered phases of rational and fixed composition. The unit of ordering is unlikely to be very large, in view of the low probability (high negative entropy) of achieving too complex an ordering pattern, although the unit cells of some ordered intermediate phases in both intermetallic and ionic structures are astonishingly large and pose some awkward questions. It might be expected, therefore, that the true equilibrium diagrams of oxide and sulfide systems should display a succession of well defined phases of such fixed compositions as lend themselves to the appropriate ordering processes. True equilibrium cannot always be attained in real systems because of the interplay between kinetic and equilibrium considerations; point defects can only be ordered or eliminated at temperatures where there is sufficient diffusional mobility. Vacancies and interstitials are trapping sites for altervalent ions; these can migrate and attain order by a series of electron switches, as long as all cation sites are tenanted by the same kind of atom, but if impurity atoms are present they can lock a measure of randomness into the cation arrangement by blocking electron transfer processes. Metastable, random, nonstoichiometric phases may then persist. It is worth speculating how far the wealth of detailed information now being obtained about the cerium, praseodymium, and terbium oxide systems is the direct consequence of the purer rare earth preparation now available, as compared with pre-ion-exchange days.

This argument needs close examination on both structural and thermodynamic grounds. Structurally, the requirements of ordering seem to be met in two distinct ways. In the first, vacant lattice sites (or interstitial atoms) undergo a superstructure ordering within the crystal lattice of the idealized composition. The superstructure may impose a change of symmetry; there may be small consequential shifts of position and changes of dimensions. In general, the ordered intermediate phase retains, for its pseudocell, a clear relation to that of the corresponding, if hypothetical, random, defective phase.

This type of ordered intermediate phase appears to arise within two of the type structures that appear especially prone to the formation of grossly nonstoichiometric compounds: the NiAs and CaF_2 structures. The former is exemplified by Jellinek's (*24*) work on the chromium sulfides (1957), CrS_{1+x}. In prewar work, Haraldsen (1937, 1938) (22) reported wide stoichiometric ranges: $CrS_{1.00}$ to $CrS_{1.18}$, $CrS_{1.22}$ to $CrS_{1.40}$, and $CrS_{1.45}$ to $CrS_{1.50}$. It now appears that after sufficiently prolonged annealing, there are six phases of rather closely defined composition: Cr_2S_3 (two forms, one of which may be deficient in sulfur), Cr_3S_4, Cr_5S_6, Cr_7S_8, and CrS (possibly not ideal in composition). The compositions of the intermediate sulfides correspond to rational ways of ordering vacant chromium sites in alternate sheets of the structure.

Bevan (1955) (*6*), Brauer and Holtschmidt (1951), and Brauer and Gradinger (1954) (*14, 15*) for the cerium oxides, and Eyring and others (1954, 1961) (*18*) for the praseodymium and terbium oxides, have found essentially analogous sequences of intermediate phases: $MO_{1.5}$, $MO_{1.65}$, $MO_{1.72}$ (= M_7O_{12}),

$MO_{1.78}$ (= M_9O_{16} or $M_{32}O_{57}$), $MO_{1.81}$ (= $M_{16}O_{29}$). These phases also almost certainly arise from the ordering of vacant oxygen sites in the defective fluorite structure.

Immediately adjacent to an anion or cation vacancy the electrostatic lattice energy is considerably reduced. An alternative way of changing the cation-anion ratio of a structure without a radical change in the coordination environment of any atom (though at the cost of increasing the repulsive terms in the lattice energy sum) is found in the remarkable series of homologous oxides of molybdenum, titanium, and vanadium, discovered by Magnéli and his collaborators (*2, 27, 28*): Mo_nO_{3n-1}, Ti_nO_{2n-1} ($n = 4, 5 \ldots 9$), and V_nO_{2n-1} (Magneli 1953, 1960; Andersson, 1954). In these oxides the octahedral coordination about the metal atoms is preserved but, at regular spacings, edge sharing is added to corner sharing in the molybdenum oxides, or face sharing to edge sharing in the rutile structure.

Both types of ordering leave little scope for nonstoichiometry without interfering with the complex long-range order of the large unit cells. There is, accordingly, some tendency for crystallographers to hold the view that grossly nonstoichiometric compounds are illusory.

Examination of Bevan's careful work on the CeO_{2-x} system shows that the cell dimensions of the intermediate phases differ significantly in the adjoining two-phase ranges. This implies a significant, if small, composition range at the temperatures at which equilibrium was frozen into the crystal lattice (Table I).

Table I. Nonstoichiometry of Intermediate Phases in Cerium Oxide Systems

Nominal Formula	*Upper and Lower Limits*	*Dimensions of Equivalent Hexagonal Cell, A. (Rhombohedral)*		*Dimensions of Cubic Cell,* a_c, A.
		a	*c*	
CeO_2	$CeO_{2.000}$	(3.825)	(9.368)	5.409
	?	(3.826)	(9.372)	5.411
$Ce_{16}O_{29}$	$CeO_{1.812}$	3.890	9.531	
	$CeO_{1.804}$	3.900	9.538	
Ce_9O_{16}	$CeO_{1.785}$ No detectable range	3.910	9.502	
Ce_7O_{12}	$CeO_{1.722}$	3.912	9.657	
	$CeO_{1.710}$	3.921	9.637	
Ce_8O_{13}	$CeO_{1.650}$	(2 × 3.934)	(2 × 9.365)	11.126
	$CeO_{1.681}$	(2 × 3.929)	(2 × 9.625)	11.114

From the thermodynamic standpoint, the conclusion that ΔG is dominated by a very large positive ΔH term turns entirely on whether the calculation of the endothermicity of random, defective crystals is valid. In so far as direct thermodynamic measurements or phase equilibrium studies are available for oxide systems (and these, as the most truly ionic of allegedly nonstoichiometric compounds, should be the ones for which the Bertaut type of calculation should be least unreliable), it seems clear that the endothermicity of the random, compared with the ordered, structure has been grossly overestimated.

Thus, for the phases derived from the fluorite structure, Bevan's room temperature observations can be supplemented by the high temperature x-ray work and tensiometric measurements of Brauer and Gingerich (1960) (*12*). Above 600° C. the composition ranges of the $CeO_{1.82}$ and $CeO_{2.00}$ oxides broaden, so that they merge into a single cubic phase. Although the phase boundaries have not been traced, the lower intermediate oxides also transform or merge into the same single cubic phase at high temperatures (*10*), extending from $CeO_{2.00}$ to at least $CeO_{1.65}$. In the corresponding praseodymium oxide series, Eyring's equilibrium pressure measurements not only show the intermediate phases, but also that the univariant ranges between them narrow and disappear at higher temperatures. Another related system, with interstitial atoms in a fluorite-type structure, is that of the uranium oxides UO_{2+x}, covered by the very detailed free energy and phase equilibrium studies of Roberts and Walter (1961) (*36*), Blackburn (1958) (*8*), Aronson and Belle (1958) (*4*), etc.

Since Roberts has discussed nonstoichiometric fluorite-type oxides in several papers, the thermodynamics need be only briefly summarized. Below 1123° C., the distinct nature of the nonstoichiometric $\overline{UO_2}$ and $\overline{U_4O_9}$ phases, and the more highly ordered nature of the latter, are shown by the differences in partial molar enthalpy of oxygen in the two phases, and by the considerable decrease in entropy accompanying the $UO_{2+x} \rightarrow U_4O_{9-y}$ phase reaction (Table II).

Table II. U-O System at 1300° K.

		ΔG, *Kcal.*	$\Delta H/Mole$ O_2, *Kcal.*	$\Delta S/Mole$ O_2, *E.U.*
UO_{2+x} phase	$UO_2 + 0.0995\ O_2 \rightarrow UO_{2.199}$	−4.09	−60	−14.6
	$UO_{2.199} + 0.0185\ O_2 \rightarrow UO_{2.236}$	−0.619	−118	−61
U_4O_{9-x} phase	$UO_{2.236} + 0.007\ O_2 \rightarrow UO_{2.250}$	−0.216	−86	−46

Above 1123° C. the UO_{2+x}—which is not unsatisfactorily interpreted directly in terms of a simple statistical thermodynamic model—replaces the partially ordered U_4O_{9-y} phase over the whole composition range up to about $UO_{2.26}$ at 1400° C. It does not appear that a very large heat effect can be ascribed to the partial order $\rightleftharpoons$ complete disorder process relating to these two phases.

Similarly, the phase equilibria are known with certainty, and free energy measurements are available (although not as closely spaced as one might wish) to define the ferrous oxide phase as having continuity over a wide stoichiometric range at 1000° K. The evidence is incompatible with the idea that these and other compounds owe their existence to ordering processes or are metastable with respect to discrete intermediate phases.

Other classes of compounds, such as the nonstoichiometric hydrides, fall within the same argument. Thus, for the classical example of palladium hydride, it is possible to describe the constitution more precisely than by the former designation as an interstitial hydride. If the α phase is described in terms of the NaCl structure (cf. the neutron diffraction work), it is a defective one, with the hydrogen sublattice only partly filled. Aston's low temperature specific heat work [Nace and Aston, 1957 (*31*)] suggests that the hydrogen atoms become ordered to impose an idealized formula, Pd_4H. But this is at low temperature; the diffusion coefficient of hydrogen in palladium and the bivariant range of the equilibrium diagram show that at, or a little above, room temperature the structure is disordered.

Problem 3. The Interaction of Lattice Defects

This problem is fundamental to an understanding of the real structure of nonstoichiometric and intermediate phases. Superstructures and shear structures, nucleation and reconstructive transformations, the quantitative details of the equilibrium of a compound with its components: all these hinge upon the interactions between point defects and valence defects.

The Virtual Charge Approximation. Lattice defects are necessarily created in complementary pairs. In the stoichiometric crystal, this means a pair of point defects; in stoichiometric unbalance, a point defect plus an electronic defect. These are not independent entities. Relative to the normal lattice constituents, cations of higher or lower valence bear a charge of $+e$ or $-e$, respectively; an interstitial cation represents a charge of $+ze$ at a position which would normally bear no charge; a vacant site bears a virtual charge of opposite sign to that of the ion properly located on it. Thus a cation vacancy is an interruption in the regular periodicity of the crystal lattice. Electrostatically, the results of removing a cation of charge $+ze$ or of superimposing a charge of $-ze$ on the occupied site are the same, and the latter can be regarded as an equivalent description. Hence, complementary point defects bear opposite virtual charges and attract each other; valence defects are attracted by (and in the state of lowest energy will be trapped at) their complementary point defects. Association of defects in this sense has been fairly fully discussed in relation to F-centers and defects in alkali halides. It has been less thoroughly pursued in a more general context.

A useful analogy, which has not yet been fully exploited, can be drawn between complementary defect pairs and electrolytes in solution. The Schottky-Wagner approximation (valid for highly dilute defects) corresponds to the Arrhenius strong electrolyte. Thus Wagner represents the nonstoichiometric equilibrium of cuprous oxide as

$$Cu_2O + O_2 \rightleftharpoons Cu_2O + 4e^+ + 4\,\square_+ + 2O^{-2}$$

for which, in so far as vacancies and positive holes are independent entities,

$$K.p_{O_2} = [e^+]^4[\square_+]^4$$

and since $e^+ = \square_+$, the conductivity and stoichiometric excess of oxygen should be proportional to $p_{O2}^{1/8}$. The experimentally observed relation between oxygen pressure and stoichiometric defect (x in $Cu_2O_{1+x} \infty p_{O2}^{1/5}$) *indicates some fairly* strong association between positive holes and copper vacancies.

In other nonstoichiometric systems—and in this context, as in others, there is a serious lack of quantitative data—Debye-Hückel effects and incomplete dissociation are much more pronounced. In some as yet unpublished work in my laboratory, Barraclough made extensive measurements on the nicely reversible $CaUO_{4-x}$ system and some relevant information can be extracted from his $(p,X)_T$ data. The equilibrium here involves

$$2UO_2^{+2} + O^{-2} \rightleftharpoons 2UO_2^+ + \square_- + {}^1/_2O_2$$

Trapped electrons and virtual charge on the oxygen vacancy together constitute the analog of a 2 to 1 electrolyte. At 700° C. the oxygen deficit varies as $P_{O2}^{-1/4}$, implying that one electron—i.e., one UO_2^+ altervalent ion—is firmly bound to the vacancy. From the behavior at higher temperatures, the further dissociation can be followed and the interaction energy found to be about 17 kcal. per mole of defect pairs.

Association effects clearly vary widely in magnitude from one substance to another. As with electrolytes in solution, the nonionic terms in the potential function for interaction may be critically important. Bloem's detailed analysis of equilibria in the $Pb_{1\pm x}S$ system shows that although the total stoichiometric defect is very small, trapping of electrons at sulfur vacancies, and of positive holes at lead vacancies, dominates the behavior.

This way of looking at defect interaction could profitably be developed further. There is a useful parallel to be drawn between solvated ions or ion-pair complexes in solution, and defects or defect complexes in their crystal lattice environment. The idea is worth using when considering the growing hints of short range order and defect association in nonstoichiometric phases.

Clustering of Defects. In a crystal of almost ideal composition, vacant sites or interstitial ions are relatively widely separated: A random distribution implies that they are as far apart as possible. It might be adjudged, at first sight, that the interaction between defects—due to their real or virtual charges, or to the strain induced in the surrounding crystal lattice—was inherently repulsive.

This is, however, not the whole of the matter. The superstructure ordering of point defects; the collection of interstitial ions along certain lines or sheets, as in Magneli's model for the precursor of his shear structures; the temperature-dependent adjustment of composition of a nonstoichiometric phase at the boundary of the bivariant range; the nucleation of a new phase of different stoichiometry—these depend on accumulating vacancies or interstitials in some regions of the crystal lattice at the expense of others.

Thus the behavior of lattice defects bears some analogy to phase separation in fluids, or to the treatment of adsorption on localized sites. At low relative temperatures, the defects adopt a random distribution if they are sufficiently dilute; if their concentration exceeds a certain value they segregate into defect-poor and defect-rich regions which can coexist. The concentration at which this occurs, and the relative temperature scale, depend on what can be represented as a nearest-neighbor attraction in the interaction potentials. The magnitude of the attractive interaction energy defines a critical temperature above which no segregation of defects occurs.

On this view, interaction between defects determines the concentration at which a phase becomes saturated with defects, and also the manner in which defects aggregate or order. It can be foreseen that stoichiometrically defined intermediate phases are likely to undergo an order-disorder transition at higher temperatures and that, in general, some detectable stoichiometric range is likely before the disordering temperature is reached.

There is evidence that attainment of superstructure ordering, or the segregation of lattice defects, can be a fast process. Reference has been made to the conversion of the ordered intermediate phases in CeO_{2-x} system into a broad-range cubic defective fluorite phase at moderately high temperatures. In Bevan's and Brauer's work it was impossible to freeze the high temperature equilibrium by quenching. In some recent work on cuprous oxide, Stone and O'Keeffe (1962) (*43*) found that when homogeneous $Cu_2O_{1.0034}$ was quenched from 1000° with the utmost rapidity, the cuprous oxide retained only 4% of the copper vacancies and positive holes, as shown by measurements of the paramagnetism. Most of the cation vacancies, with their associated positive holes, segregated rapidly to build up nuclei of the higher oxide, CuO.

Defect Complexes. The argument this far has reached the following stage. The state of minimum energy of any system at very low temperatures corresponds, without question, to the attainment of order. Third law considerations imply that a nonstoichiometric phase, with its inherent randomness, should be metastable at 0° K. with respect to a mixture of ideal, stoichiometric compounds. The relative status of complex intermediate phases and of stoichiometrically simple compounds, with small unit cells and derived from clearly defined valence states, is less clear—e.g., of the series Ti_nO_{2n-1} as compared with TiO_2 and Ti_2O_3. It is also certain that, wherever room temperature structural information has been supplemented by high temperature equilibrium data, univariant two-phase regions of the phase diagram are progressively invaded by bivariant equilibria. Simple lattice energy calculations indicating that disordered nonstoichiometric states are very highly endothermic are quantitatively incompatible with the experimental evidence.

Ordered intermediate phases, based either on superlattice ordering of defects or on shear structures, etc., necessarily have rather large unit cells. Ordering forces have to operate over distances that are large compared with nearest neighbor distances. Thus in Magneli's shear structures, based on the ReO_3 or the rutile type, the essential features are one- or two-dimensional arrays of lattice misfit, configurations in which the distinction between normal lattice site and interstitial site loses and changes its meaning. The arrays can be regarded as built up by the logical packing of a particular kind of defect cluster. That a given stoichiometry results in a fully ordered structure, rather than in a statistical distribution of stacking sequences, depends on a more subtle long range factor. In any case, to establish order of this kind implies a substantial decrease of configurational entropy per unit cell, which partly offsets, in the free energy, the exothermicity of the ordered state.

Because there is a disparity between the predicted endothermicity of random structures and the observed ΔH and ΔG for the breakup of intermediate phases, there is merit in an alternative hypothesis—that it is not long-range ordering but short-range interactions of defects, with each other and with the immediately surrounding crystal lattice, that stabilize significant deviations from stoichiometry. Reverting to the analogy of electrolytes in solution, it may be noted that calculations ignoring the role of the solvent would show the energy of charge separation to be so great that ionic compounds could not be dissolved, nor their ions be dispersed. In fact, most of the lattice energy is recovered by ion-solvent interaction (dipole orientation and coordinate bond formation) in the first coordination shell; more can be regained if complex ion formation occurs. Analogy suggests that relaxation of the crystal lattice must equally be brought into the picture.

This suggests the need to look critically at what is really known about the nature of lattice defects. Here Roth's paper on ferrous oxide (1960) (*37*), $Fe_{0.87}O$, marks an important stage. Methods of diagnosing how nonstoichiometry arises—e.g., that ferrous oxide is cation-deficient, $Fe_{1-x}O$—strictly go no further than an enumeration of the number of atoms of each kind per unit cell. That the changes in unit cell contents signify a corresponding number of simple vacancies or interstitials is purely inferential and, as now appears, questionable.

Roth's neutron diffraction work indicates that it is wrong to infer from the over-all nonstoichiometric reaction

$$2Fe^{+2} + \frac{1}{2}O_2 \rightleftharpoons O^{-2}|\square_- + 2\,Fe^{+3} + \square_+$$

two positive holes on normal cation sites and one additional cation vacancy arise from each atom of oxygen in stoichiometric excess; the products are one positive hole in the cation lattice, together with a defect complex of a type not hitherto postulated. The expected positive hole-vacancy pair $(Fe^{+3}|\square_+)(\square_+)$ transforms itself by movement of the Fe^{+3} ion to the interstitial site adjacent to the vacancy—i.e., to a site tetrahedrally coordinated with oxygen:

$$(Fe^{+3}|\square_+)(\square_+) + \Delta \rightleftharpoons (Fe^{+3}|\Delta)(\square_+)_2$$

This defect complex is important in three respects: It maximizes the energy of interaction between real and virtual charges on the defects, and so contributes stabilization; surrounded, as it is, by iron cations on octahedrally coordinated sites in a close-packed oxygen lattice, the defect complex and its immediate environment are like a microdomain out of the spinel structure of Fe_3O_4, the next higher oxide; and the iron atom in a tetrahedral position between two octahedral vacancies corresponds to the transition state for a normal cation diffusion step. Apart from the (probable) trapping of the positive holes at these positions, this configuration of atoms will be represented by a certain steady-state population in the crystal lattice at temperatures where diffusion and equilibration can occur. There is a sense in which the germ of the next higher phase is already latent in the ideal stoichiometric structure.

The very recent work of Wallace and Craig (1961) on tantalum hydride is relevant here. Above 53° C. the system is stoichiometrically indeterminate (α phase) and completely random in structure; at low temperatures Ta_2H, of more or less definite composition (β phase), exists in equilibrium with metallic tantalum. It appears to be established that, for material of this ideal composition, the long-range order in the crystal lattice disappears at a temperature well below that at which the main energy absorption and entropy increase occur, associated with the $\beta \rightarrow \alpha$ transition. The interpretation placed on the combination of neutron diffraction and thermodynamic work is that, below the $\alpha \rightleftharpoons \beta$ transition point, hydrogen atoms in tetrahedral sites associate in clusters of four, in a definite configuration, and that most of the energy of the order-disorder transformation is gained in establishing this short-range order. Transitions and energy changes below the $\alpha \rightleftharpoons \beta$ transition point correspond to the mutual arrangement of the clusters or complexes, so as to achieve long-range order, but this is associated with only a small further decrease in entropy.

This situation may well be more general than has been hitherto realized. If the essential condition for gross stoichiometric deviations is that energy is gained by transforming simple point defects plus valence anomalies into some new configuration, the interaction of this configuration with the surrounding crystal lattice (its "solvation") may be energetically important. An atomic arrangement which, infinitely repeated, constitutes the stable structure of the next phase in a succession may, in isolation, provide the favored pattern for defect complexing.

It is postulated that defect complexes of this kind, independent and randomly distributed at medium or high temperatures, are the entities that undergo ordering to yield superstructures, shear structures, etc., as intermediate compounds of complex formula. In their turn, depending on the free energy of formation of the complexes, they must be dissociable at high enough temperatures or in high dilutions. The Schottky-Wagner model for random point defects and electronic defects should therefore be applicable at high temperatures. There is not much experimental evidence about the properties of well defined systems close to stoichiometry, where defects would be very dilute. In the number of cases—e.g., the beginning of the stoichiometric range of UO_{2+x} at high temperatures, or the approach of oxygen-deficient $CaUO_{4-x}$ to the ideal composition—the free energy and partial molar entropy vary very steeply with composition. This might be a range in which the dissociation equilibrium between free and complexed defects is subject to sensible displacement. The situation over the whole temperature range can be summarized as in Table III.

Table III. Relation between Nonstoichiometric Compounds and Ordered Intermediate Phases

High Temperatures				*Low Temperatures*
Isolated, random point defects and valence defects	Defect pair association	Rearrangement of coordination environment in isolated defect· clusters or "microdomains"	1- or 2-dimensional assays of ordered defects or reorganized defect complexes	Fully defined superstructures or shear structures
Essentially disordered		Stabilization by short-range ordering effects	Partial order; random stacking sequences, etc.	Complete ordering; long-range interactions
Random structures			Ordered structures	
Nonstoichiometric phases				Stoichiometric phases

Russian workers have advanced some apparently related ideas. Ariya and his colleagues (1958, 1961) (3, 17) have pointed out that the standard heat of formation of a compound across its stoichiometric range frequently falls rather smoothly on the curve joining the value for the stoichiometric compound and that of the next phase in the equilibrium diagram (Figure 2). Furthermore, there is

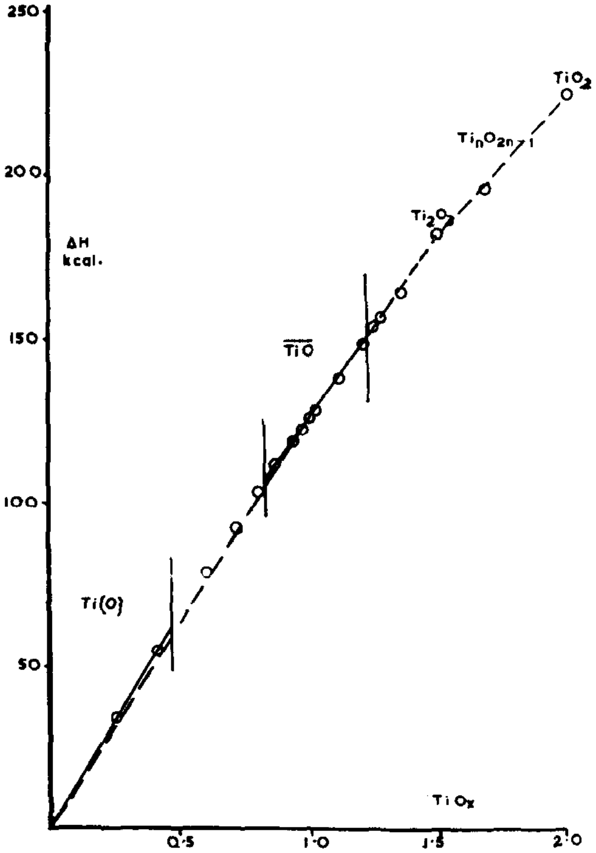

Figure 2. Integral formation of oxides in nonstoichiometric Ti-O system