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NON-STOICHIOMETRIC COMPOUNDS

Leo Brewer

1965

Non-Stoichiometric Compounds

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The concept of stoichiometric compounds or compounds with integral combining ratios of the elements has played an important role in the development of the atomic theory of matter. The distinction between elements, compounds, and mixtures and the concept of pure substances was first clearly introduced by Boyle in the seventeenth century and further extended toward the end of the eighteenth century when Cavendish found simple integral combining volumes of hydrogen and oxygen gases in the reaction to form water and when Lavoisier established the law of conservation of mass and applied gravimetric analysis to determine the composition of water, carbon dioxide and other compounds. These observations were used by Dalton as the basis of his atomic hypothesis, but the experimental verification was not clear. Without the understanding that elemental gases could be diatomic, volumetric combining ratios of many gases did not work out properly. Although Avogadro recognized the existence of diatomic molecules in 1811, his hypothesis was not generally

accepted until after 1860. Also the densities of some gases did not correspond to a simple formula and not until the work of Deville in 1864 was it recognized that the deviation was due to dissociation of the gases.

Thus the key step leading to the Dalton hypothesis was based primarily on the question of whether compounds contained fixed simple combining ratios of the elements, e.g. were stoichiometric. Berthellot vigorously attacked the assumption of constant combining ratios of reactants and was in fact the first to discover reversible reactions for which the yield depended upon the amount of excess of a reactant. Over the period 1799-1807 Berthellot's views were strongly refuted by Proust who did establish clearly, within the accuracy of measurements of those days, the law of Definite Proportions or the existence of solid compounds that were stoichiometric. It was fortunate for the advance of science that stoichiometric compounds, now known as daltonides, were established. However, we now know that the concept of a daltonide is, in general, an approximation and that compounds must have a finite composition range and must therefore be berthollides, compounds with variable composition.

The basis for deviations from the laws of definite combining proportions and simple combining ratios can be illustrated by contrasting gaseous molecules and solid compounds. For the gaseous molecule NO, the smallest change that one can produce in this molecule is either the addition or removal of one atom. For example, one could add one nitrogen atom to produce N_2O or one oxygen atom to produce NO_2 , both of which are compounds with properties drastically different from those of nitric oxide. As the atom is the smallest unit which can be added or removed

from a molecule, it is clear that the smallest change that one can produce in a gaseous molecule will produce a large change in its properties. If, on the other hand, we consider solid sodium chloride, for example a single crystal weighing 10 g, its formula would be $\text{Na}_{10}^{23}\text{Cl}_{10}^{23}$. Here again, the smallest change that one can bring about is the addition or removal of one atom. If we remove one chlorine atom, the new formula is now $\text{Na}_{10}^{23}\text{Cl}_{10}^{23-1}$. When one is dealing with condensed phases with infinite lattices, the removal or addition of single atoms produces such minute changes in the formula that one can have essentially minute and gradual changes in the properties of the phase as one changes its composition. Thus it is not surprising that condensed phases have ranges of composition and are not restricted to definite compositions or simple combining proportions. In fact, one can prove thermodynamically that no condensed phase can be restricted to a unique composition except at a congruent melting or boiling point, a peritectic point, or at temperatures approaching absolute zero. Except for these singular points, condensed phases under all other equilibrium conditions must have appreciable ranges of composition or appreciable homogeneous ranges.

Consider the sodium chloride phase again. The phase in equilibrium with chlorine at 1 atm cannot be the same sodium chloride phase which is in equilibrium with sodium metal. It is impossible to have sodium metal and chlorine gas at 1 atm in equilibrium with one another. From available thermodynamic data one can calculate that the chlorine partial

pressure at room temperature increases from less than 10^{-130} atm to a value of 1 atm as one varies the composition by adding chlorine from the sodium chloride composition in equilibrium with sodium to the sodium chloride composition in equilibrium with chlorine. Likewise the water to hydrogen ratio at equilibrium with alumina at 1000°K will lie between 10^{10} and 10^{-14} depending upon whether the composition corresponds to the oxygen-rich or the aluminum-rich end of the composition range.

The changes in properties of sodium chloride across its homogeneous range are quite substantial. For example, its color changes from deep blue at the sodium-rich end to a white color at the chlorine-rich end (1). Likewise, its electrical and many other properties change quite markedly as one moves across the homogeneous range. For sodium chloride the range in composition is rather small, although it can be detected analytically without much difficulty. One finds that the homogeneous ranges will vary greatly from one phase to another. In some instances, a system of two components may correspond to a phase diagram with a complete homogeneous range from one component to the other. In other instances there may be a number of intermediate phases, some of which have moderately wide homogeneous ranges and others which have fairly narrow homogeneous ranges.

It is important to recognize that the compositions at the limits of these phases would normally have no particular significance of their own. These limiting compositions will be different at each temperature and are not determined alone by the properties of the phase in question.

but are equally well determined by the properties of the phases that exist in equilibrium with the phase in question. Thus, under some circumstances, when it is possible by proper seeding to have a choice of phases which might be saturating a given phase, then the limit of homogeneous range will be different under the two conditions. The reader may consult the literature (2) to become familiar with the plots of free energy versus moles of one component per fixed amount of the other component for a series of phases which illustrate that the limits of the homogeneous ranges occur when there is a common tangent to two free energy curves corresponding to equal partial molal free energies for the two phases. Such plots clearly show the influence of the saturating phases upon the homogeneous range of a given phase.

It is quite customary to designate a phase by a formula which corresponds to some simple combining ratio. For example, the sodium chloride homogeneous range is referred to as the NaCl phase region; the iron(II) oxide homogeneous range, or the wüstite phase, is referred to as the FeO phase region. The use of these names does not imply any commitment about the range of compositions nor that the simple composition chosen to name the phase has any special significance within this phase region. Thus in the instance of the iron(II) oxide phase region, the composition FeO does not exist in an equilibrium system (3). Nevertheless it is useful to refer to wüstite as the FeO phase region because of the fact that X-ray patterns for compositions in this phase region correspond to an ideal lattice of the sodium chloride type, which would have the composition FeO if it were an ideal lattice with no vacant lattice sites.

Except at the absolute zero, it is not possible to have an ideal crystal for any substance at equilibrium and there will always be vacancies in the lattice. The vacancies in the cation sites need not be equal to those in the anion sites. In the instance of wüstite, any attempt to equalize the vacancies in anion and cation sites would result in a phase unstable with respect to disproportionation to metallic iron and an oxide phase richer in oxygen. Thus the terms FeO phase, TiO phase, NaCl phase, etc. do not imply that the phase has a fixed composition corresponding to the ideal crystal structure. No other commitment is made than the designation of the crystallographic arrangement. For those who are accustomed to dealing with intermetallic compounds, this is quite obvious. However, many people who have dealt with nonmetallic compounds under rather restricted conditions often have not been aware of the importance of recognizing the existence of homogeneous ranges for all compounds.

There are many important respects in which not recognizing this can greatly handicap the understanding of chemical processes. The designation of a vapor pressure for a phase causes difficulty unless one recognizes that the existence of a homogeneous range for a phase implies a range of vapor pressures as a function of composition. The designation of a single vapor pressure for a phase is normally meaningless unless one can characterize the composition of the phase and can use a method of vapor pressure determination that does not appreciably alter the composition; so that one can associate the vapor pressure with a specific composition within a homogeneous range. The phase

will normally be saturated at either end of its range by some other phase. In a binary system at fixed temperature, the two condensed phases together with a gaseous phase constitute an invariant system with a unique characteristic vapor pressure. Thus if one does not measure the vapor pressure as a function of composition in the homogeneous range, one must normally insure that a saturating condensed phase is present to characterize the system.

In most systems this means that one does not wish to use a "pure" sample which would correspond to some composition in the single phase region, as the system would not be uniquely characterized and the vapor pressure measurement would have no significance. One of the two phases which could saturate the phase in question must be added in order to produce a completely characterized system before measuring the vapor pressure. In some instances a constant boiling composition exists within the homogeneous range and if one uses a method of vapor pressure determination which allows the system to approach this constant-boiling composition, there will be a third composition within the homogeneous range for which the vapor pressure measurement can be made without characterizing the composition of the phase. This is not general and one must verify that the constant-boiling condition is possible and insure that the method of determination allows one to reach this condition before attempting to make a measurement on a single phase system without carefully specifying the composition. In some systems the pressure may vary a millionfold across a homogeneous range, and it is quite meaningless to publish vapor pressures for a

phase as is sometimes done unless one has made the system invariant by adding a saturating phase or by insuring constant boiling conditions. As the constant boiling composition as well as the limiting compositions will vary with temperature, one must be somewhat cautious in using the temperature coefficient of the vapor pressure to obtain heats of sublimation or vaporization as the heat may not correspond to any standard heat unless one has corrected for the changing composition with temperature.

The prediction of chemical behavior by means of thermodynamic data can be seriously in error if one does not take into account the homogeneous range of each phase. The thermodynamic data in the literature are normally given for one standard composition. The standard compositions may be hypothetical and need not correspond to any actual composition. In carrying out the calculations to predict actual behavior one must be prepared to calculate free energy changes for changes in composition from the standard state composition to the composition actually present at equilibrium. It is in this area that there is a most serious limitation to the use of thermodynamic data for prediction of chemical behavior, particularly in high temperature systems. This calculation of the free energy change in going from the standard composition to the actual equilibrium composition corresponds to knowing the activity coefficient as a function of composition within the homogeneous range. The few examples that have been studied indicate that the activity coefficients may vary in a complex manner in such homogeneous ranges. More data are needed to confidently predict activity coefficients in these homogeneous ranges and therefore reliably predict chemical equilibrium behavior.

Other properties can vary considerably across the homogeneous composition range of a compound. It has been noted earlier that color and vapor pressure change markedly. In addition, thermal shock properties, thermal conductivity, chemical reactivity, and, particularly, electrical conductivity can change very rapidly with changing concentrations of crystal defects due to changing composition. The two common types of crystal defects can be illustrated for a non-stoichiometric compound with excess metal. If the excess metal is at a cation site with an associated anion vacancy, the defect is termed a Schottky defect. Metal atoms in interstitial position in the crystal lattice are termed Frenkel defects. The names are those of the men who first proposed their existence.

The effect of non-stoichiometry upon electric conductivity is most marked for the poorly conducting semi-conductors. If the crystal defects are due to atoms with excess electrons which can act as donors of electrons, the compound is designated as an n-type conductor. A deficiency of electrons or presence of acceptor sites results in a p-type conductor with conductivity due to migration of the positive defects. If the homogeneous range of a compound extends on both sides of stoichiometric, the conductivity will often change from n-type to p-type near the stoichiometric composition. Deviations from stoichiometry of as little as one part per million can make significant changes in conductivity of semi-conductor materials.

Diffusion of reactants through a solid may depend strongly upon vacancies and the chemical reactivity of a solid can change drastically

with composition. As both the equilibrium and kinetic behavior can vary strongly with composition, the degree of non-stoichiometry must be fixed to fix the chemical behavior of a compound.

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