

SOLUTION MODELS AND PATTERNS IN ALLOY THERMODYNAMICS

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Abstract - The thermodynamics of binary and dilute ternary alloys are discussed in terms of the electron theory of metals and the constant pair-wise bonding model. It is shown that both aspects can contribute to our understanding, but the important phenomenon of electron transfer is, at present, poorly understood. This affects the predictive capabilities of these models, but the major development of computerized data banking may not require that significant development be made to what is essentially an experimental body of knowledge.

INTRODUCTION

The development of our quantitative knowledge of the stabilities of metallic solutions has undergone a transformation in the post-war years to a state where the thermodynamics of all of the industrially important metallic elements and a large number of the significant binary systems have been measured at least over a few hundreds of degrees temperature range. From the point of view of the practising metallurgist, the stabilities, i.e. Gibbs energies of systems, are all important, and the separation of these into heats and entropies of mixing is of interest only in connection with the need to extrapolate data beyond the temperature range which might be the limits of applicability of a particular experimental technique. For example, the Knudsen effusion technique which has been used to provide a great deal of our present data is practically limited to a total pressure range of 10^{-10} - 10^{-4} atmos., because of detection problems at the lower limit, and the onset of molecular beam collisions at the upper limit. Much of the needed information can be obtained from phase diagrams, but there is always a possibility that solid systems have not been allowed to reach the state of equilibrium during a particular laboratory study, which they might achieve in long-term service at modest temperatures e.g. 500°C. The chemical metallurgist perceives the need for a separation of the two components of a Gibbs energy from this standpoint, and from the theoretical point of view a knowledge of the partial heats and entropies of the components of a binary system is vital to any model analysis. Much of our present literature is far less useful in connection with the quantitative aspects of the atomic modelling of alloy systems because of experimental inaccuracies, and we remain at the point where it is only patterns of behaviour of a less precise quantitative nature which can be provided. In metallurgical systems where the lower limit of temperature of measurements might be 800 K and the upper limit 2200 K, an error limit of ± 500 joules/g atom should be regarded as quite accurate. In any one investigation, a temperature range of 200 K would be regarded as successful. Within these limitations, I will endeavour to bring together some of the main thrusts of experimental and theoretical study of alloy systems in the post-war period, relating these to the needs of metallurgical industry which is where the information must eventually be applied.

THE EVOLUTION OF MODELS FOR BINARY SYSTEMS

The special nature of metallic solutions, and the importance of the role of the conduction electrons in their stabilities was first brought out by the phase diagram studies of Hume-Rothery and co-workers (1). He pointed out that many features of the diagrams for alloys of the Group 1B metals with those of Groups II B - V B could be closely related to one another if the electron/atom ratio was identified with the Periodic Group of each element, and the electron concentration in the conduction band, the free electron concentration, was used as a composition variable in drawing the diagrams rather than the more conventional atomic concentration. The occurrence of a common depression of freezing point curve and solid solution ranges for alloys of a given Group I solvent, could be accounted for on this basis, as could the occurrence of certain intermetallic "compounds" of a characteristic average composition. These substances typically showed a range of composition in the equilibrium diagrams.

To the thermochemist the depression of freezing point, where a liquid is in equilibrium with a continuous solid solution range, should be described by an equation having one particular

form

$$\frac{dX_B}{dT} = - \frac{X_A^S \left\{ \Delta H_{\ell} - \Delta H_s + (X_B^S - X_B^{\ell}) (\partial \Delta H_s / \partial X_B) \right\}}{(\partial \mu_B^S / \partial X_B) (X_B^{\ell} - X_B^S) T}$$

where A is the solvent, B the dilute solute, and s and ℓ the solid and liquid solutions respectively, and X is the atom fraction of each component. The term $\partial \mu_B^S / \partial X_B$ represents the change of chemical potential of the solute in the solid solution, and it has been shown that this term controls the behaviour of the depression of freezing point curves. It is constant for solutes such as cadmium, indium and tin in solution in silver when the electron concentration is used instead of atomic concentration (2).

Further evidence for the relatively simple electron/atom ratio effects in alloys come from the calorimetric studies of Kleppa (3) of liquid zinc and cadmium alloys with elements of Groups III - VB. Kleppa found for the first time that the endothermic heats of mixing of these alloys showed an increasing asymmetry, as a function of atom fraction, as the distance between the Groups in the Periodic Table of the alloying elements became larger. It has subsequently been shown, as a corollary to this discovery, that elements from the same sub-group of the Periodic Table e.g. Cd-Zn, Ga-In, (4) Sn-Pb (5) form liquid alloys which closely approximate the ideal regular solution behaviour i.e. $\Delta H^m / X_A X_B$ has a constant value, the so-called " α function".

Hildebrand and Scott (6) had proposed that metallic alloys should obey the equation

$$\Delta H^m = \frac{V_1 + V_2}{2} \left\{ \frac{\Delta E_1^V}{V_1} - \frac{\Delta E_2^V}{V_2} \right\}^2 \phi_1 \phi_2$$

where ϕ_1 and ϕ_2 are the volume fractions. Using the known data for these constants, we would expect values of the volume α function, $\Delta H^m / \phi_1 \phi_2$ to be somewhat larger than the experimental values at the equimolar composition (Table 1).

TABLE 1. Evaluation of the volume α function for binary alloys Zn-Cd, Ga-In, Sn-Pb

	Zn	Cd	Ga	In	Sn	Pb	
Atomic volume	9.63	14.05	11.24	16.4	17.07	19.36	cc
Energy of vaporization	28	24	63	56	70	44	Kcal/g.atom
Alloy	ΔH^m (calc.)	Expt. (at the equimolar composition)					
Cd-Zn	469	500 cal					
Ga-In	930	300					
Sn-Pb	1219	327					

The calculated values also do not show the correct trend in these alloy systems, but considering the magnitude of the effect, this seems too much to expect. The idea that the volume plays an important part in alloy thermodynamics had also been suggested earlier by Hume-Rothery et al. (7), and Predel (8) has recently shown that alloys of a given B group metal do show a direct relationship between the maximum heat of mixing and the difference in atomic volumes between the alloying elements. This "misfit" energy appears to be the only source of a positive component to the heat of mixing of alloys for which we have a readily tested model at the present time.

These two aspects of metallic cohesion, the explanations of the depression of freezing point in terms of the electron/atom ratio and the effect of the volume difference on the heat of mixing, represent the two approaches which are still current. The free electron theory considers the conduction band and its density to be all-important in the placing of ion cores on their equilibrium sites. Although the ion core of copper is Cu^+ and that of zinc is Zn^{2+} , Mott (9) showed that the conduction electrons would spend a longer time in the vicinity of

the more highly charged zinc ion, thus tending to screen the extra charge. He calculated that in the equimolar Cu-Zn mixture the volumes occupied by copper and zinc, the Wigner-Seitz polyhedra, would have residual charges after screening of $-0.075e$ and $+0.075e$ respectively. The Madelung energy associated with these residual charges in the ordered CuZn intermetallic compound which would disappear in the disordered state would account for the order-disorder transformation energy of about 1 Kcal/mole. The alternative view of metals which is more akin to Pauling's resonance theory of the metallic bond (10), considers the bond strength between an atom and its coordination shell in terms of individual bond energies and the number of neighbours. Thus the heat of vaporization may be considered as the energy to break $\frac{1}{2} NZ$ bonds/g atom where N is Avogadro's number and Z is the first coordination number. If it can be assumed that the bond energy associated with each two-particle contact depends only on the nature of the two atoms and not on the other atoms surrounding the contact, then a simple statistical theory can account for the regular solution model of randomly mixed binary alloys (constant pairwise bonding model) (11).

A difference in atomic volume in a binary system does not necessarily mean that there will be immiscibility in the solid state. On the contrary, when the atoms of each type can be so packed in the solid state that there is an increase in coordination of either species, or both, then Kubaschewski (12) has shown that the resulting ordered structure will be an intermetallic compound with definite sites for each type of atom and a negative heat of formation. This heat of formation can be calculated if it is assumed that the energy of interaction between like atoms is the same as that in the pure metals with an inverse dependence on the interatomic difference. Many phases described by Laves (13) should be of this nature. However, it is usually found that the internuclear distance between the centres of unlike atoms cannot normally be obtained from those of the constituent species, and this suggests that part of the cohesion, at least, is due to electron transfer from one species to the other, leading to a so-called "electrochemical" contribution, or something similar to an ionic contribution to the bonding. In the earlier calculations, appeal was made to Pauling's electronegativity scale to make this calculation. A more fundamental analysis based on free electron theory suggested that the electron chemical potential in the pure components should replace the electronegativity which originally used data for gaseous diatomic molecules. Varley (14) made a calculation using a "two-band" model of alloy formation in which electrons were transferred from the Fermi surface of one component to a level corresponding to the Fermi surface of the second, dilute, component in the pure state. Thus

$$\Delta E^m \propto E_F^A - E_F^B$$

This contribution is necessarily negative in sign and thus provides a basis for the understanding of strong compound formation bordering on the formation of an ionic compound, which is found in some binary alloy systems. Intermetallic compounds are known such as Mg Sn and Mg₃Bi₂, where the electrical conductivity is orders of magnitude less than that in typical metals. Miedema (15) has made an extensive analysis of the trends in bonding in binary metallic systems making use of the electron transfer model, with the Fermi energy as a measure of the tendency to transfer, and the compressibilities as a measure of the positive contribution to the heat of formation. The extraordinary stabilities of some intermetallic compounds involving Pd and Pt (16) must be accounted for in this treatment by the addition of a third term which is representative of the contribution of d electrons. The general equation employed by Miedema to discuss a very large number of binary metal solutions and compounds is

$$\Delta H^m \sim -Pe (\Delta W)^2 + Q (\Delta n_{ws}^{1/3})^2 - R$$

where the first term uses the square of the difference between the work functions of the metals, ΔW , the second is related to the density of electrons at the surface of the atoms, n_{ws} , and the third is a contribution due to d bonding. The first and third terms lead to negative contributions to the heat of mixing whilst the second leads to the positive component. The term, n_{ws} , has been related to the compressibility, B , empirically, using data from the alkali metals, and the relationship

$$n_{ws}^2 \propto B/V$$

where V , the atomic volume, was derived from established data.

The transfer of charge which is implicit in this model would lead to a change in size of the atoms, the donor undergoing a decrease in volume and vice versa for the acceptor. This change in size has been detected in a number of intermetallic compounds, and the case of the Laves phases AB_2 is particularly favourable. In these compounds, of which greater than 200 are known, the ideal radius ratio of the elements, R_A and R_B , is 1.225, when the atoms of like kind are in contact with each other. When the radius ratio is less than the critical value, it is found that the A-A distance is greater than the value found in pure element A. Conversely if the radius ratio is greater than the critical value the A-A distance is less than that in pure element A (17). Measured values for the internuclear distances of the A atoms show that contraction usually occurs on compound formation with a correspondingly smaller expansion of the B atoms. These changes of size on compound formation are too small to be accounted for by the complete transfer of an electron from one species to the other, being at the most 0.6Å and more typically 0.1-0.3Å. Generally speaking the extent of electron transfer does follow the difference in electronegativity of the elements forming the compound.

The free electron theory of metals suggests that if there were in principle a large transfer of charge, greater than $\pm e$ between the atoms in a compound, the charge separation would be largely screened out by the conduction electrons, so that the ion-core interactions would be somewhat less than would be obtained by the assumption of a Madelung energy arising from the ionic structure. Such an interaction is not screened out entirely but greatly attenuated by the presence of the conduction band. It is therefore to be expected that the bonding of intermetallic compounds will be less strong than the corresponding ionic substances for this reason. Recent theoretical studies (18) have indicated a proportionality between the chemical potentials of electrons in pure metals, and the electronegativity scale of Pauling, and hence the conclusions drawn from the use of electronegativities should be in the right direction, even if the use of simple formula

$$\Delta H_{\text{ionic}} = 23 |x_A - x_B|^2 \text{ Kcal.}$$

where x_j is the electronegativity, should fail on a quantitative basis. Typical values of the heats of formation of some highly 'ionic' intermetallic compounds are shown in Table 2.

TABLE 2. Some heats of formation of stable intermetallic compounds

Compound	ΔH_{298}^0 Kcal/mole	Structure
NaTl	- 9.0 \pm 1.0	
NaPb	-11.0 \pm 1.0	F.C. tetragonal
NaBi	-15.6 \pm 1.0	F.C. tetragonal
Mg ₂ Sn	-19.25 \pm 1.3	CaF ₂
Mg ₂ Pb	-11.5 \pm 0.7	CaF ₂
Mg ₃ Sb ₂	-71.7 \pm 4	La ₂ O ₃
Mg ₃ Bi ₂	-30.3	La ₂ O ₃
LiAl	-11.7	NaTl
LiTl	-12.8 \pm 1.0	CsCl
NiAl	-28.3 \pm 1.2	CsCl

INTERACTIONS IN LIQUID ALLOYS

It will be clear from the discussion of electron transfer in solid systems, that a dominant effect in binary systems forming stable compounds is that of electron transfer, and that there can be no discussion of any molecular structure such as that found in covalently bonded solids. The closest approach to this situation is in NaTl-type compounds in which each atom has eight neighbours, four of which are of one kind and four of the other. The fact that Tl can achieve in s^2p^2 configuration on receiving an electron, accounts for the four-coordination of the thallium atoms with one another using sp^3 hybrid orbitals. The compound can be described by the ionic symbolism Na^+Tl^- .

It has been frequently suggested (19) that the thermodynamics of binary alloys in which there is a strong interaction should be described in terms of "associations" of the atomic species into "molecules". An example of this is that the thermodynamics of liquid Hg-Tl were accounted for quite well by Predel (20) making use of the existence of the compound Hg_5Tl_2 in the solid alloys (referred to as Hg_3Tl in the paper) to explain the properties of the liquid alloys. It is a corollary of such treatment that the entropy of mixing has a cusp at compositions around that of the solid state compound. Neutron and x-ray diffraction studies of these liquids (21) show the existence of a hump on the radial distribution curve which is often observed in systems for which such molecular association is invoked. Predel suggests that there are two structures in the liquid alloy, one a random mixture of Hg and Tl atoms with a regular heat of mixing, and the other having an Hg_5Tl_2 -related structure. The intermetallic phase is face-centered cubic in the solid state and is also a disordered phase.

The model therefore suggests two different coordination modes for the atoms, but coordination numbers at least as large as eight, the experimental value for the disordered liquid. Clearly the term "molecule" is quite out of place in this context, and the term "microdomain" would seem to fit the requirement more usefully. The extreme situation would represent a majority of the melt in the intermetallic compound coordination with microdomains of random structure interspersed. The transition from a random metallic melt to the nearly ionic molten compound would then be similar to the situation which must apply in the continuous range of liquid solutions which can be formed between liquid Na and NaCl, liquid Cs and Cs_3O and liquid Ag and Ag_2S .

It appears to have been conclusively demonstrated that liquid salts such as the alkaline or alkaline earth halides, oxides and sulphides, have two sub-lattices on which cations mix only with cations, and anions only with anions. This gives a simple basis for Temkin's rule, since it is the entropy of mixing which gives rise to the idealized activities. Thus in Na_2O - K_2O mixtures

$$a_{\text{Na}_2\text{O}} = x_{\text{Na}_2\text{O}}^2$$

because there are two g. ions of sodium ions to mix for every mole of the molecule Na_2O . One must presume that in Na-NaCl mixtures, the population of the chloride sites is a direct function of NaCl concentration and that these sites occur in proximity to one another. There will be no vacancy concentration similar to the state in F-centre NaCl, but regions of liquid containing the major proportion of the halide sites.

In the solid state, the coexistence of an ordered and a disordered state can only occur in the relatively narrow temperature range of an order-disorder transformation. In the liquid state where sites cannot be localized and atoms identified with a given type of site, the order-disorder state should probably be related to fluctuations in the number and type of neighbouring atoms to a given atom.

Oxygen solutions in liquid metals have been studied for a number of elements now that the solid state electrochemical technique has been established. In this method the EMF of a cell containing the metal/oxygen solution as one electrode and a reference metal/metal oxide mixture of known oxygen potential, used in conjunction with an oxide ion conducting solid electrolyte, is measured as a function of oxygen content of the metal (22). This content can be varied under control by the passage of current through the cell. The electrolyte is a solid solution of CaO or Y_2O_3 in ZrO_2 or ThO_2 which has the CaF_2 structure. The transport number of oxygen ions is practically unity over a wide range of oxygen potentials and temperatures (23).

The results, most of which are shown in Table 3, show a close link between the partial molar heat of solution of oxygen in the metal and the heat of formation of the corresponding lowest metal oxide per g. atom of oxygen. The saturation solubilities are normally less than 1 atom percent, and so Henry's law, or at least a close approximation to it, seems to apply to these dilute solutions. A substantial range of solution in a liquid metal is established for the case of caesium, but the only other metal for which a high solubility has been reported is barium (24). Typically then, a dilute solution of oxygen in the metal is succeeded, as the oxygen content increases by the separation of an oxide.

Similarly in sulphur-containing systems, the partial heat of solution of sulphur in the few metals for which information exists, seems to be proportional to the heat of formation of the lowest sulphide. The saturation solubilities of sulphur in liquid metals are, however, usually substantially larger than the corresponding oxygen solubilities. There have recently been published analyses of sulphur solutions in terms of molecular species (25) but again the concept of a molecule which may contain two or three atoms clustered together as a separate entity in a surrounding non-interacting liquid metal seems an unlikely concept. One might think that if such molecules are formed in liquid metals, there would be a closer connection between the heats of solution and the heats of formation of the gaseous molecules,

but the data for oxygen systems do not appear to support this suggestion (Table 3).

TABLE 3. Comparative stability data for metal/oxygen systems.

Metal	$-\Delta\bar{H}_{\frac{1}{2}O_2}$ (Kcal)	$-\Delta H_{298}^0$ oxide (Kcal)	ΔH_{298}^0 gaseous monoxide (26)
Silver	4	7.3 (Ag_2O)	76
Copper	20	40 (Cu_2O)	58
Thallium	15	40 (Tl_2O)	>>28
Indium	32	74 ($1/3 In_2O_3$)	>41
Gallium	35	86 ($1/3 Ga_2O_3$)	57
Lead	23	54 (PbO)	16.8
Tin	25	69.4 ($\frac{1}{2}SnO_2$)	5
Germanium	39	69.3 ($\frac{1}{2}GeO_2$)	- 9.2
Iron	28	65	63
Cobalt	16	57	74
Nickel	19	57	74

It should be emphasized that because of the nature of the liquid metal solutions the partial Gibbs energy data cover only a relatively narrow temperature range (100-200 K) and the heats of solution quoted above are second law values only.

TERNARY SOLUTIONS

The metallurgist is interested in more complex metallic systems than binary systems in many industrial applications. Thus, the production of stainless steel begins with a quaternary system Fe-Ni-Cr-C to which further additions must be made to produce alloys for practical use. It is not surprising that metals chemists have pushed the study of alloys into ternary systems as an approach to understanding the complex real alloys. The ternary Gibbs-Duhem equation was first solved by Darken (27) who showed that activities of all three components of a ternary system could be obtained from measurements of the activity of one component in the whole composition range. The general solution equation

$$\Delta G_{x_1, x_3}^{XS} = (1-x_2) \int_1^{x_2} \frac{-xs}{(1-x_2)^2} \cdot dx_2 \quad - \quad x_1 \int_1^0 \frac{-xs}{(1-x_2)^2} \cdot dx_2 \quad - \quad x_3 \int_1^0 \frac{-xs}{(1-x_2)^2} \cdot dx_2$$

(I)

x_1/x_3 $x_3=0$ $x_1=0$

can be approximated for the dilute solution of one component in the complete range of composition of the binary alloy of the other two components thus

$$\Delta G_{x_1, x_3}^{XS} = x_1 \Delta G_{2(x_1=1)}^{-XS} + x_3 \Delta G_{2(x_3=1)}^{-XS} - \Delta G_{2(x_1/x_3)}^{-XS} \quad (II)$$

providing that all three binary systems are regular solutions. This equation has been found to describe a number of ternary solutions with a dilute concentration of one component (28) and is the basis for the calculation of concentrated ternary alloy thermodynamics from a knowledge of the constituent binary systems. The treatments due to Kohler (29) and Toop (30) differ in the integration paths which are chosen in the ternary field but are basically dependent on additive behaviour of the atomic interactions. An example of these treatments is the Toop equation

$$\Delta G_2^{-XS} = \frac{X_1}{1-X_2} \cdot \Delta G_{1-2}^{-XS} + \frac{X_3}{1-X_2} \cdot \Delta G_{2-3}^{-XS} - (1-X_2)^2 \cdot \Delta G_{1-3}^{XS} \quad (\text{III})$$

which is frequently used today for the calculation of ternary system thermodynamics from binary data. Here ΔG_{1-2} is the partial Gibbs energy of solution of component 2 at the given mole fraction X_2 in the binary 1-2 system ΔG_{2-3} is for the corresponding 2-3 system and ΔG_{1-3}^{XS} is the integral excess Gibbs energy of the binary 1-3 system at the given ratio of atom fractions X_1/X_3 .

Although these equations can be formally derived from the Darken integral, it is found experimentally that the dilute solution equation which can be derived from that given above for the activity coefficients

$$\log \gamma_2^{1-3} = X_1 \log \gamma_2^1 + X_2 \log \gamma_2^3 - \Delta G_{1-3}^{XS}/RT \quad (\text{IV})$$

can be used to account for several situations even where the constituent binaries 1,2 and 2,3 are patently not regular solutions. An atomic model using constant pairwise bonding and a constant coordination number for these dilute ternary alloys, in which random distribution is assumed, also leads to this equation (31). Proceeding from this model it is straightforward to calculate the quasi-chemical equivalent of the random distribution model. The equation is

$$\left[\frac{1}{\gamma_2^{1-3}} \right]^{1/Z} = X_1 \left[\frac{\gamma_1^{1-3}}{\gamma_2^1} \right]^{1/Z} + X_3 \left[\frac{\gamma_3^{1-3}}{\gamma_2^3} \right]^{1/Z} \quad (\text{V})$$

where again component 2 is the dilute constituent. This equation demonstrates that the random and non-random cases show practically the same variation of γ_2 as a function of X_1/X_3 ratio, when the binary values γ_2^1 and γ_2^3 differ by up to three orders of magnitude, when Z has the high value typical of metallic coordination viz 8-12.

The fit of experimental data in the situation where the coordination number is known to be constant is demonstrated by the fact that the activity coefficients of indium, germanium and tin in dilute solutions in Cu + Au face centred cubic alloys are predicted quite well (32). Similarly, dilute hydrogen and nitrogen solutions in liquid alloys can be predicted to values within the experimental error (33).

The equations fail with the normal values of the coordination number of liquid metals for oxygen dissolved in liquid alloys, and can only be made to fit the extensive data if an unusually low value of the coordination number around 4 is used (34). From the form of the quasi-chemical equation given above, it is clear that a case could be made for a low coordination for oxygen i.e. in tetrahedral or octahedral sites, but this could not be done for the metallic atoms which surround the oxygen solute. Because of the electron affinity of oxygen it seems quite probable that at least one electron is subtracted from the conduction band, and located on or about the oxygen atom. To compensate for this localization, the conduction band electron density would be expected to be lower in the metallic coordination shell of oxygen. Thus, the effective number of atoms with which each metal atom surrounding the oxygen atom can interact could be reduced considerably in line with the empirical fit to the quasi-chemical equation.

This now raises the question of the existence of microdomains containing a number of oxygen atoms (ions) in which the broken metal-metal bonds of the coordination shell of each oxygen atom could be partially compensated for by further oxygen bonding in "oxide" clusters.

Because of the extremely small solid solubility of oxygen in most metals, the interaction of oxygen-metal groupings in solids cannot be extensively studied for subsequent extrapolation to the liquid state. It is known that hydrogen in solids tends to agglomerate (35), but this is mainly to reduce strain energy, a factor which is presumably absent in liquids. This would probably be the case with oxygen solutions in metals. However, some detailed structural information is available from x-ray and neutron diffraction studies of defects in non-stoichiometric oxides such as FeO_{1+x} , which has the rocksalt structure. The value of x can extend up to 0.17 in this phase before the next higher phase, the inverse spinel Fe_3O_4 , is formed. The defects which are introduced into the NaCl structure by oxygen addition are Fe^{3+} interstitial ions in the cubic coordination shell of which are four oxygen ions, two Fe^{2+} cations and two cation vacancies (36). These defect units cluster by sharing faces or edges and corners until the most stable cluster has 4 such units joined by edge and corner sharing. The aggregate so formed is an element of the inverse spinel structure Fe_3O_4 . Thus, FeO_{1+x} contains microdomains which are precursors of the next oxide phase (37).

It is suggested here that such a clustering of units involving oxygen atoms with a lower coordination of metal atoms than is typical of the melt could join to form microdomains in liquid metals and alloys which are precursors of the oxide phase which forms at saturation. The long-term stability of such microdomains is not essential to the argument, and clearly these could be analogous to the unstable nuclei which are formed and disperse again in undersaturated vapours. The formation of microdomains with some structural similarity to the oxide phase might help to explain the puzzling relationship between the partial heat of solution of oxygen in a liquid metal, and the heat of formation of the lowest corresponding oxide.

In conclusion, the evidence for departure of dilute ternary solutions from the simple high-coordination assumptions of equation IV when the dilute constituent has a high electron affinity, such as oxygen or sulphur, should be related to the use of equation III for the computer generation of ternary phase diagrams using binary data only. It would seem that when significant electron transfer can occur in any of the binary components of a given ternary, and where there are strong interactions from this source, it is quite possible that the use of equation III will involve significant error. Evidently, when there is little or no electron transfer, and by inference, even when there is a strong interaction involving d electrons, but which may not involve electron transfer, then equation III may be quite satisfactory. There obviously remain many interesting studies of dilute ternary alloys to be carried out before we can be certain on this point.

THE CREATION OF ALLOY DATABANKS

It seems very likely that the ultimate depository for alloy thermodynamic data will be computer-based data processing systems, and the question arises concerning the most appropriate form of storing such data. Based on the models of alloy systems which have been developed from experimental studies it seems clear that the α function $\Delta G^{XS}/X_1X_2$ is a useful function to consider since a composition-temperature independent value of this function is the strictly regular solution, and a linear dependence on composition only is the sub-regular model. This last model can be understood in terms of free electron theory when there is a difference in the chemical potentials of electrons between the two pure components and ion-core interactions are insignificant thus following Wagner (38) the chemical potential of the atomic species can be written as the simple sum of the ion core and electron chemical potentials

$$\mu_{\text{atom}} = \mu_{\text{ion}} + Z\mu_{\text{electron}}$$

where Z is the number of conduction electrons/atom. Although computers have been traditionally employed with polynomial representations in a single variable eg.

$$\Delta G^{XS}/X_1X_2 = \alpha + \beta X_1 + \gamma X_1^2 + \delta X_1^3 \dots \dots \dots \text{etc.}$$

there is considerable merit in the use of the Scatchard polynomial

$$\Delta G^{XS}/X_1X_2 = \alpha + \beta(X_1 - X_2) + \gamma(X_1 - X_2)^2 \dots \dots \text{etc.}$$

Given the experimental scatter which is normally associated with results for alloy thermodynamics, the unconstrained use of computer fitting to simple polynomials of the first kind can lead to physically impossible values between the experimental results. The Scatchard expansion in being more directly related to the results of atomic models can be subjectively

more readily controlled in terms of the actual experimental error associated with each experimental point. Thus, the first term is clearly the strictly regular model, the second term is the sub-regular model, the third term allows for asymmetry arising from changes in the electron/atom ratio or to electron transfer, and the fourth term allows for strong interactions. There seems little point in going much further with the expansion unless very accurate results are at hand. It should also be noted that the Scatchard polynomial terms are closely related in shape to the Legendre polynomials which, being orthogonal, allow the addition of further terms as required without significant changes of the coefficients of the earlier terms (39).

These compositional effects ignore the possibility of an excess entropy change on alloy formation, which would introduce a temperature dependence into the α function. This term will be unimportant in alloys where there are weak interactions, but, as shown by Slough (40), there is almost a proportionality between the excess entropy and the heat of solution which will be of significance in systems with a strong interaction. It is true to say that what is regarded as insignificant now will be an object of precise measurement at some time in the future, and it is only to be expected that more precise measurement will mean a more complicated picture of the thermodynamics of alloys. The question which this raises at the present time is "To what extent can we hope to develop models beyond the present simple stage, to predict properties at a more complicated level?" The functions of models must be to summarize existing data and to guide the search for new information, but in alloy systems where small differences in Gibbs energies can sometimes lead to metastable solid systems of long duration, these important fine details cannot be predicted. Furthermore, the need of the practising metallurgists to have accurate data for refining reactions and minor phase segregations is not only beyond the limits of modelling but also outside the realms of accurate measurement at the present time. It becomes important to continue the development of experimental methods not only to provide more reliable input data in known circumstances but to make what might be the qualitative indications of models take on a quantitative aspect of use in alloy design. Indeed the major role of modelling would seem no longer to be an attempted description of the real world, but as a sign post to valuable areas for precise measurement.

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