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THE COORDINATION CLUSTER THEORY FOR METALLIC SOLUTIONS*

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1. INTRODUCTION

The coordination cluster theory (CCT) is a statistical mechanical theory for the thermodynamic properties of a dilute solute in a binary or higher order solvent.¹⁻⁴ Although the CCT has been applied to liquids, it can be modified for solids. The theory permits one to describe the thermodynamic properties of a solute in a binary solvent in terms of the solute properties in the pure solvent components, the properties of the binary mixture and one unknown parameter. In principle, the properties of solutes in multicomponent solvents can be calculated from those in the subsidiary binary solvents. Modern quantum mechanical methods for the calculation of the energetics of metal solutions could be used to place the theory on a firm fundamental basis by testing the approximations in the theory and determining the unknown parameters.

2. THE THEORY

The dissolution of a solute S in a binary solvent $A - B$ leads to the formation of coordination clusters $S(Z-i, B_i)$, where S is coordinated by Z solvent atoms of which i are B atoms and the remainder are A atoms. If one considers the equilibria for the formation of these coordination clusters,

then one can write a set of $(Z + 1)$ equilibrium constants, K_i , given by

$$K_i = \frac{a_i}{a_S a_A^{Z-i} a_B^i}, \quad i = 0, \dots, Z. \quad (2)$$

where the a 's are activities of the species indicated. In dilute enough solutions of S , all the coordination clusters will obey Henry's law. If standard states are defined so that the activity coefficients of the clusters are unity at infinite dilution, then the activity of the i^{th} coordination cluster species, a_i , is equal to its atomic fraction, X_i . It follows that

$$\frac{1}{\gamma_S} = \sum_{i=0}^Z K_i a_A^{Z-i} a_B^i = \sum_{i=0}^Z K_i (X_A \gamma_A)^{Z-i} (X_B \gamma_B)^i. \quad (3)$$

where the γ 's are activity coefficients of the species in solution. The calculation is thus reduced to evaluating the equilibrium constants, K_i , or the standard Gibbs free energy of formation of the i^{th} species at infinite dilution, $\Delta G_i^\circ (= -RT \ln K_i)$. This evaluation

can be performed by relating the equilibrium constants to identifiable energetic and statistical factors for the formation of the i^{th} species and the interaction of that species with the solvent. A statistical mechanical calculation¹ leads to the relation:

$$-\ln K_i = -\ln \frac{Z!}{(Z-i)!i!} + \frac{(Z-i)}{Z} \ln \gamma_{S(A)} + \frac{i}{Z} \ln \gamma_{S(B)} + \frac{g_i^E}{RT} + (1-t)[(Z-i) \ln \gamma_A + i \ln \gamma_B]. \quad (4)$$

The first term on the right hand side is a statistical factor. The second and third terms represent simple additivity of the pair interactions between S and the solvent atoms, and the fourth term, g_i^E/RT , represents the extent to which the bonding is nonadditive, that is, the extent to which the linear relationship given by the second and third terms does not hold. When $i = 0$ and $i = Z$, g_i^E is zero, so that this fourth term is analogous to an excess Gibbs free energy of mixing of A and B in the coordination shell. Thus, the first four terms on the right-hand side represent the standard free energy of formation of the i^{th} species from the end-member species, $S(A_Z)$ and $S(B_Z)$, in the end-member solvents A and B . The last term on the right-hand side represents the difference between the interactions of the A or B atoms in the i^{th} species with the mixed solvent and the interactions of these same atoms in the end-member species with the respective end-member solvents (pure A or pure B). The factor $(1-t)$ represents the relative extent to which the interaction with the solvent is the same as the interaction of a "free" A or B atom that has no solute atoms as nearest neighbors. The statistical mechanical calculation¹ leads to an expression for the activity coefficient of a solute, γ_S , in the binary solvent $A-B$

$$\frac{1}{\gamma_S} = \sum_{i=0}^Z \frac{Z!}{(Z-i)!i!} \left(\frac{X_A \gamma_A^t}{\gamma_{S(A)}^{1/Z}} \right)^{Z-i} \left(\frac{X_B \gamma_B^t}{\gamma_{S(B)}^{1/Z}} \right)^i \exp \left(\frac{-g_i^E}{RT} \right) \quad (5)$$

where X_A , γ_A , and X_B , γ_B are the mole fractions and activity coefficients of components A and B , respectively; $\gamma_{S(A)}$ and $\gamma_{S(B)}$ are the activity coefficients of component S at high dilution in the pure solvents A and B ; and t is a geometric factor. The value of t is $1/Z$ for a substitutional alloy and can range from $1/Z'$ to $1/2$ for an interstitial alloy, with Z' being defined as the coordination number of the solvent atoms. It has been shown that calculations based on Eq.(5) are relatively insensitive to a reasonable choice of values for the parameters Z and t .² We have used a value of $t = 1/3$ for interstitial alloys, and $t = 1/Z$ for substitutional alloys, with Z ranging from 6 to 12.²

Since g_i^E is an excess free energy of mixing of solvent atoms in the coordination shell, it can be expressed as a power series involving the concentrations of the atoms, $((Z-i)/Z)$ and (i/Z) , in the coordination shell of the α cluster. Up to second-order terms it is given by the expression

$$g_i^E = \sum_{j < j'} \frac{(Z-i)jh}{2} + \dots \quad (6)$$

where h is an unknown parameter. Equation (6) implies that the mixture of atoms in the coordination shell forms a regular solution. We have shown that Eq. (6) can

Fig. 1. Relative activity coefficients of oxygen in the Cu-Ni-O system. Curves (1), (2), and (3) refer to calculations from equations in References 5-7, in Reference 8, and from the CCT, respectively.

Fig. 2. Relative activity coefficients of sulfur in the Ag-Sn-S system. Curves (1), (2), and (3) refer to calculations from equations in References 5-7, in Reference 8, and from the CCT, respectively.

be used to accurately represent the solubility of oxygen or sulfur in a large number of binary alloys.²

3. COMPARISONS WITH EXPERIMENT

A comparison of all reliable data on a number of solutions of oxygen and sulfur in binary liquid alloys indicates that all the data in each system could be very well represented by the use of a single unknown parameter. Figure 1 illustrates this for the Cu-Ni-O system. It also illustrates the fact observed here and in the other cases where measurements were made at more than one temperature, that the same param-

Fig. 3. Relative activity coefficients of Li in Al-Sn alloys. Curves (1), (2), (3), and (4) refer to calculations from equations in References 5-7, modified from References 5-7, in Reference 8, and from the CCT, respectively.

eter correctly predicts the temperature dependence of the activity coefficients. This means that the configurational entropy of solution predicted by the theory adequately describes the entropies in these melts. Figure 1 illustrates the fact that the theory in References 5-7 does not describe the data well and Figure 2 similarly illustrates this fact for Reference 8. Thus, the CCT is the only theory which provides a simple accurate description of a large number of measurements on alloy solutions. With the very accurate measurements on dilute solutions of Li in Al-Sn,⁹ it can be seen in Figure 3 that the CCT provides the only good representation of the data.

4. THE POSSIBLE ROLE OF QUANTUM MECHANICAL THEORIES

Modern quantum mechanical calculations of the energetics of alloys present the possibility for testing the approximations and enhancing the utility of the CCT. There are two aspects of the energetics which can be investigated. One aspect is related to the relative energetics for the equilibria between the different coordination clusters in a solution

where A and B are atoms in the bulk solvent which are not near an S atom. The theory and its ability to represent data well implies that, to a good approximation, the energies for reaction (7) change in increments of h as a function of i so that

$$\Delta E_i \sim \Delta E_0 - ih \quad (8)$$

This first order approximation for the non-additivity of "pair bond" energies requires a theoretical examination. In addition to this, the absolute values of the energetic parameters could, in principle, be predicted *a priori* by quantum mechanical methods. This would require calculations of the energetics of solutions of $Z+1$ clusters with central S atoms and $2(Z'+1)$ clusters with central A or B atoms. The initial implementation of such calculations could be made on a solid or liquid solution which is simple enough

to readily perform calculations with current capabilities. There are several other requirements for initial work. The solution could be substitutional or interstitial and the expected energetics should be unique enough to provide an adequate test of the CCT. In addition, it should be possible to make precise measurements on the chosen alloy system. The coupling of quantum mechanical calculations with the theory could greatly enhance the usefulness of theories such as the CCT and provide guidance for improving their ability to describe real systems.

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