Relation of Regular Solution Theory of Liquid Metal Alloys to Miedema's Work

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Relation of Regular Solution Theory of Liquid Metal Alloys to Miedema's Work

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In a binary liquid alloy, regular solution theory leads to the concentration fluctuations $\langle (\Delta c)^2 \rangle$ as

$$\langle (\Delta c)^2 \rangle = \frac{c(1-c)}{1 - 2wc(1-c)/k_B T} \qquad \text{(i)}$$

where w is the interchange energy in the theory. It is pointed out that Miedema's work gives an explicit expression for w in an AB alloy in terms of

   a) the boundary densities ρ_A and ρ_B in pure metals A and B

and

   b) the electronegativity difference $(x_A - x_B)$.

   Since w has been been estimated both from thermodynamic data and from phase diagrams, a link is thereby forged between the chemical theory of solutions embodied in Eq. (i) and the electron theory of metals.
   Some numerical consequences for the interchange energy w are explored briefly for mixtures of two alkali metals. It is finally stressed that the type of theory based on Eq. (i) is not applicable when size differences become large.

1 INTRODUCTION

The work of Miedema and his colleagues[1] on binary AB metal alloys has brought pattern into the field of heats of formation. These are expressed in terms of the electronegativity difference $(x_A - x_B)$ and the boundary

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electron densities ρ_A and ρ_B of pure metals A and B. The remaining factor is concentration dependent, being essentially $c_A(1 - c_A)$ for a disordered alloy, where c is the concentration. If the atomic volumes V_A and V_B are different, $c_A^s(1 - c_A^s)$ is used instead, where c^s is the surface concentration given by $c_A^s = c_A V_A^{2/3}/(c_A V_A^{2/3} + c_B V_B^{2/3})$.

We show in Section 2 below that contact can be established between Miedema's treatment and the chemical theory of regular solutions. This later theory has been employed by a number of workers to discuss various thermodynamic properties of solutions, the work of Bhatia, Hargrove and March[2] on liquid Na–K alloys being referred to again below. The basic formulae of regular solution theory are summarized in Section 2. This theory has been shown to be based fundamentally on statistical mechanics by Longuet–Higgins,[3] in what is now known as the theory of conformal solutions. This fundamental treatment is, however, crucially dependent on the pair potentials $\phi_{ij}(r)$ in the AB alloy being obtainable from the pair potential $\phi(r)$ of a reference liquid, through the scaling

$$\phi_{ij}(r) = A_{ij}\phi(\lambda_{ij}r) \qquad (1.1)$$

plus the assumption that the A's and λ's are sufficiently near to unity to use perturbation theory about the reference liquid.[4]

The fact that λ_{ij} must be near to unity clearly limits the applicability of the theory to size differences that are not too large. The A's being near to unity suggests that, in metals, the theory should be best when the valence difference is also small or zero. Bhatia et al.[2] show that the theory works well for Na–K, and we summarize the way their results were obtained in Section 2, in order to make contact with Miedama's work. Conformal solution theory[3,4] leads to the interchange energy w, defined precisely below, as a function of thermodynamic state, but is otherwise the same in its predictions as regular solution theory.

2   REGULAR SOLUTION THEORY

Interchange energy in terms of boundary densities and electronegativity differences

Bhatia et al.[2] focused on the concentration fluctuations $\langle(\Delta c)^2\rangle$ in their work. Thermodynamically, this quantity is related to the Gibbs free energy of the solution, say $G(c)$, and structurally, in the liquid, to the long wavelength limit of the concentration-concentration structure factor $S_{cc}(q)$. The result

they used for liquid Na–K alloys was

$$\langle(\Delta c)^2\rangle = S_{cc}(0) = k_B T/(\partial^2 G/\partial c^2)$$

$$= \frac{c(1 - c)}{1 - 2wc(1 - c)/k_B T}. \qquad (2.1)$$

Contact can now be established with Miedema's work through the heat of solution, which is directly related to w. In fact, w is an interchange energy such that if we start with two pure metals A and B and exchange an interior A atom with an interior B atom, the total change in the energy of the metals is $2w$. Then one can write[5]

$$w = \tfrac{1}{2}(\Delta H_s(A \text{ in } B) + \Delta H_s(B \text{ in } A)) \qquad (2.2)$$

where $\Delta H_s(i \text{ in } j)$ is the heat of solution of i in j. Thus, from Eq. (2.1) we can write

$$\frac{1}{S_{cc}(0)} = \frac{1}{c(1 - c)} - \frac{2w}{k_B T} \qquad (2.3)$$

This then is the point at which we can make contact with Miedema's work on the heats of solution. Then we obtain for w an expression of the form

$$w = \frac{V_A^{2/3} + V_B^{2/3}}{\rho_A^{-1/3} + \rho_B^{-1/3}} \left[-P(\rho_A^{1/3} - \rho_B^{1/3})^2 + Q(x_A - x_B)^2 \right] \qquad (2.4)$$

where P and Q are almost constant, through a wide class of alloys. Thus we have here a link between ρ_A and ρ_B, quantities which are obtainable from the electron theory of pure metals, the electronegativity difference $x_A - x_B$, and the interchange energy of the theory of regular solutions.

3   SOME NUMERICAL CONSEQUENCES FOR LIQUID MIXTURES OF TWO ALKALI METALS

We show in the Table below some numerical consequences of the above formula (2.4) for the interchange energy w. We use the experimental results of Yokokawa and Kleppa[6] in Eq. (2.2) to obtain the final column of the Table.

There is gross correlation between experiment used in Eq. (2.2) and w calculated from Eq. (2.4), but more than that cannot be claimed. Two specific comments are called for. One is that, as Bhatia and March[7] have shown, NaCs has too large a size difference to be treated by regular solution

TABLE I

Alloy (AB)	w (units are KJ/g at. solute)	Experiment
NaK	5.5	2.9
CsK	0.0	0.45
(NaCs)	10.0	5.0
RbCs	0.0	−0.5
KRb	0.0	0.5
NaRb	7.5	5.4

theory and in particular, in Eq. (2.3), the symmetry around $c = \frac{1}{2}$ is badly violated by the measured $S_{cc}(0)$. Secondly, the formula (2.4) gives to $w/k_B T$ for liquid Na–K alloys a value twice as large as that used by Bhatia,[8] and this factor of 2 is unacceptable in calculating the concentration fluctuations, which are very sensitive to the value of w. Thus it is clear from Eq. (2.1) that for $w/k_B T = 2$, $S_{cc}(0)$ is infinite at $c = 0.5$.

Therefore, while there is interesting contact between Miedema's work and regular solution theory, refinements will be called for before Miedema's work can be used quantitatively in conjunction with regular solution theory.

4 POTENTIAL RELATIONSHIP TO PHASE DIAGRAMS AND SURFACE SEGREGATION

It is of interest to draw attention here to the fact that Bhatia and March[9,10] have studied the way in which the phase diagrams of binary alloys depend on the difference between the concentration fluctuations in the liquid and solid alloys. In this context, we note that Miedema has demonstrated that the constants P and Q in Eq. (2.4) do exhibit systematic differences between solid and liquid for certain classes of alloys. For example, $w_{\text{liquid}} \neq w_{\text{solid}}$ for alloys formed from one transition metal and one polyvalent simple metal. But in contrast his work leads to $w_{\text{liquid}} = w_{\text{solid}}$ for alloys of two transition metals. Thus again, Miedema's treatment will need further refinement if it is to be used in conjunction with regular solution theory to calculate phase diagrams.

In addition to the estimates of $w_{\text{liquid}} - w_{\text{solid}}$ given by Bhatia and March,[10] these workers have also discussed the way in which the problem of surface segregation depends on the concentration fluctuations.[11] It has been pointed out by Burton and Machlin[12] that surface segregation and phase diagrams are closely linked.

5 SUMMARY

The main result of this note is to derive the interchange energy of an AB alloy in terms of the boundary electron densities in the pure metals A and B, and the difference in electronegativity. Contact is made between the numerical predictions of Eq. (2.4) for liquid Na–K alloys and the interchange energy required to obtain correctly the concentration fluctuations. The Miedema treatment is not yet sufficiently refined for this latter purpose, giving the interchange energy to be about a factor of two too large. However, it is the correlation of w with boundary density and with electronegativity which is the important point we wish to stress here. We are continuing to work on refinement of the results presented here.

Acknowledgement

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