"Constant-Volume Alloy" Formulation of Enthalpy of Mixing for Metallic Systems

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We present an exact statistical thermodynamic expression for the partial enthalpy of mixing for metals which avoids the problems of evaluating the large internal energy of the pure metals from the plasma state. This method is applied to the homovalent alloys Al-Ga, Al-In and Al-Tl. The results show clearly the tendency towards a critical mixing point in these systems when using a pseudopotential theory for these metals. An estimate for the critical point of the Al-Tl system and reasonably correct values for the partial enthalpies at infinite dilution are obtained.

1. Introduction

Previous attempts [1, 2] at predicting the enthalpy and free energy of mixing of two metals rested on the difference of the large internal energies (mostly electrostatic) of the alloy and the metals involved. This difficulty could be avoided by investigating substitutional systems [3] for which there is little difference of atomic volumes and thus only small variations of electrostatic and electron gas energies. For non-substitutional systems of higher valency, this problem essentially involves finding a fraction of one eV (a typical enthalpy of mixing) out of differences of cohesive energies of the order of 50 eV, thus a problem described as "looking for a needle in a haystack".

The problem of the enthalpy of mixing is important because it enables one to study mixing and demixing phenomena for liquid alloys and thus the approach to a critical point of mixing. We shall study this problem in homovalent metallic mixtures, because for such systems immiscibility may occur and also because we can more easily maintain the electron gas in known conditions.

We shall, in a first part, transform the problem of the enthalpy of mixing at constant pressure P and temperature T into partial energies at constant molar volume V_m and T. The latter problem allows one to use the internal energy expressions in terms of pair potentials and correlation functions [3]. Using a pseudopotential theory of metals and experimental correlation functions, we shall obtain the partial enthalpy of mixing at infinite dilution, on the average, for the two components in Al-Ga, Al-In and Al-Tl. These results clearly show the tendency towards immiscibility for Al-Ga and the immiscibility for the Al-In and Al-Tl systems.

2. Formulation of the "Constant-Volume Alloy" Method

The internal energy (per mole) of a binary alloy can be written at finite temperature as follows [3]:

$$U = N U_0(Z, V_m) + N\varrho/2 \int d^3r [x_1^2 g_{11}(r) u_{11}(r) + 2 x_1 x_2 g_{12}(r) u_{12}(r) + x_2^2 g_{22}(r) u_{22}(r)]; \quad (1)$$

x_1 and x_2 are the molar fractions, $U_0(Z, V_m)$ is the large internal energy per ion of the electron gas including the electrostatic binding energy to the ions, $u_{ij}(r)$ is the pair potential between ions and $g_{ij}(r)$ is their pair correlation function at density $\varrho = N/V_m$. In magnitude, the term NU_0 overshadows the other term and is the one most dependent on volume or density. The reference state of the system in (1) is the plasma state with infinite distances. When one tries to obtain the molar enthalpy of mixing

$$\Delta H = H(Z, V) - x_1 H_1^0 - x_2 H_2^0 \quad (2)$$

from Eq. (1), one quickly realizes that the variations in the term U_0 are usually too large which implies that, although U_0 represents well individual metallic atoms, the variation of the simple analytical forms of U_0 do not represent reality. In other words, the electron gas properties are not well represented by these analytical forms, particularly when one takes differences or derivatives.

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We now develop a method of calculation for the partial enthalpy of mixing which will not involve taking derivatives of U_0. We recall that the partial enthalpy of mixing is related to the molar enthalpy of mixing ΔH by

$$\overline{\Delta H}_1 = \Delta H + (1 - x_1)(\partial \Delta H/\partial x_1)_{T,P}\,. \qquad (3)$$

Using the definition (2) for ΔH, we obtain immediately

$$\overline{\Delta H}_1 = H - H_1{}^0 + (1 - x_1)(\partial H/\partial x_1)_{T,P}, \quad (4)$$

where H refers to one mole of the alloy, and $H_1{}^0$ to the pure metal 1. The result (4) depends directly on the derivative $(\partial H/\partial x_1)_{T,P}$ or essentially $(\partial U/\partial x_1)_{T,P}$, which would involve taking the derivatives for the alloy of the expression for U in Equation (1). For infinite dilution of the constant 1, Eq. (4) becomes

$$\overline{\Delta H}_1{}^{\infty} = H_2{}^0 - H_1{}^0 + (\partial H/\partial x_1)_{T,\,P,\,x_1 \to 0}\,. \qquad (4\,a)$$

For the element 2 the symmetric relation is obtained:

$$\overline{\Delta H}_2{}^{\infty} = H_1{}^0 - H_2{}^0 + (\partial H/\partial x_2)_{T,\,P,\,x_2 \to 0}\,. \qquad (4\,b)$$

The limits of the partial enthalpy of mixing (partial enthalpy of dissolution) still depend on the enthalpy difference of the pure metal but, their average does not:

$$(\overline{\Delta H}_1{}^{\infty} + \overline{\Delta H}_2{}^{\infty})/2 = \tfrac{1}{2}\left[(\partial H/\partial x_1)_{T,\,P,\,x_1 \to 0} + (\partial H/\partial x_2)_{T,\,P,\,x_2 \to 0}\right]. \qquad (5)$$

In the following we shall evaluate these two partial derivatives from the pseudo-potential theory and thermodynamic parameters. The formation of a dilute alloy with constant valency and constant volume per electron (which is equivalent here to constant atomic density) will keep the NU_0 term in (1) constant, i.e. $(\partial U_0/\partial x_1)_{T,P} = 0$.

Thus the problem becomes to relate the partial derivatives at constant P, which appears in Eq. (5), to those at constant ϱ. Then this last derivative can be evaluated from the structure terms of (1) as if we formed in a first step a constant molar volume alloy and added in a second step the corresponding mechanical energy deduced from thermodynamics.

In fact, classical thermodynamic calculations lead to the relation [4]

$$\left(\frac{\partial H}{\partial x_1}\right)_{T,P} = \frac{\alpha(\bar{V}_1 - \bar{V}_2)\,T}{\chi_T} + \left(\frac{\partial U}{\partial x_1}\right)_{T,\varrho}, \qquad (6)$$

where $\bar{V}_1$ and $\bar{V}_2$ are respectively the partial molar volume of 1 and 2 such that $1/\varrho = x_1\bar{V}_1 + x_2\bar{V}_2$.

α is the thermal expansion coefficient and χ_T the isothermal compressibility of the alloy. When $x \to 0$ the Eq. (6) becomes *

$$\left(\frac{\partial H}{\partial x_1}\right)_{T,\,P,\,x_1 \to 0} = \frac{\alpha_2(\bar{V}_1{}^{\infty} - V_2{}^0)\,T}{\chi_{T_2}} + \left(\frac{\partial U}{\partial x_1}\right)_{T,\,\varrho = \varrho_2,\,x_1 \to 0}. \qquad (7\,a)$$

A symmetric relation (7 b) for component 2 infinitely diluted in 1 can be obtained. The first term on the right hand side of (7 a) is the mechanical energy. The second term can be expressed from the relation (1)

$$(\partial U/\partial x_1)_{T,\,\varrho = \varrho_2,\,x_1 \to 0} = \varrho_2(\varepsilon_{12} - \varepsilon_{22}^0) \qquad (8\,a)$$

with

$$\varepsilon_{12} = \lim_{x_1 \to 0} 4\pi \int_0^{\infty} g_{12}(R)\, u_{12}(R)\, R^2\, \mathrm{d}R\,,$$

and

$$\varepsilon_{22}^0 = 4\pi \int_0^{\infty} g_{22}^0(R)\, u_{22}^0(R)\, R^2\, \mathrm{d}R\,.$$

The equivalent of the Eq. (8) for the component 2 infinitely diluted in 1 is

$$(\partial U/\partial x_2)_{T,\,\varrho = \varrho_1,\,x_2 \to 0} = \varrho_1(\varepsilon_{21} - \varepsilon_{11}^0)\,, \qquad (8\,b)$$

$$\varepsilon_{21} = \lim_{x_2 \to 0} 4\pi \int_0^{\infty} g_{21}(R)\, u_{21}(R)\, R^2\, \mathrm{d}R\,,$$

$$\varepsilon_{11}^0 = 4\pi \int_0^{\infty} g_{11}^0(R)\, u_{11}^0(R)\, R^2\, \mathrm{d}R\,.$$

From the relations (5) and (7 a), (7 b) follows

$$\overline{\Delta H}_1{}^{\infty} + \overline{\Delta H}_2{}^{\infty} = \left(\varrho_2\,\varepsilon_{12} - \frac{\varrho_1\,\varepsilon_{11}^0 + \varrho_2\,\varepsilon_{22}^0}{2}\right) + \left(\varrho_1\,\varepsilon_{21} - \frac{\varrho_1\,\varepsilon_{11}^0 + \varrho_2\,\varepsilon_{22}^0}{2}\right) + \frac{\alpha_2}{\chi_{T_2}}(\bar{V}_1{}^{\infty} - \bar{V}_2{}^0)\,T + \frac{\alpha_1(\bar{V}_2{}^{\infty} - V_1{}^0)}{\chi_{T_1}}\,T\,. \qquad (9)$$

The first two terms in parentheses look like the generlisation of the classical interchange energy in the nearest neighbour approximation. Independently of the elastic terms, it would be tempting to identify these terms with the corresponding partial enthalpies of dissolution. But this could be com-

* The superscript (0) refers to the pure metal in all cases.

pletely wrong. In fact the calculation will show that the difference between the value of these two terms is considerably larger than the difference in the partial enthalpies, which comes from the fact that ε_{12} and ε_{21} correspond to different metallic solvents.

In the following, we will proceed to the evaluation of ε_{12}, ε_{21}, ε_{11}^0 and ε_{22}^0 from the pseudo-potentials.

3. Evaluation of the Effective Pair Potentials

We shall be guided by the following considerations:

1. The model pseudopotentials of Heine, Abarenkov and Shaw, fitted to the spectral energies of the free ion do not require a different pseudopotential calculation for the alloys, but the pair potentials (even homoionic) will differ;

2. The average medium approximation (reasonable in a disordered medium) allows a decoupling into separate pair potentials;

3. As shown by Inglesfield [5] the "on the Fermi sphere" approximation of these pseudopotentials is more valid for alloys, than for pure metals and allows us to use the pure metal pseudopotentials in all cases.

Also, since we are dealing with alloys, we shall use the valencies uncorrected for depletion holes since this effect is very difficult to estimate in alloys and amounts to at the most 5 or 6%. This would increase our pair potentials by perhaps 10%. The effects due to the differing screening at different densities will predominate, as our results clearly show.

The expression for homoatomic pair potentials is well known and is similar (even though differing in values) to the pure metal case. Thus, we turn to the heteroatomic pair potentials, which are obtained by Heine and Weaire [6] in the average medium approximation as

$$u_{ij}(r) = \frac{Z_i Z_j}{r} + \frac{\Omega}{4\pi^3} \cdot \int \mathrm{d}^3 q \, e^{i\mathbf{q}\cdot\mathbf{r}} [v_i(q)\, v_j(q)\, \varepsilon(q)\, \chi(q)],$$

where Ω is the atomic volume of the alloy, $v_i(q)$ $(i=1, 2)$ is the screened pseudopotential of constituant i, $\varepsilon(q)$ the usual dielectric function (normalized to the vacuum) and $\chi(q)$ the perturbation characteristic. Using the linear screening theory, one obtains

$$u_{ij}(r) = \frac{Z_i Z_j}{r} + \frac{\Omega}{\pi^2} \int_0^\infty q \, \mathrm{d}q \, \frac{\sin q r}{r} \cdot [V_i^{\mathrm{ps}}(q)\, V_j^{\mathrm{ps}}(q)\, \chi(q)/\varepsilon(q)],$$

$$u_{ij}(r) = \frac{Z_i Z_j}{r} \frac{2}{\pi} \int_0^\infty \mathrm{d}q \, \frac{\sin q r}{q} \cdot \left\{1 + \left[\frac{V_i^{\mathrm{ps}} q^2 \Omega}{4\pi Z_i} \frac{V_j^{\mathrm{ps}} q^2 \Omega}{4\pi Z_j} \frac{1-\varepsilon(q)}{\varepsilon(q)} \right]\right\}, \quad (10)$$

where $V_i^{\mathrm{ps}}(q)$ is the unscreened pseudopotential form factor in the on-Fermi-sphere approximation [7].

This is indeed the generalization of the homoatomic potentials in terms of the characteristic function

$$F_N^{ij}(q) = -\frac{V_i^{\mathrm{ps}} q^2 \Omega}{4\pi Z_i} \frac{V_j^{\mathrm{ps}} q^2 \Omega}{4\pi Z_j} \frac{1-\varepsilon(q)}{\varepsilon(q)}. \quad (11)$$

Expression (10) is the Fourier transform of the expression found by Ashscroft in q-space [8].

It is worthwhile to look at this expression in more detail. Clearly, the characteristic function for the case $i \neq j$ is rather close to the geometric average of the two functions for $i=j=1$ and for $i=j=2$. Thus, it is not surprising that the Fourier transform itself shows a geometric average behavior, which in some cases may look like the arithmetic average, particularly when the pseudopotentials V_1^{ps} and V_2^{ps} are close near $q=2k_{\mathrm{F}}$. Thus, when the pseudopotentials of the constituents are rather close near $q=2k_{\mathrm{F}}$, the long-range part of the heteroatomic potential will tend to the arithmetic mean of u_{11} and u_{22}. However, when the pseudopotentials are dissimilar, the u_{12} will tend more towards the geometric average of u_{11} and u_{22}.

Equation (10) has one more advantage:

$$V_i^{\mathrm{ps}} q^2 \Omega / 4\pi Z_i$$

is the normalized $v_{\mathrm{N}}(q)$ pseudopotential which in the Heine-Abarenkov-Shaw formalism should stay the same in the alloys as in the pure metal because the constants are determined by the energies of electrons added to the free ion. This is a considerable simplification over the OPW formalism, which necessitates a complete calculation of pseudopotentials for each concentration.

Also, it is clear that the Friedel oscillations of $u_{ij}(r)$ for dilute j atoms will be the same as for $u_{ii}(r)$ with a coefficient essentially given by the second

derivative of F_N^{ij} at $q = 2k_F$. Thus, the coefficient of these in $u_{ij}(r)$ will be the geometric average of the Friedel coefficients of $u_{11}(r)$ and $u_{22}(r)$.

For the numerical computations of the $u_{ij}(r)$ values, we used the model potential parameters tabulated by Heine and Appapillai [7] and the screening constant dielectric function of Vashishta and Singwi [9]. We are thus in the same conditions as for the metal computations of Kumaravadivel and Evans [10], except for the on-Fermi-sphere approximation which we want to use for the alloy, until a non-local, heteroatomic characteristic function is obtained. Thus, we have a check on our pure metal homoionic potentials.

The range in q-values was well subvided into 200 intervals and the range in r extended to 10 Å. Indeed, we found as before that the Friedel oscillations, in aluminium particularly, extend to these distances, which involve three orders of neighbours. However, the alloys enthalpy differences depend on differences of structural energies, and there one could stop integrating at 7.5 Å or over two layers of neighbouring ions from the original ion. Since we shall use here experimental pair correlation functions, it is not much more accurate to go beyond the second neighbours.

We present here the pair potentials for the infinitely dilute situation, since we know best how to approximate their correlation functions in our constant volume formalism. In Fig. 1 we present all pair potentials for the Al-In alloy (for $x_{In} = 1$) and

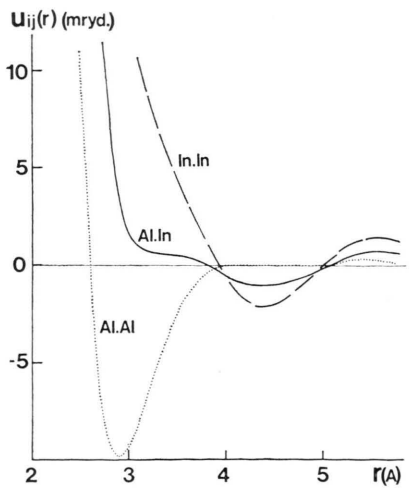

Fig. 1a. Ionic pair potentials for the Al-In alloy when $x_{In} = 1$. Note that the solute Al ion has by far the deepest potential.

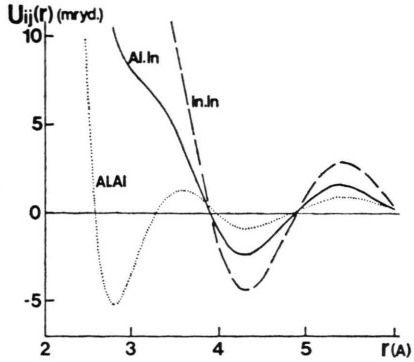

Fig. 1b. Ionic pair potentials for Al-In when $x_{Al} = 1$. Note the more repulsive Al-In interaction.

the In-Al alloy (for $x_{Al} = 1$). It is interesting to note first the obvious dissymmetry of these two figures, i.e. it is more difficult to dissolve the large In pseudo-ion into the smaller Al pseudo-ion than in the opposite situation. The atom which is placed in solution chooses the Friedel oscillations of the matrix and sees its pair potential deepened, i.e. both indium and aluminium have deeper pair potentials when being solutes than when beeing pure. Thus, the solute pairs stabilize themselves with respect to the heteroionic pairs, whether placed in a medium of higher (Al) or lower (In) density. The pair potential Al-Al in Fig. 1 is rather close to the Evans pair potential, although a bit shallower: the effective hard-sphere radius, determined by the approximate thermodynamic perturbation (10), is found to be the same as for Evans. The Al-In and In-Al pair potentials are close to the arithmetic mean of the corresponding homopotentials in the oscillating region, but not near the first peak of the correlation function. Hence a strong positive enthalpy contribution for the structure term (8a), (8b). Thus, it is quite clear that, in the trivalent metals, the pair potentials are stronly influenced by rather small changes in density, whereas in the monovalent metals this does not seem to be the case at all. In Fig. 2, we present the remaining pair potentials.

4. Application to the Systems Al-Ga, Al-In and Al-Tl and Discussion of Results

In order to calculate the partial enthalpy of mixing for these systems, we need also the corresponding partial pair correlation functions. In our "constant volume alloy" method, we need these

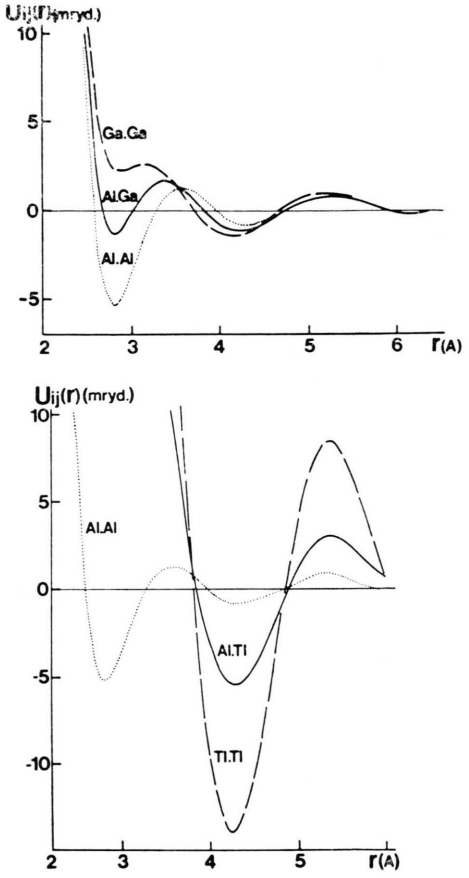

Fig. 2. Some remaining pair potentials for Al-Ga and Al-Tl, when $x_{Al} = 1$. Note that these two alloys show very different pair interactions, where the Al-Tl case perhaps exaggerates the second minimum.

only at constant volume, which is a considerable simplification over the calculation of the true partial correlation functions. All our calculations will be for $T = 943$ K, i.e. a temperature slightly above the melting point of Al. The reason is that the pair correlation function of Al is well measured for both Al (Ruppersberg [11]) and In (Hoehler and Steeb [12]) around this temperature. Liquid Tl seems to be known only at 593 K [13] and liquid Ga at 423 K [14]. Thus, $T = 943$ K is a convenient temperature from the point of view of pair correlation functions. There will be a slight error because not all correlation functions are known at this temperature: the results for the Al-In system will be the most accurate ones from this point of view. Another problem is that the pair correlation functions (being Fourier transform) are not known accurately beyond 9 to 10 Å in r-space. Fortunately, this covers already three orders of neighbours and thus these errors are not very significant. These errors would exist also if we transformed our results into the q-space, because the structure factors are also limited in the q-range.

Since we work here with an alloy formed at constant molar volume in the first step, we shall take all partial pair correlation functions equal to that of the solvent. This is nearly true since we force the solute atom (at constant atomic volume) into the matrix and we do not expect a strong heteroionic interaction in these homovalent alloys. Thus, here we feel justified in using the pair correlation functions of the solvents which are the only ones known at the present time anyway.

The thermal expansion coefficient α and the isothermal compressibility χ_T have been well measured as a function of temperature for the group III metals, and thus we had little trouble in finding good values, although the densities are still not very accurate. The partial volumes $\bar{V}_i^{\infty}$, on the other hand, have not been measured. Here, we shall approximate $\bar{V}_i^{\infty} \cong V_i^0$. Anyway, the elastic or mechanical energy contribution is a small fraction of the "constant volume alloy" energy.

Table 1. Structure terms and elastic term in the partial enthalpies at infinite dilution of Al-Ga, Al-In, and Al-Tl (the metal underlined is the solvent).

	Al-Ga	Ga-Al	Al-In	In-Al	Al-Tl	Tl-Al
$\alpha T/\chi_T$ (dynes/cm^2)	$4.467 \cdot 10^{10}$	$3.53 \cdot 10^{10}$	$4.467 \cdot 10^{10}$	$2.726 \cdot 10^{10}$	$4.467 \cdot 10^{10}$	$2.646 \cdot 10^{10}$
$\varrho_j \varepsilon_{ij}$ (cal/mole)	6306	3792	43253	8568	116970	29244
$\varrho_i \varepsilon_{ii}^0$ (cal/mole)	− 3137	8967	− 3137	32739	− 3137	67264
$\frac{1}{2}\left(\frac{\alpha_2 T}{\chi_{T2}} - \frac{\alpha_1 T}{\chi_{T1}}\right)(V_1^0 - V_2^0)$ (cal/mole)	94		1307		1965	
$\frac{1}{2}(\overline{\Delta H_1} + \overline{\Delta H_2})$ theoretical (cal/mole)	2200		12400		42800	
$\frac{1}{2}(\overline{\Delta H_1} + \overline{\Delta H_2})$ experimental	700		6500		?	

Thus, the calculation was carefully done and the main terms are listed in Table 1. The integrals in the $\varrho_j \varepsilon_{ij}$ and $\varrho_{ii} \varepsilon_{ii}^0$ were evaluated with a step of 0.1 Å up to 4.5 Å and 0.2 Å up to 7.5 Å. The oscillations beyond these become quite weak and, our final result being differences of bond energies, there is a cancellation of any remaining oscillations.

Table 1 shows first the strong dissymmetry of the heteroionic bonds: the situation where one tries to dissolve (at constant volume) the bigger ion into Al has a stronger repulsive energy by a factor of 2 to 4 than the reverse case where one dissolves Al in the large atom matrix. This energy, however, is much larger than the dissymmetry of experimental enthalpies. The average enthalpy of dissolution shows very conclusively the increasing tendency towards immiscibility from Ga to Tl alloyed with aluminium: Al-Ga has an average $\Delta \bar{H}_i^{\infty}$ (experimental) of about 700 cal/mole, whereas Al-In has one of about 6500 cal/mole. Al-Tl is visibly strongly immiscible: no contribution of $T\Delta S$ will make this system miscible before reaching the boiling point, since conformal solution theory gives a critical mixing point $T_C = 10700$ K. Although the agreement with the experimental enthalpy of mixing is not completely satisfactory, this method of calculation represents well the trend of the experimental data and the increasing instability from Ga to Tl alloyed with Al.

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