Heat of Mixing and Activities in Liquid Al-Sn Alloys

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The microscopic electron theory based on the pseudopotential formalism has been applied to the calculation of the heats of mixing and of activities in liquid Al-Sn alloys. The calculated values for both quantities were found to be in reasonable agreement with the experimental data.

Introduction

Experimental results on thermodynamic functions of liquid metals and alloys have often been interpreted qualitatively or semi-quantitatively by using molecular theories [1]. A theoretical basis for an understanding of the thermodynamic properties of liquid metals and alloys has been obtained by developments in the pseudopotential theory of metals [2—9].

The main purpose of this paper is to present the results of calculations on the heat of mixing and activities of liquid Al-Sn alloys using a method which is similar, in principle, to that of Young [2] and Hafner [7]. The applicability of the microscopic electron theory in the calculation of the thermodynamic properties of alloys is, however, limited to alloys formed of Group III and IV elements.

Basic Equations

On the basis of the Gibbs-Bogoliubov inequality [3] we could obtain the following equation for the Helmholtz's free energy:

$$F \leqq F_0 + \tfrac{1}{2} \sum U(q) [a(q) - 1] , \tag{1}$$

where F_0 is the free energy of the so-called reference system, $a(q)$ its structure factor and $U(q)$ the pair wise interaction. The experimental structure factors of liquid metals are well expressed by the hard sphere model [5]. Therefore, if we use the structure factor approximated by the hard sphere model as a reference system and the hard sphere term F_{hs} which includes the contribution of the electron gas, the free energy of the system may practically be written as

$$F = F_{\mathrm{ps}} + F_{\mathrm{hs}} , \tag{2}$$

where F_{ps} contains the total energy of the electrons and ions in the metal and F_{hs} the entropy of the hard spheres. An expression for the total energy E_{tot} in liquid metals and alloys based on the pseudopotential theory has been discussed previously [6, 7]. The basic equations necessary for the discussion are:

$$F_{\mathrm{ps}} = E_{\mathrm{tot}} - \tfrac{3}{2} k_{\mathrm{B}} T , \tag{3}$$

$$F_{\mathrm{hs}} = \tfrac{3}{2} k_{\mathrm{B}} T - T S_{\mathrm{hs}} , \tag{4}$$

$$\begin{aligned} E_{\mathrm{tot}} = {} & E_{\mathrm{elec}} + E_{\mathrm{H}} + E_{\mathrm{es}} + E_{\mathrm{bs}} \\ & + E_{\mathrm{cc}} + \tfrac{3}{2} k T , \end{aligned} \tag{5}$$

$$\begin{aligned} E_{\mathrm{elec}} = {} & \frac{2.21}{r_{\mathrm{s}}{}^2} Z - \frac{0.916}{r_{\mathrm{s}}} \\ & \cdot Z - (0.115 - 0.031 \ln r_{\mathrm{s}}) Z , \end{aligned} \tag{6}$$

$$E_{\mathrm{H}} = \lim_{q \to 0} \left(w^{\mathrm{bp}} + \frac{8\pi}{q^2} Z \right) \frac{Z}{\Omega} , \tag{7}$$

$$\begin{aligned} E_{\mathrm{eff}} = {} & E_{\mathrm{es}} + E_{\mathrm{cc}} && (8) \\ & + \left[E_{\mathrm{bs}} - \frac{1}{2} \sum_{q \neq 0} \frac{q^2}{8\pi} \, | w^{\mathrm{bp}} |^2 \left(\frac{1}{\varepsilon(q)} - 1 \right) \right] \\ = {} & \tfrac{1}{2} \sum \varphi_{\mathrm{eff}}(q) [a(q) - 1] \\ = {} & \frac{1}{2\Omega} \int_0^\infty \varphi_{\mathrm{eff}}(r) \, g(r) \, 4\pi r^2 \, \mathrm{d}r , && (9) \end{aligned}$$

$$\begin{aligned} S_{\mathrm{hs}} = {} & k_{\mathrm{B}} \left[\ln \left\{ \frac{e}{n} \left(\frac{e \, m \, k_{\mathrm{B}} T}{2\pi \hbar^2} \right)^{3/2} \right\} \right] \\ & + k_{\mathrm{B}} \left[\ln(1 - \eta) + \frac{3}{2} \left\{ 1 - \frac{1}{(1 - \eta)^2} \right\} \right] , \end{aligned} \tag{10}$$

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where w^{bp} is the bare pseudopotential, $\varepsilon(q)$ the dielectric function, $\varphi_{\mathrm{eff}}(r)$ the effective interionic potential, $g(r)$ the pair distribution function, n the number density of the ions and η the packing density. The other symbols have their usual meaning [6—8]. In the expression for the entropy, the electron entropy has been neglected because it is very small compared with S_{hs} [9]. The above expression is easily extended to a binary alloy, although the equations become somewhat complicated [7, 8].

The heat of mixing of a binary alloy $\mathrm{A}_{1-x}\mathrm{B}_x$ is

$$\Delta E = E_{\mathrm{tot}}(\mathrm{A}_{1-x}\mathrm{B}_x) - (1-x)\,E_{\mathrm{tot}}(\mathrm{A}) - x\,E_{\mathrm{tot}}(\mathrm{B})\,, \qquad (11)$$

where $E_{\mathrm{tot}}(\mathrm{A}_{1-x}\mathrm{B}_x)$, $E_{\mathrm{tot}}(\mathrm{A})$ and $E_{\mathrm{tot}}(\mathrm{B})$ are the total energy of the alloy $\mathrm{A}_{1-x}\mathrm{B}_x$, and the pure metals A and B, respectively.

On the other hand, the activity a_{A} in a binary A-B alloy is given by

$$a_{\mathrm{A}} = \exp\frac{\mu_{\mathrm{A}} - \mu_{\mathrm{A}}{}^0}{k_{\mathrm{B}}T}\,, \qquad (12)$$

where μ_{A} and $\mu_{\mathrm{A}}{}^0$ are the chemical potentials of element A in the alloy and in the pure standard state. The chemical potential μ_{A} is given by

$$\mu_{\mathrm{A}} = (\partial G/\partial n_{\mathrm{A}})_{P,\,T,\,n_{\mathrm{B}}} = \mu_{\mathrm{A}}^{\mathrm{hs}} + (\partial F_{\mathrm{ps}}/\partial n_{\mathrm{A}})_{P,\,T,\,n_{\mathrm{B}}}\,, \qquad (13)$$

where $n_{\mathrm{A}} + n_{\mathrm{B}} = n$. As mentioned before, F_{ps} can be described by the electron theory of metals, and the partial differentiation $(\partial F_{\mathrm{ps}}/\partial n_{\mathrm{A}})$ is also easily obtained from the plot of F_{ps} versus n_{A} [8]. The full expression for the activity of a liquid binary alloy in terms of the microscopic electron theory of metals has already been described [8]. The essential equations are summarized in the Appendix.

Method of Calculation and Comparison with Experiment

The information required to estimate the total energy are the pseudopotentials of the bare ions the dielectric function and the structure factors. Several treatments have been reported for evaluating the pseudopotentials of bare ions in metals. The empty-core potential [10] is useful for the present calculation. This potential with the core radius r_{c} is written as

$$w^{\mathrm{bp}} = (4\pi z/q^2)\cos(q\,r_{\mathrm{c}})\,, \qquad (14)$$

where r_{c} is determined so as to satisfy the equilibrium condition $(\partial E_{\mathrm{tot}}/\partial\Omega) = 0$ [2, 4]. We have assumed that r_{c} does not change with alloy composition so that the core-core repulsion potential between the atoms A and B, $\Phi_{\mathrm{cc}}^{\mathrm{AB}}(r)$, is equal to the root mean square of the AA and BB pair potentials. To proceed with the calculation, we have used Born-Meyer type repulsion potentials [11] for $\Phi_{\mathrm{cc}}(r)$ and the Hubbard-Sham approximation [12, 13] for the dielectric function $\varepsilon(q)$. The values for the Born-Mayer repulsion parameters are given in Table 1. The small volume effect on alloying was taken from the experimental density data [18].

Table 1. A list of parameters used in the calculations.

Packing density	0.408				
Hard sphere diameter	Al	2.46 Å			
	Sn	2.83 Å			
Core radius for model pseudopotential	Al	1.19 (a. u.)			
	Sn	1.23 (a. u.)			
		A (eV)	B	C	r_0 (Å)
Core repulsion parameters	Al	0.908	9.97	−19.6	2.82
	Sn	1.32	8.95	−20.3	3.23

$\Phi_{cc}(r) = A\exp[B + C(r/r_0)]$

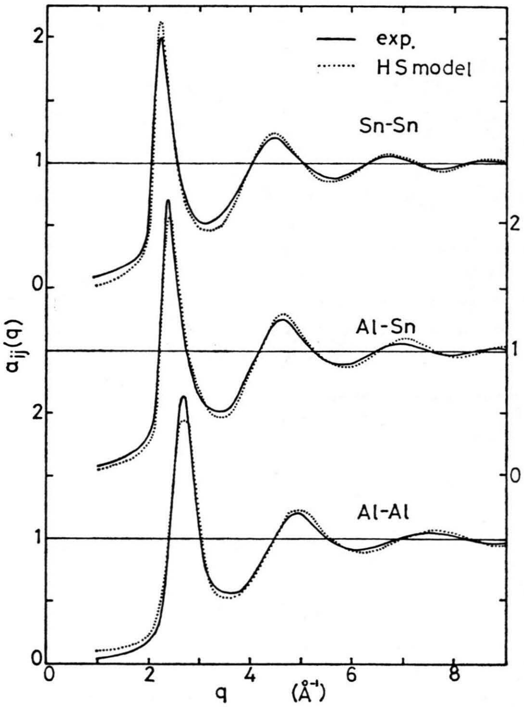

Fig. 1. Partial structure factors obtained experimentally for a liquid Al-50 at % Sn alloy at 800 °C.

Figure 1 shows the partial structure factors for a liquid Al-50 at% Sn alloy at 800 °C obtained experimentally by the present authors. Most strikingly the general profiles of the partial structure factors are rather similar to those of liquid binary alloys of simple metals such as Na-K, i.e. they all show a relatively sharp symmetrical first peak followed by small oscillations in amplitude. Thus these results indicate that the Al and Sn atoms act, to a first approximation, like the hard spheres in the hard sphere mixture model by Ashcroft and Langreth [14]. Based on the experimental structural data of Fig. 1, the partial structure factors given by the hard sphere model were used in the present calculation. This is consistent with the condition of the Gibbs-Bogoliubov inequality in Equation (1). The packing density and the hard sphere diameters of the hard sphere mixture model [14] were determined by fitting the experimental structure factors of the Al-50 at% Sn alloy. A comparison between experiment and calculation is given in Fig. 1. The relevant parameters are summarized in Table 1. It has been confirmed that the hard sphere model with these parameters also reproduces the experimental structure factors of the alloys with 20, 40, 60 and 80 at% Sn. The hard sphere diameters in Table 1 are close to the position of the repulsive part in the effective interionic potentials. This is consistent with the previous results of Hafner [7].

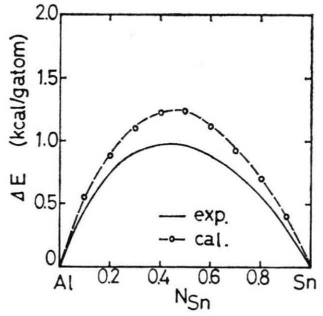

Fig. 2. Calculated and experimental heats of mixing of liquid Al-Sn alloys at 800 °C. The experimental data are taken from the work of Wittig and Keil [15].

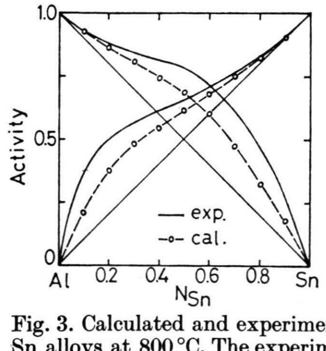

Fig. 3. Calculated and experimental activities in liquid Al-Sn alloys at 800 °C. The experimental data are taken from the work of Lee and Yazawa [16].

The variation of the estimated heat of mixing and the activities with the composition of liquid Al-Sn alloys is shown in Figs. 2 and 3 together with the experimental data [15, 16] from the compilation of Hultgren et al. [17]. The calculated curves are in fair agreement with the measured data. It will be interesting to extend the present method to other systems.

Concluding Remarks

The microscopic electron theory based on the pseudopotential formalism seems to be a useful framework for the theoretical estimation of the thermodynamic properties of liquid binary alloys which involve the elements of Group III and IV. This is consistent with the calculation of Hafner [7] on alloys formed from elements of Groups I and III. Although the number of available points for a comparison between calculation and experiment is still limited, the present work suggests that the pseudopotential method in conjunction with the hard sphere model as a reference system is useful for rationalizing the activity behaviour of liquid binary alloys.

Appendix

The purpose of the appendix is to indicate the method for estimating the chemical potential and activity in a binary alloy ($A_{1-x}B_x$) so that the present method can be readily extended to other systems.

The Gibbs' free energy G is defined as

$$\begin{aligned} G &= F_{\mathrm{hs}} + P_{\mathrm{hs}}\, n + F_{\mathrm{ps}} \\ &= (1-x)\,\mu_{\mathrm{A}}^{\mathrm{hs}} + x\,\mu_{\mathrm{B}}{}^{\mathrm{hs}} + F_{\mathrm{ps}}\,, \end{aligned} \tag{A.1}$$

where $\mu_{\mathrm{A}}^{\mathrm{hs}}$ and $\mu_{\mathrm{B}}^{\mathrm{hs}}$ are the chemical potentials of A and B in the A-B alloy based on a hard sphere (HS) model. The pressure of the HS system, P_{hs}, is given as

$$\begin{aligned} \frac{P_{\mathrm{hs}}}{k_{\mathrm{B}}T} &= \frac{n(1+\bar{\eta}+\bar{\eta}^2)}{(1-\eta)^3} \\ &\quad - \frac{1}{2}\,\frac{\pi\, n_{\mathrm{A}}\, n_{\mathrm{B}}(\sigma_{\mathrm{A}}-\sigma_{\mathrm{B}})^2(\sigma_{\mathrm{A}}+\sigma_{\mathrm{B}}+\sigma_{\mathrm{A}}\,\sigma_{\mathrm{B}}\,X)}{(1-\bar{\eta})^3}\,, \end{aligned} \tag{A.2}$$

where

$$X = \frac{\pi}{6}\,(n_A\,\sigma_A{}^2 + n_B\,\sigma_B{}^2)\,. \tag{A.3}$$

The chemical potential of atom A in the binary system A-B is then given by

$$\mu_A \equiv \left(\frac{\partial G}{\partial n_A}\right)_{P,\,T,\,n_B} = \mu_A^{\mathrm{hs}} + \left(\frac{\partial F_{\mathrm{ps}}}{\partial n_A}\right)_{P,\,T,\,n_B}. \tag{A.4}$$

Denoting $\mu_A{}^0$ as the chemical potential of element A in its pure state, we may express the activity a_A as follows:

$$\begin{aligned} k_B T \ln a_A &= \mu_A - \mu_A{}^0 \qquad\qquad \text{(A.5)}\\ &= [\mu_A - \mu_A{}^0]^{\mathrm{hs}} + [\mu_A - \mu_A{}^0]^{\mathrm{kin}}\\ &\quad + [\mu_A - \mu_A{}^0]^{\mathrm{exch}} + [\mu_A - \mu_A{}^0]^{\mathrm{corr}}\\ &\quad + [\mu_A - \mu_A{}^0]^{\mathrm{unif}} + [\mu_A - \mu_A{}^0]^{\mathrm{Mad}}\\ &\quad + [\mu_A - \mu_A{}^0]^{\mathrm{bs}} + [\mu_A - \mu_A{}^0]^{\mathrm{c-c}}\,. \end{aligned}$$

μ_A^{hs} is given by

$$\begin{aligned} \frac{\mu_A^{\mathrm{hs}}}{k_B T} &= \left[n\left(\frac{2\pi\hbar^2}{m_A\,k_B T}\right)^{3/2}\right] - \ln(1-\eta)\\ &\quad + \frac{3X\sigma_A}{(1-\eta)} + \frac{3}{2}\left[\frac{3X^2}{(1-\eta)^2} + \frac{2Y}{(1-\eta)}\right]\sigma_A{}^2\\ &\quad + \frac{\pi\,P_{\mathrm{hs}}\,\sigma_A{}^3}{6k_B T}\,, \end{aligned} \tag{A.6}$$

where

$$Y = \frac{\pi}{6}\,(n_A\,\sigma_A + n_B\,\sigma_B)\,. \tag{A.7}$$

$(\mu_A{}^0)^{\mathrm{hs}}$ is deduced from the limiting case $n_A \to n$ and $n_B \to 0$ in Equation (A.7). The terms in Eq. (A.5) are

$$[\mu_A - \mu_A{}^0]^{\mathrm{kin}} = 2.21\left[\left(\frac{1}{\bar{r}_S{}^2} - \frac{1}{\bar{r}^2{}_{S,A}}\right) + \frac{2}{3}\,\frac{x}{\bar{r}_S{}^5}\,(r^3{}_{S,B} - r^3{}_{S,A})\right]\bar{Z}\,, \tag{A.8}$$

$$[\mu_A - \mu_A{}^0]^{\mathrm{exch}} = -\,0.916\left[\left(\frac{1}{\bar{r}_S} - \frac{1}{r_{S,\,A}}\right) + \frac{1}{3}\,\frac{x}{\bar{r}_S{}^4}\,(r^3{}_{S,B} - r^3{}_{S,A})\right]\bar{Z}\,, \tag{A.9}$$

$$[\mu_A - \mu_A{}^0]^{\mathrm{corr}} = 0.031\left[(\ln\bar{r}_S - \ln r_{S,\,A}) - \frac{x}{\bar{r}_S{}^3}\,(r^3{}_{S,B} - r^3{}_{S,A})\right]\bar{Z}\,, \tag{A.10}$$

$$\begin{aligned} [\mu_A - \mu_A{}^0]^{\mathrm{unif}} = 4\pi\Bigg[&\left(\frac{(1-x)\,r^2{}_{C,A} + x\,r^2{}_{C,B}}{N\Omega} - \frac{r^2{}_{C,A}}{N\Omega_A}\right)\\ &+ \frac{x}{N\Omega^2}\,\{(1-x)\,r^2{}_{C,A} + x\,r^2{}_{C,B})\,(\Omega_B - \Omega_A)\} - \frac{x}{N\Omega}\,(r^2{}_{C,B} - r^2{}_{S,B})\Bigg]\,, \end{aligned} \tag{A.11}$$

$$\begin{aligned} [\mu_A - \mu_A{}^0]^{\mathrm{Mad}} = \frac{1}{2}\Bigg[&\left(\frac{1}{N\Omega} - \frac{1}{N\Omega_A}\right)R_{AA}\\ &+ \frac{x}{N\Omega^2}\{(1-x)^2\,R_{AA} + 2x(1-x)\,R_{AB} + x^2\,R_{BB})\,(\Omega_B - \Omega_A)\}\\ &+ \frac{x^2}{N\Omega}\,(2\,R_{AB} - R_{AA} - R_{BB})\Bigg]\,, \end{aligned} \tag{A.12}$$

$$\begin{aligned} [\mu_A - \mu_A{}^0]^{\mathrm{bs}} = \frac{1}{2}\Bigg[&\left(\frac{1}{N\Omega} - \frac{1}{N\Omega_A}\right)\psi_{AA} + \frac{x}{N\Omega^2}\{(1-x)\,\psi_{AA} + x\,\psi_{BB})\,(\Omega_B - \Omega_A)\}\\ &+ \frac{1}{2}\left(\frac{1}{N\Omega} - \frac{1}{N\Omega_A}\right)\varphi_{AA} + \frac{x}{N\Omega^2}\\ &\times\{(1-x)^2\,\varphi_{AA} + 2x(1-x)\,\varphi_{AB} + x^2\,\varphi_{BB})\,(\Omega_B - \Omega_A)\}\\ &+ \frac{x^2}{N\Omega}\,(2\,\varphi_{AB} - \varphi_{AA} - \varphi_{BB})\Bigg]\,, \end{aligned} \tag{A.13}$$

$$\begin{aligned} [\mu_A - \mu_A{}^0]^{\mathrm{c-c}} = \frac{1}{2}\Bigg[&\left(\frac{1}{N\Omega} - \frac{1}{N\Omega_A}\right)\xi_{AA} + \frac{x}{N\Omega^2}\\ &\times\{(1-x)^2\,\xi_{AA} + 2x(1-x)\,\xi_{AB} + x^2\,\xi_{BB})\,(\Omega_B - \Omega_A)\}\\ &+ \frac{x^2}{N\Omega}\,(2\,\xi_{AB} - \xi_{AA} - \xi_{BB})\Bigg]\,, \end{aligned} \tag{A.14}$$

$$R_{ij} = \frac{1}{(2\pi)^3} \int_0^\infty \frac{8\pi}{q^2} Z_i Z_j [a_{ij}(q) - 1]\, 4\pi q^2 \, \mathrm{d}q \,, \tag{A.15}$$

$$\varphi_{ij} = \frac{N\Omega}{(2\pi)^3} \int_0^\infty \frac{\langle \boldsymbol{k} | w_i{}^{\mathrm{bp}} | \boldsymbol{k}+\boldsymbol{q} \rangle \langle \boldsymbol{k}+\boldsymbol{q} | w_j{}^{\mathrm{bp}} | \boldsymbol{k} \rangle}{8\pi/q^2} \frac{1-\varepsilon(q)}{\varepsilon(q)} [a_{ij}(q) - 1]\, 4\pi q^2 \, \mathrm{d}q \,, \tag{A.16}$$

$$\psi_{ij} = \frac{N\Omega}{(2\pi)^3} \int_0^\infty \frac{\langle \boldsymbol{k} | w_i{}^{\mathrm{bp}} | \boldsymbol{k}+\boldsymbol{q} \rangle \langle \boldsymbol{k}+\boldsymbol{q} | w_j{}^{\mathrm{bp}} | \boldsymbol{k} \rangle}{8\pi/q^2} \frac{1-\varepsilon(q)}{\varepsilon(q)} \, 4\pi q^2 \, \mathrm{d}q \,, \tag{A.17}$$

$$\xi_{ij} = \int_0^\infty \Phi_{ij}^{\mathrm{c-c}}(r)\, g_{ij}(r)\, 4\pi r^2 \, \mathrm{d}r \,. \tag{A.18}$$

If we assume that the packing density η does not change over the whole range of composition of the alloy and that $\sigma_{\mathrm{A}} = \sigma_{\mathrm{B}}$ and $Z_{\mathrm{A}} = Z_{\mathrm{B}}$, Eq. (A.5) then can be simplified as follows:

$$\mu_{\mathrm{A}} - \mu_{\mathrm{A}}{}^0 = k_{\mathrm{B}} T \ln x + \frac{x^2}{2} \frac{(2\Phi_{\mathrm{AB}} - \Phi_{\mathrm{AA}} - \Phi_{\mathrm{BB}})}{N\Omega} \,, \tag{A.19}$$

where Φ_{ij} is equal to $(R_{ij} + \varphi_{ij} + \xi_{ij})$. This expression is equivalent to the classical one. It is noteworthy that the Gibbs-Duhem equation

$$n_{\mathrm{A}} \, \mathrm{d}\mu_{\mathrm{A}} + n_{\mathrm{B}} \, \mathrm{d}\mu_{\mathrm{B}} = 0 \,,$$

stands for each term in Eq. (A.5), independently.

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