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Activities in Liquid Na–K and Al–Mg Alloys Estimated Using the Pseudopotential Theory of Metals

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ABSTRACT

The microscopic electron theory of metals based on the pseudopotential formalism and the Gibbs-Bogoliubov inequality has been applied to the calculation of activities in liquid Na-K and Al-Mg alloys. The results were found to be in reasonable agreement with the experimental data, although the calculated values depend slightly on the expression for the dielectric function.

INTRODUCTION

An electron theory for the thermodynamic properties of liquid alloys has been sought for some time now because a systematic linkage between microscopic electron theory and macroscopic thermodynamic behaviour would be important to a range of problems in basic materials science and engineering. Most experimental results of thermodynamical functions of liquid metals and alloys have been interpreted qualitatively or semi-quantitatively in terms of molecular theories /1/. Following these works, the electron theories on thermodynamic properties of liquid metals and alloys have been investigated recently by the pseudopotential method and the agreement between theoretical and experimental data was found to be fairly reasonable /2-9/. However, the systematic investigations are still limited, particularly for activities in liquid alloys using modern electron theory of metals.

The main purpose of this paper is to present the results of calculations for activities of liquid Na-K and Al-Mg alloys by the pseudopotential theory of metals coupled with the Gibbs-Bogoliubov inequality scheme /3/.

CHEMICAL POTENTIAL AND ACTIVITY IN A BINARY LIQUID ALLOY

On the basis of the Gibbs-Bogoliubov inequality /3/, the Helmholtz free energy F can be expressed by the equation:

$$F \leqslant F_0 + \tfrac{1}{2} \Sigma U(q)[a(q) - 1] \qquad (1)$$

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. X-ray and neutron diffraction studies have been widely employed for the determination of the structure of liquid metals and alloys. Although there are some exceptions, structural features such as the structure factor and the radial distribution function look similar for various metallic liquids and the hard sphere model appears to satisfy well such structural features /5/. This includes liquid Na-K and Al-Mg alloys. Therefore, if the structure factor approximated by the hard sphere model is used as a reference system and if the hard sphere term F_{hs} includes the entropy of the hard spheres and the contribution of the electron gas, the Helmholtz free energy F of the system may be practically expressed as:

$$F = F_{ps} + F_{hs} \qquad (2)$$

where F_{ps} contains the total energy of the electrons and ions in the metal. Then, the Gibbs free energy G can be written as follows:

$$G = F_{hs} + P_{hs}/n + F_{ps} \qquad (3)$$

$$= (1 - x)\mu_A^{hs} + x\mu_B^{hs} + F_{ps} \qquad (4)$$

where μ_A^{hs} and μ_B^{hs} are the chemical potentials of A and B in an A-B liquid alloy based on a hard sphere (HS) model. The pressure of the HS system P_{hs} is given by:

$$\frac{P_{hs}}{k_B T} = \frac{n(1 + \bar{\eta} + \bar{\eta}^2)}{(1 - \bar{\eta})^3} - \frac{1}{2} \frac{\pi n_A n_B (\sigma_A - \sigma_B)^2 (\sigma_A + \sigma_B + \sigma_A \sigma_B X)}{(1 - \bar{\eta})^3} \qquad (5)$$

$$X = \frac{\pi}{6}(n_A \sigma_A^2 + n_B \sigma_B^2) \qquad (6)$$

$$\bar{\eta} = \frac{\pi}{6}(n_A \sigma_A^3 + n_B \sigma_B^3) \qquad (7)$$

where $n = N/V$, $n_A = (1 - x)n$, $n_B = xn$ and σ_A and σ_B are the hard sphere diameters of ions A and B, respectively. The other symbols have their usual meaning, k_B is the Boltzmann constant and x the atomic fraction of the B component /4-9/.

The full expression for the activity of a component in a binary liquid alloy in terms of the microscopic electron theory of metals has already been described /5, 10/. The essential equations for the present calculation are summarized below.

The chemical potential of atom A in a binary system of A-B is given by:

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{P,T,n_B} = \mu_A^{hs} + \left(\frac{\partial F_{ps}}{\partial r_A}\right)_{P,T,n_B} \quad (8)$$

Denoting μ_A^0 as the chemical potential of component A in its pure state, the activity a_A in a binary A-B alloy may be expressed as:

$$\begin{aligned} k_B T \ln a_A &= \mu_A - \mu_A^0 \\ &= [\mu_A - \mu_A^0]^{hs} + [\mu_A - \mu_A^0]^{kin} \\ &+ [\mu_A - \mu_A^0]^{exch} + [\mu_A - \mu_A^0]^{corr} \\ &+ [\mu_A - \mu_A^0]^{unif} + [\mu_A - \mu_A^0]^{Mad} \\ &+ [\mu_A - \mu_A^0]^{bs} + [\mu_A - \mu_A^0]^{c-c} \end{aligned} \quad (9)$$

The hard sphere term of μ_A^{hs} is given in the form:

$$\begin{aligned} \frac{\mu_A^{hs}}{k_B T} &= \ln\left[n\left(\frac{2\pi\hbar^2}{m_A k_B T}\right)^{3/2}\right] - \ln(1-\bar{\eta}) \\ &+ \frac{3X\sigma_A}{(1-\bar{\eta})} + \frac{3}{2}\left[\frac{3X^2}{(1-\bar{\eta})^2} + \frac{2Y}{(1-\bar{\eta})}\right]\sigma_A^2 \\ &+ \frac{\pi P_{hs}\sigma_A^3}{6k_B T} \end{aligned} \quad (10)$$

$$Y = \frac{\pi}{6}(n_A\sigma_A + n_B\sigma_B) \quad (11)$$

The term of $(\mu_A^0)^{hs}$ is easily obtained from the limiting case $n_A \to n$ and $n_B \to 0$ in Eq. (10). Each term in Eq. (9) is given by the following equations when the pseudopotential method /4, 5/ is employed.

$$\begin{aligned} [\mu_A - \mu_A^0]^{kin} &= 2.21\left[\left(\frac{1}{\bar{r}_S^2} - \frac{1}{r_{S,A}^2}\right)\right. \\ &\left. + \frac{2}{3}\frac{x}{\bar{r}_S^5}(r_{S,B}^3 - r_{S,A}^3)\right]\bar{Z} \end{aligned} \quad (12)$$

$$\begin{aligned} [\mu_A - \mu_A^0]^{exch} &= -0.916\left[\left(\frac{1}{\bar{r}_S} - \frac{1}{r_{S,A}}\right)\right. \\ &\left. + \frac{1}{3}\frac{x}{\bar{r}_S^4}(r_{S,B}^3 - r_{S,A}^3)\right]\bar{Z} \end{aligned} \quad (13)$$

$$\begin{aligned} [\mu_A - \mu_A^0]^{corr} &= 0.031\left[(\ln \bar{r}_S - \ln r_{S,A})\right. \\ &\left. - \frac{x}{\bar{r}_S^3}(r_{S,B}^3 - r_{S,A}^3)\right] Z \end{aligned} \quad (14)$$

$$\begin{aligned} [\mu_A - \mu_A^0]^{unif} &= 4\pi\left[\left(\frac{(1-x)r_{C,A}^2 + xr_{C,B}^2}{N\Omega} - \frac{r_{C,A}^2}{N\Omega_A}\right)\right. \\ &+ \frac{x}{N\Omega^2}\langle(1-x)r_{C,A}^2 + xr_{C,B}^2)(\Omega_B - \Omega_A)\rangle \\ &\left. - \frac{x}{N\Omega}(r_{C,B}^2 - r_{C,B}^2)\right] \end{aligned} \quad (15)$$

$$\begin{aligned} [\mu_A - \mu_A^0]^{Mad} &= \frac{1}{2}\left[\left(\frac{1}{N\Omega} - \frac{1}{N\Omega_A}\right)P_{AA}\right. \\ &+ \frac{x}{N\Omega^2}\langle(1-x)^2 R_{AA} + 2x(1-x)R_{AB} \\ &\left. + x^2 R_{BB})(\Omega_B - \Omega_A)\rangle \right. \\ &\left. + \frac{x^2}{N\Omega}(2R_{AB} - R_{AA} - R_{BB})\right] \end{aligned} \quad (16)$$

$$\begin{aligned} [\mu_A - \mu_A^0]^{bs} &= \frac{1}{2}\left[\left(\frac{1}{N\Omega} - \frac{1}{N\Omega_A}\right)\psi_{AA}\right. \\ &+ \frac{x}{N\Omega^2}\langle(1-x)\psi_{AA} + x\psi_{BB})(\Omega_B - \Omega_A)\rangle \\ &+ \frac{1}{2}\left(\frac{1}{N\Omega} - \frac{1}{N\Omega_A}\right)\psi_{AA} + \frac{x}{N\Omega^2} \\ &\times\langle(1-x)^2\varphi_{AA} + 2x(1-x)\varphi_{AB} \\ &\left. + x^2\varphi_{BB})(\Omega_B - \Omega_A)\rangle \right. \\ &\left. + \frac{x^2}{N\Omega}(2\varphi_{AB} - \varphi_{AA} - \varphi_{BB})\right] \end{aligned} \quad (17)$$

$$[\mu_A - \mu_A^0]^{c-c} = \frac{1}{2}\left(\frac{1}{N\Omega} - \frac{1}{N\Omega_A}\right)\xi_{AA}$$

$$+ \frac{x}{N\Omega^2}\left\langle (1-x)^2\xi_{AA} + 2x(1-x)\xi_{AB} + x^2\xi_{BB}\right)(\Omega_B - \Omega_A)\rangle$$

$$+ \frac{x^2}{N\Omega}(2\xi_{AB} - \xi_{AA} - \xi_{BB})] \qquad (18)$$

$$R_{ij} = \frac{1}{(2\pi)^3}\int_0^\infty \frac{8\pi}{q^2} Z_i Z_j [a_{ij}(q) - 1]\, 4\pi q^2\, dq \qquad (19)$$

$$\varphi_{ij} = \frac{N\Omega}{(2\pi)^3}\int_0^\infty \frac{\langle k|\omega_i^{bp}|k+q\rangle\langle k+q|\omega_j^{bp}|k\rangle}{8\pi/q^2}$$

$$\times \frac{1-\epsilon(q)}{\epsilon(q)}[a_{ij}(q) - 1]\, 4\pi q^2\, dq \qquad (19a)$$

$$\varphi_{ij} = \frac{N\Omega}{(2\pi)^3}\int_0^\infty \frac{\langle k|\omega_i^{bp}|k+q\rangle\langle k+q|\omega_j^{bp}|k\rangle}{8\pi/q^2}$$

$$\times \frac{1-\epsilon(q)}{\epsilon(q)}\, 4\pi q^2\, dq \qquad (19b)$$

$$\xi_{ij} = \int_0^\infty \Phi_{ij}^{c-c}(r)\, g_{ij}(r)\, 4\pi r^2\, dr$$

$$\left.\begin{aligned} \bar{Z}\bar{r}_s^3 &= Z_A(1-x)r_{s,A}^3 + Z\ xr_{s,B}^3 \\ Z &= (1-x)Z_A + xZ_B \\ \bar{\omega}^{bp} &= (1-x)\omega_A^{bp} + x\omega_A^{bp} \end{aligned}\right\} \qquad (20)$$

where ω_i^{bp} represents the pseudopotential of bare ion i and $\epsilon(q)$ the dielectric function, respectively. If it is assumed that the packing density $\bar{\eta}$ does not change over the whole range of composition of the alloy which is confirmed for several binary liquid alloys /5/, and $\sigma_A = \sigma_B$ and $Z_A = Z_B$, Eq. (9) then can be simplified as:

$$\mu_A - \mu_A^0 = k_B T \ln x + \frac{x^2}{2}\frac{(2\Phi_{AB} - \Phi_{AA} - \Phi_{BB})}{N\Omega} \qquad (21)$$

where Φ_{ij} is equal to $(R_{ij} + \varphi_{ij} + \xi_{ij})$. This expression is known to be equivalent to the classical one. In addition, the so-called Gibbs-Duhem equation $n_A d\mu_A + n_B d\mu_B = 0$ is satisfied for each term in Eq. (9) independently /5, 10/.

CALCULATION OF ACTIVITIES OF LIQUID NA-K AND AL-MG ALLOYS

The main information required to estimate the activities of liquid alloy by the pseudopotential formalism are the pseudopotentials of the bare ions, the dielectric function and the structure factor. Regarding the structure factor, a comparison between the experimental data and the calculations based on the hard sphere model /11/ indicates that the structural features of liquid Na-K and Al-Mg alloys are well interpreted by random mixing of hard spheres /12/. Thus, the partial structure factors given by the hard sphere model with a packing density of 0.45 /5/ were used in the present calculation and this is also consistent with the condition of the Gibbs-Bogoliubov inequality expressed by Eq. (1). On the contrary, there have been several proposals for the pseudopotential of the bare ion in metals. However, the empty-core model potential is convenient for the present calculation. The empty-core potential with a core radius r_C is written as follows /13/:

$$\omega^{bp} = -\frac{4\pi Z}{q^2}\cos(q \cdot r_C) \qquad (22)$$

where r_C is determined in order to satisfy the equilibrium condition $(\partial F_{ps}/\partial\Omega) = 0$. 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, $\Phi_{AB}^{c-c}(r)$, 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 /14/ for the core-core interaction.

The dielectric function $\epsilon(q)$ is given by /15/:

$$\epsilon(q) = 1 - \frac{(4\pi|e|^2/q^2)X(q)}{1 + (4\pi|e|^2/q^2)G(q)X(q)} \qquad (23)$$

$$X(q) = -\frac{mk_F}{m^2h^2}\left(\frac{1}{2} + \frac{4k_F^2 - q^2}{8k_Fq}\ln\left|\frac{2k_F + q}{2k_F - q}\right|\right) \qquad (24)$$

Several proposals for G(q) are available and each approach has its own advantages and disadvantages. On the basis of previous works, the expressions for G(q) proposed by Hubbard-Sham /16, 17/, Kleinman-Sham /17, 18/ and Shaw /19/ have been employed in this study. For illustration, the numerical values for these three cases are plotted in Fig. 1 and the relevant parameters required in the calculation are summarized in Table 1.

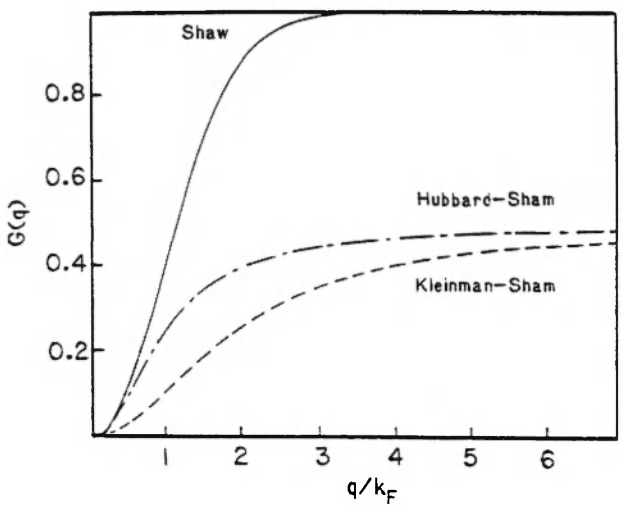

Fig. 1. Variation of the factor G(q) for three different expressions. k_F: the Fermi wavevector.

TABLE 1
A List of Parameters Used in the Present Calculations

Hard sphere diameter (nm)	Na	0.331	Al	0.253	
	K	0.410	Mg	0.284	
Empty core radius (a.u.)	Na	1.68	Al	1.13	
	K	2.26	Mg	1.32	
Core repulsion parameters		A (eV)	B	C	r_0 (nm)
	Na	0.605	5.56	-12.1	0.382
	K	0.934	7.30	-13.6	0.464
	Al	0.908	9.97	-19.6	0.282
	Mg	1.269	4.91	-11.0	0.321

$$\Phi^{c-c}(r) = A \exp [B + C(r/r_0)]$$

The variation of the estimated activities are shown in Figs. 2 and 3 together with experimental data /20/. The calculated values are slightly dependent upon the expression of dielectric function. However, the present

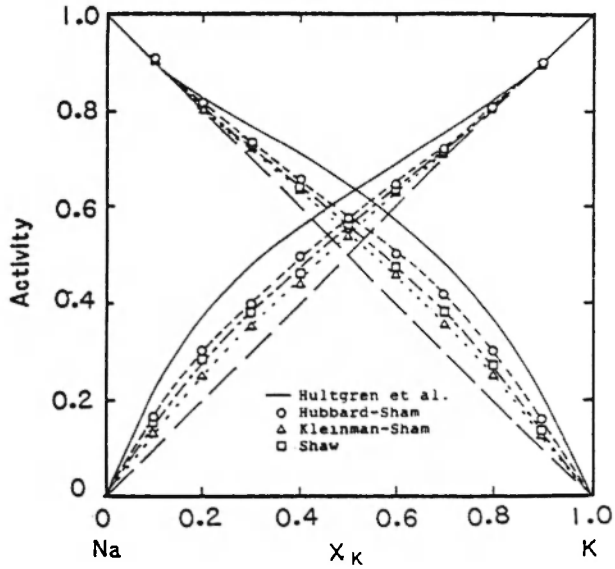

Fig. 2. Calculated and experimental activities in liquid Na-K alloys at 384 K. The experimental data are taken from the compilation /20/.

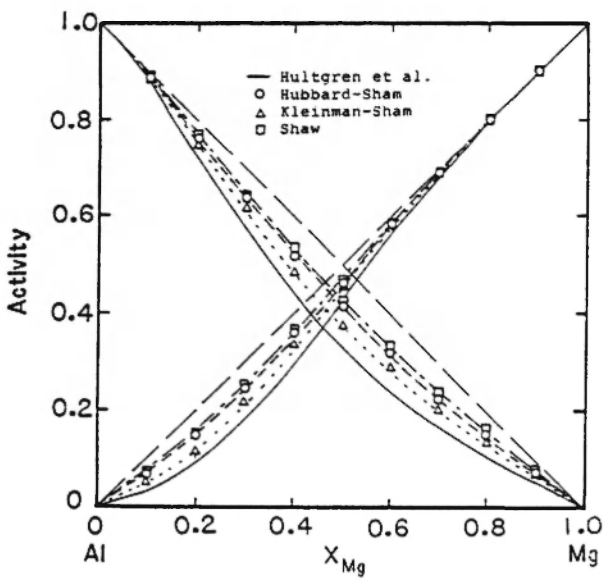

Fig. 3. Calculated and experimental activities in liquid Al-Mg alloys at 1073 K. The experimental data are taken from the compilation /20/.

calculations which employ the pseudopotential formalism are in reasonable agreement with experimental data. The calculated values reproduce the essential features of the composition dependence of the activities for both alloys, although there are differences in detail. Thus the present authors maintain the view that the results

in this work well represent a step forward towards the estimation of activities in liquid alloys using only fundamental physical constants of constituents, although some further improvement in selecting the best physical parameters may be required for reproducing exactly the experimental data.

CONCLUDING REMARKS

Microscopic electron theory based on the pseudopotential formalism seems to be a useful framework for the theoretical estimation of the thermodynamic properties of binary liquid alloys. Although the number of available systems 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 binary liquid alloys.

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