A Theory of the Excess Chemical Potential of Metals in Alloys as Related to Electrochemical Measurements

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Recent measurements of electromotive forces in electrochemical cells have shown the feasibility of measuring relative chemical potentials of alloy components. The excess chemical potential is formulated from the excess Gibbs free energy $\Delta G^{\mathrm{E}} = \Delta U^{\mathrm{E}} + P\,\Delta V^{\mathrm{E}} - T\,\Delta S^{\mathrm{E}}$ (at constant P and T). The excess internal energy ΔU^{E} is evaluated from the structure-dependent internal energy of the metals. $T\,\Delta S^{\mathrm{E}}$ is taken as zero (to a good approximation in lithium-magnesium). $P\,\Delta V^{\mathrm{E}}$ is found to be negligible at atmospheric pressure. A calculation is made for the alloy Li–Mg at about 600 °C for the excess chemical potential

$$\Delta\mu_i{}^{\mathrm{E}} = \left(\frac{\partial}{\partial N_i}\,\Delta G^{\mathrm{E}}\right)_{N_j,\,T,\,P}$$

where N_i is the number of lithium ions, which is found to be of the right magnitude compared to two sets of experimental results.

Theory

The electromotive force in a galvanic cell, involving no concentration gradients, is proportional to the difference between the chemical potentials of the two metallic electrodes[1, 2]. The chemical potential μ of a metal is the Gibbs free energy per atom

$$G = U + P\,V - T\,S\,. \qquad (1)$$

More accurately, $\mu_i = (\partial G/\partial N_i)_{T,P}$ for a mixture of particle species $i\,(i = 1, 2, 3)$ where temperature T and pressure P are kept constant.

In Eq. (1), the unknown quantity is the internal energy U of the metal[3], since the volumes V are measured or interpolated linearly for alloys (to a good approximation), whereas the entropy can be approximated by that of an ideal mixture[4]. Thus, the possibility of predicting the Gibbs free energy of a metallic electrode depends largely on the prediction of the internal or cohesive energy of the metal. Fortunately, considerable progress has been made on this last problem with the pseudopotential theory of metals[3] which, although still poor for defects in metals, provides good results for the cohesive energy of metals and the relative stability of crystal structures.

We summarize here the main results for the cohesive energy in the pseudopotential theory of metals[3] (per atom at density n):

$$U = \frac{a\,Z}{r_{\mathrm{s}}{}^2} - \frac{b\,Z}{r_{\mathrm{s}}} - c\,Z - \mathrm{d}Z \ln r_{\mathrm{s}} - \frac{e\,Z^{5/3}}{r_{\mathrm{s}}} \qquad (2)$$
$$+ \frac{3\,R_{\mathrm{c}}{}^2\,Z}{r_{\mathrm{s}}{}^3} + \frac{n}{2}\int_0^\infty 4\,\pi\,r^2\,\mathrm{d}r\,g(r)\,u_{\mathrm{eff}}(r) + \frac{3}{2}\,k\,T\,.$$

In Eq. (2), a, b, c, d, e are numerical constants representing the internal energy of the electron gas which we shall choose according to the results of Nozière and Pines (a, b, c, d)[5] and Sholl (e)[6]. The sixth term is written in the Aschcroft pseudopotential approximation[3] with a core of radius R_{c} for the electron-ion potential *. This term is referred to as the Hartree term. The seventh term, which depends strongly on the structure of the metal, represents the Coulomb direct and indirect interaction between the ions of density n and pair correlation function $g(r)$[7]. $\frac{3}{2}\,k\,T$ is the average kinetic energy of the ions. Equation (2) is characterized by strong separation between the conduction electron gas (the first four terms) and the ionic gas (the last two terms) of valency Z. The remaining two terms represent interaction terms between ions and electrons. r_{s} is the radius of the sphere occupied by one electron $r_{\mathrm{s}} = (3/4\,\pi\,n_{\mathrm{e}})^{1/3}$.

Finally, we remark that Eq. (2) looks deceptively simple because it depends still on two unknowns: (1) $u_{\mathrm{eff}}(r)$ or the effective interaction between two ions which depends among other things on the order of perturbation theory in the electron-ion potential (usually a pseudopotential) and the screening used to represent the electron gas; (2) $g(r)$ or the radial distribution function $4\,\pi\,r^2\,g(\mathrm{r})$ which is usually determined by x-ray diffraction.

Method of Analysis and Results

We shall proceed in three steps: (1) obtain the cohesive energy U of the pure metal (lithium), (2) obtain the cohesive energy of the alloy (lithium-magnesium), (3) obtain $\Delta G_i{}^{\mathrm{E}}$ and $\Delta\mu_i{}^{\mathrm{E}}$ for lithium ions. We choose this example because of our previous experience with lithium metal[7]. We have indeed, in previous publications, obtained $g(r)$ and $u_{\mathrm{eff}}(r)$ in equation (2): these are the most accurate available so far. Four our present purpose, we shall simplify term number 7, the ion interaction, as follows (per unit volume):

$$\frac{n^2}{2}\int_0^\infty 4\,\pi\,r^2\,\mathrm{d}r\,g(r)\,u_{\mathrm{eff}}(r) \cong \frac{\eta\,n}{2}\,u_{\mathrm{eff}}(r_0)\,, \qquad (3)$$

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* $R_{\mathrm{c}} = 1.415$ a.u. $= 0.7488$ Å for lithium.

where $u_{\text{eff}}(r_0) = u_{\text{LiLi}}(r_0$ for pure lithium,

$$u_{\text{eff}}(r_0') = x^2\, u_{\text{LiLi}}(r_0') + 2(1-x)\, x\, u_{\text{LiMg}}(r_0') + (1-x)^2\, u_{\text{MgMg}}(r_0')$$

for the Li – Mg alloy. In the above, η is the coordination number of the ions (about 9.1 for liquid lithium) and r_0 is the equilibrium distance between ions in the metal[9] (r_0' for the alloy).

Thus, in Table I, we present the results for the detailed calculation of U for pure lithium and for 50 a/o lithium-magnesium at the same temperature of 453 K. The result for pure liquid lithium is remarkably close to the experimental result[8] shown in parentheses, since no adjustment whatsoever has been made to Equation (2). This is remarkable for the present calculation since most other calculations of absolute cohesive energies of metals need some adjustment in the Hartree energy (term 6). The results on Li – Mg deserve some explanation: Equation (3) is used to evaluate term 7 of Eq. (2) where $g(r)$ is assumed to be the same for the distribution of Mg and Li ions (as for Li ions around Li), because Li^+ an Mg^{++} ions have nearly the same radii and thus only the electron gas differs, but this shows only secondary effects on the distribution of Li – Mg ions. The other parameters in Eq. (2) are defined as usual, i. e.,

Table I. Cohesive energy of pure liquid lithium and 50 atomic percent lithium-magnesium (1 ryd = 13.6 ev) at temperature 453 K (melting point of lithium).

	Lithium	Lithium-Magnesium (50 at%)
Terms 1+2+3+4	−0.15334	−0.20620
Term 5	−0.52023	−1.15731
Term 6	+0.16314	+0.23619
Term 7	−0.01752	−0.01629
Term 8	+0.00431	+0.00431
U (ryd/ion)	−0.523 (−0.510)	−1.139 (−1.171)

$$Z = x\, Z_{\text{Li}} + (1-x)\, Z_{\text{Mg}}\,,$$

$$r_s^3 = 1/Z\,\left(x\, r_s{}^3{}_{\text{Li}} + (1-x)\, r_s{}^3{}_{\text{Mg}}\right).$$

The result U is seen to be in fair agreement with experiment for Li – Mg.

Now, we turn to the $\Delta G^{\text{E}} = \Delta U^{\text{E}} + P\,\Delta V^{\text{E}} - T\,\Delta S^{\text{E}}$ for lithium ion, which we approximate as follows[4] $\Delta G^{\text{E}}_{\text{Li}} = N_{\text{i}}[\Delta U_{\text{Li}} + P\,\Delta V]$, where ΔU_{Li} is the part of ΔU which depends explicitly on the number of lithium ions, i. e.,

$$\Delta U_{\text{Li}} \cong \frac{\eta}{2}\,[x\, u_{\text{LiLi}}(r_0') + 2(1-x)\, u_{\text{LiMg}}(r_0')] - \frac{\eta}{2}\, u_{\text{LiLi}}(r_0)\,. \tag{4}$$

The rest of ΔU depends on the number of magnesium ions and electrons. $r_1 = 3.20$ Å for pure Mg, $r_0 = 3.110$ Å for pure Li and $r_0' = 3.115$ Å for Li – Mg[8]: these are values for the solids which we assume the same as for the liquid, in the absence of liquid data. To justify Eq. (4), we note that Eq. (2) depends, per unit volume, on the Li ion number only through the two last terms, since the first six terms depend on the electron density only and we consider the electron fluid to be distinct from the ionic fluid.

In Table II, we find the results for each term discussed above. As expected, $P\,\Delta V$ is extremely small and only ΔU_{Li} is of a significant magnitude. For ΔU_{Li}, we have used the densities appropriate for about 887 K as much as possible, so there is a difference between this and the value in Table I from term 7. We obtain here a value about six times as large as the $\partial/\partial N_{\text{i}}(\Delta G^{\text{E}}_{\text{Li}}) = \Delta\mu^{\text{E}}_{\text{Li}}$ obtained experimentally by Saboungi and Blander[1]. Thus, we believe Eq. (4) only gives a rough estimate of ΔU_{Li} as somewhat expected. The coordination number η is probably not the same for Li – Li as for the Li – Mg liquid: unfortunately it has not been determined experimentally for the Li – Mg alloy in the liquid phase. Hopefully, this wil be corrected in the future.

Table II. Excess Gibbs free energy per lithium ion between lithium and 50 a/o lithium-magnesium at temperature of 887 K.

ΔU_{Li}	−0.00748 ryd/ion
$P\,\Delta V$	10^{-7} ryd/ion
$\frac{\partial}{\partial N_i}(\Delta G^{\text{E}}_{\text{Li}}) = \Delta\mu^{\text{E}}_i$	−0.00748 ryd/ion = −2346 cal/mole (−420 cal/mole)

In summary, we conclude that our effective potentials in condensed lithium allow us to compute with some precision

(1) the cohesive energy of liquid lithium and lithium-magnesium,
(2) the excess chemical potential of lithium in lithium-magnesium in the condensed phase.

We also conclude our information about the electronic and ionic energies in lithium alloys is thus of sufficient accuracy to allow determination and prediction of differences of energies between systems.

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