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CALORIMETRIC STUDIES OF LIQUID Li–Zn ALLOYS

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ABSTRACT

The concentration dependence of the enthalpies of mixing of liquid Li–Zn alloys has been determined at 820 K using reaction calorimetry. The experimental results of these alloys can be described by Krupkowski's method and the association model. The association model predicts the temperature dependence of the enthalpy and entropy of mixing.

INTRODUCTION

In the phase diagrams of lithium alloys several solid intermetallic compounds are usually present. At concentrations close to the most stable intermetallic compound maximum chemical short-range order is frequently present in the liquid state which influences the thermodynamic functions. Extremal values of these functions, e.g. integral enthalpy and excess entropy, are often correlated with a similar behaviour of various physical properties [1,2]. Information on structure from X-ray diffraction studies can be related to the thermodynamics of the system and therefore structure factors can be calculated from thermodynamic data and vice versa [3]. To be able to observe mutual correlations, precise and properly evaluated thermodynamic

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data are necessary. Experimental studies on lithium alloys are extremely difficult due to the high reactivity with oxygen, nitrogen and moisture. Most of the thermodynamic data originate from e.m.f. studies, some from vapour pressure measurements and, more recently, from calorimetric techniques [4].

In previous studies on magnesium alloys [5,6] the results of e.m.f. and calorimetric measurements have been combined to obtain accurate enthalpy and entropy values which have been connected with structure. The same procedure has been applied to lithium alloys; however in Li–Sn alloys [2] a linear dependence of e.m.f. vs. temperature was obtained (as in other e.m.f. studies), indicating that the enthalpy is independent of temperature. In calorimetric measurements, it was not possible to investigate the entire range of concentrations due to the high melting temperatures of the intermetallic compounds; thus it was not possible to detect any temperature dependence of the integral enthalpy. In liquid Li–Pb alloys the enthalpy has been found to be temperature dependent [7]. The maximum value of ΔC_p of 15.7 ± 2.4 J $\mathrm{mol^{-1}\ K^{-1}}$ occurs at a concentration close to Li_4Pb. Higher ΔC_p values are expected for the Li–Sn system, which exhibits more negative values for ΔH than Li–Pb. For liquid Al–Li alloys the maximum ΔC_p value at 973 K calculated using the association model amounts to 9.5 J $\mathrm{mol^{-1}\ K^{-1}}$. In this system the ΔH values are less negative than those of liquid Li–Pb alloys [8].

As in Li–Sn and Al–Li alloys it was not possible to carry out calorimetric measurements in the middle range of lithium concentrations due to experimental difficulties. However, in Li–Zn alloys it was possible to cover the entire concentration range. Our interest in this system stems from the fact that, as yet, we have only been able to find e.m.f. data at one temperature (773 K) for moderately dilute lithium solutions (Hoshino et al. [9]).

The main aim of this study is to present the calorimetric data for liquid Li–Zn alloys at temperatures exceeding 800 K and to compare them with the e.m.f. results of Nagel and Schwitzgebel which were presented at the Calphad XV conference [10].

EXPERIMENTAL AND RESULTS

The integral enthalpy of mixing of Li–Zn was measured in a high-temperature calorimeter under a protective argon atmosphere in a similar manner to Mg–Ga [5], Li–Sn [2] and, recently, Al–Li [8]. The solid components (Li or Zn) were added to a liquid bath consisting of pure metal (at the beginning), or to the alloy (to which several consecutive additions were made). According to the phase diagram [11] the measurement temperature should exceed 800 K to cover the entire concentration range for liquid alloys. The lithium-rich alloys were contained in iron reaction crucibles. The temperature change due to the addition of a component sample or a calibration sample was detected by an Ni–NiCr thermopile situated below the reaction crucible. Calibration was performed by adding tantalum (which has a known enthalpy content) between the additions of the alloy components during the measurements. In the calorimetric studies on lithium alloys, in addition to the corrosion problems, there is a possibility that lithium or alloys with a high lithium content will creep out of the metallic containers; this will change the composition of the alloy and will also destroy the thermopile. Four sets of calorimetric measurements were performed at

TABLE 1

Calorimetric results of the integral enthalpy of mixing of liquid Li–Zn alloys

x_{Li} (at.%)	$-\Delta H$ (kJ mol^{-1})	x_{Zn} (at.%)	$-\Delta H$ (kJ mol^{-1})
$T = 820$ K		$T = 816$ K	
0.009	0.55	0.034	0.78
0.026	1.54	0.089	2.15
0.048	2.79	0.153	3.72
0.070	3.98	0.21	5.17
0.0915	5.06	0.258	6.33
0.113	6.1	0.305	7.46
0.136	7.12	0.349	8.47
0.156	7.93	0.392	9.54
0.172	8.58 ± 0.4	0.429	10.27
0.189	9.19	0.462	10.82 ± 0.6
0.203	9.65	0.491	11.23
0.217	10.08	0.516	11.53
0.2355	10.5	0.541	11.76
0.251	10.95	0.564	11.97
0.261	11.19	0.584	12.05
0.274	11.44	0.605	12.09
		0.628	12.06
$T = 820$ K			
0.285	11.59		
0.302	11.81		
0.319	11.97 ± 0.3		
0.328	12.05		
0.3535	12.17		
0.375	12.24		
$T = 818$ K			
0.397	12.27		
0.415	12.22		
0.430	12.16		
0.45	12.03 ± 1.1		
0.466	11.91		
0.481	11.78		
0.497	11.65		
0.51	11.51		
0.525	11.37		

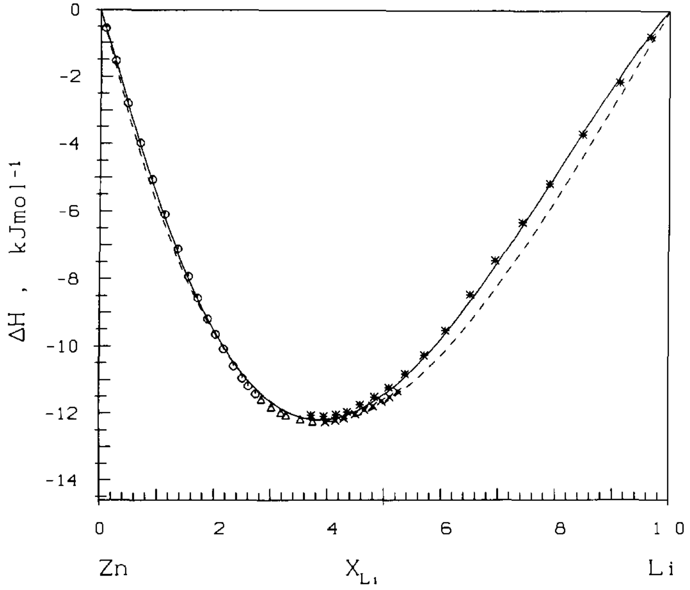

Fig. 1. Experimental results of the integral enthalpy of mixing of liquid Li–Zn alloys: o, Δ, 820 K; ×, 818 K; *, 816 K; ———, calculated results using the association model (the values for the model parameters are given in the text); – – – –, results obtained using eqn. (5).

temperatures between 816 K and 820 K. The results are given in Table 1 and plotted in Fig. 1. The mean error for the calibration ranged between 1.7% and 8.5%.

DISCUSSION

The e.m.f. data presented at Calphad XV [10] were obtained at two temperatures (803 and 833 K) over the entire range of concentration (which was changed by coulometric titration) using concentration cells with liquid electrodes and a liquid electrolyte. From the e.m.f. data the activity coefficients of lithium were calculated by Krupkowski's method [12] and these were fitted to the relation $\ln \gamma_{Li} = \omega(T)\,(1 - x_{Li})^m$. The asymmetry coefficient m which appears in this relation is independent of concentration. The relation for $\ln \gamma_{Zn}$ is obtained using the Gibbs–Duhem equation. This leads to the following equations for the activity coefficients, the partial excess entropies $\Delta \bar{S}^E$ and the integral enthalpy ΔH

$$\ln \gamma_{Li} = \left(-\frac{8333}{T} + 4.58\right)(1 - x_{Li})^{3.4} \tag{1}$$

$$\ln \gamma_{Zn} = \left(-\frac{8333}{T} + 4.58\right)\left[(1 - x_{Li})^{3.4} - 1.417(1 - x_{Li})^{2.4} + 0.417\right] \tag{2}$$

$$-\Delta\bar{S}^{\mathrm{E}}_{\mathrm{Li}} = 4.58R(1 - x_{\mathrm{Li}})^{3.4} \tag{3}$$

$$-\Delta\bar{S}^{\mathrm{E}}_{\mathrm{Zn}} = 4.58R\left[(1 - x_{\mathrm{Li}})^{3.4} - 1.417(1 - x_{\mathrm{Li}})^{2.4} + 0.417\right] \tag{4}$$

$$\Delta H = -3475R\left[1 - (1 - x_{\mathrm{Li}})^{2.4}\right]x_{\mathrm{Zn}} \tag{5}$$

In Fig. 3, the partial Gibbs free energy $\Delta\bar{G}_{\mathrm{Li}}$ calculated using eqn. (1) is compared with the experimental results of Hoshino et al. [9].

As already mentioned the liquid Li–Zn alloys should show a temperature-dependent enthalpy ΔH. Experimental verification (measuring the excess specific heat of these alloys above 820 K) is very difficult because of the high reactivity of lithium and the high vapour pressure of zinc. With the help of the association model it is possible to calculate ΔC_p starting from the experimental results for ΔH and $\Delta\bar{G}_i$ at one temperature [1].

The expressions for a binary alloy which forms a single type of associate are

$$\Delta H = \frac{n_{\mathrm{A}_1} n_{\mathrm{B}_1}}{n} C^{\mathrm{reg}}_{\mathrm{A}_1,\mathrm{B}_1} + \frac{n_{\mathrm{A}_1} n_{\mathrm{A}_i\mathrm{B}_j}}{n} C^{\mathrm{reg}}_{\mathrm{A}_1,\mathrm{A}_i\mathrm{B}_j} + \frac{n_{\mathrm{B}_1} n_{\mathrm{A}_i\mathrm{B}_j}}{n} C^{\mathrm{reg}}_{\mathrm{B}_1,\mathrm{A}_i\mathrm{B}_j} + n_{\mathrm{A}_i\mathrm{B}_j} \Delta H^{\ominus}_{\mathrm{A}_i\mathrm{B}_j} \tag{6}$$

and

$$\Delta S = -R\left(n_{\mathrm{A}_1} \ln x_{\mathrm{A}_1} + n_{\mathrm{B}_1} \ln x_{\mathrm{B}_1} + n_{\mathrm{A}_i\mathrm{B}_j} \ln x_{\mathrm{A}_i\mathrm{B}_j}\right) + n_{\mathrm{A}_i\mathrm{B}_j} \Delta S^{\ominus}_{\mathrm{A}_i\mathrm{B}_j} \tag{7}$$

n_{A_1} and n_{B_1} moles of free A and B atoms are in equilibrium with $n_{\mathrm{A}_i\mathrm{B}_j}$ moles of associates having the composition $\mathrm{A}_i\mathrm{B}_j$ $(i, j = 1,2,\ldots,n)$. x_{A_1}, x_{B_1} and $x_{\mathrm{A}_i\mathrm{B}_j}$ are the molar fractions of the assumed species for one mole of a binary alloy and n is the total number of moles. The equilibrium value for $n_{\mathrm{A}_i\mathrm{B}_j}$ is determined by a mass action law

$$\frac{\left(n_{\mathrm{A}_1}\gamma_{\mathrm{A}_1}/n\right)^i \left(n_{\mathrm{B}_1}\gamma_{\mathrm{B}_1}/n\right)^j}{n_{\mathrm{A}_i\mathrm{B}_j}\gamma_{\mathrm{A}_i\mathrm{B}_j}} = \frac{1}{K_{\mathrm{A}_i\mathrm{B}_j}} = \frac{1}{\exp\left[-\left(\Delta H^{\ominus}_{\mathrm{A}_i\mathrm{B}_j} - T\Delta S^{\ominus}_{\mathrm{A}_i\mathrm{B}_j}\right)/RT\right]} \tag{8}$$

The activity coefficient can be expressed in terms of the model parameters given in eqns. (1) and (2) [1,13]. $\Delta H^{\ominus}_{\mathrm{A}_i\mathrm{B}_j}$ and $\Delta S^{\ominus}_{\mathrm{A}_i\mathrm{B}_j}$ are the enthalpy and entropy of formation of the associates. For the calculation of the thermodynamic properties given in eqns. (1)–(3) the composition of the associates must be defined.

The phase diagram shows several zinc-rich intermetallic phases with relatively broad homogeneity ranges and similar thermal stabilities [11]. For the calculation, the stoichiometries $\mathrm{Li_2Zn_3}$ and $\mathrm{LiZn_2}$ are assumed for the associates. The best representation for the experimental ΔH and $\Delta\bar{G}_{\mathrm{Li}}$ values [9,10] are obtained using $\mathrm{LiZn_2}$ associates. The model parameters are fixed using a least-squares method [13]. The results are as follows: $\Delta H^{\ominus}_{\mathrm{LiZn_2}} = -47.3$ kJ mol^{-1}; $\Delta S^{\ominus}_{\mathrm{LiZn_2}} = -39.5$ J mol^{-1} K^{-1}; $C^{\mathrm{reg}}_{\mathrm{Li,Zn}} = -18.5$ kJ mol^{-1}; $C^{\mathrm{reg}}_{\mathrm{Li,LiZn_2}} = -26.9$ kJ mol^{-1}; $C^{\mathrm{reg}}_{\mathrm{Zn,LiZn_2}} = -18.3$ kJ mol^{-1}.

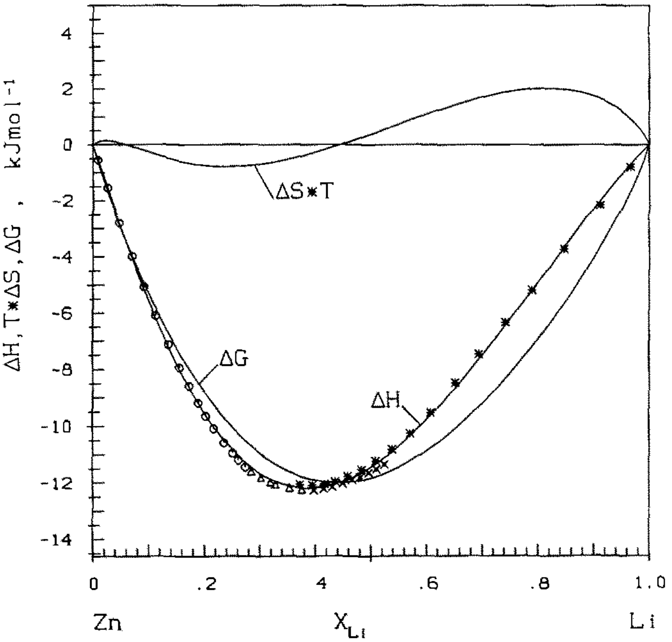

Fig. 2. Calculated enthalpy, Gibbs free energy and entropy of mixing of liquid Li–Zn alloys at 820 K using the association model; o, Δ, ×, *, experimental values.

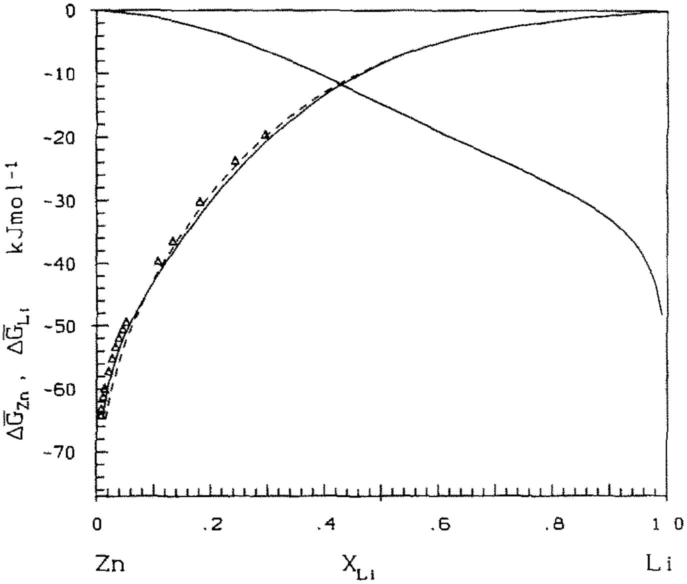

Fig. 3. Calculated partial Gibbs free energies of liquid and undercooled Li–Zn alloys at 773 K; Δ, experimental values [9]; ———, association model; – – – –, eqn. (1).

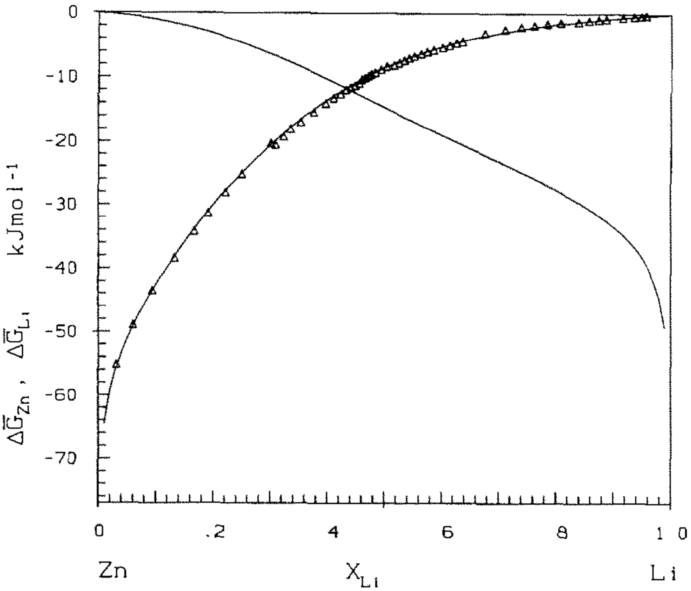

Fig. 4. Calculated partial Gibbs free energies of liquid Li–Zn alloys at 803 K; △, experimental values [10].

The results for ΔH, ΔG and $T\Delta S$ at 820 K are given in Fig. 2 and $\Delta\bar{G}_{Li}$ and $\Delta\bar{G}_{Zn}$ at 773 K, 803 K and 833 K are given in Figs. 3, 4 and 5 respectively. The model describes the experimental results within the experi-

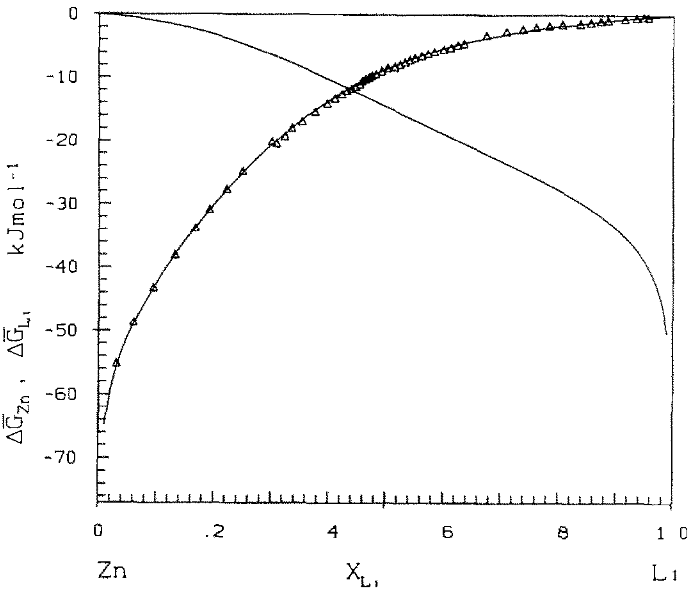

Fig. 5. Calculated partial Gibbs free energies of liquid Li–Zn alloys at 833 K; △, experimental values [10].

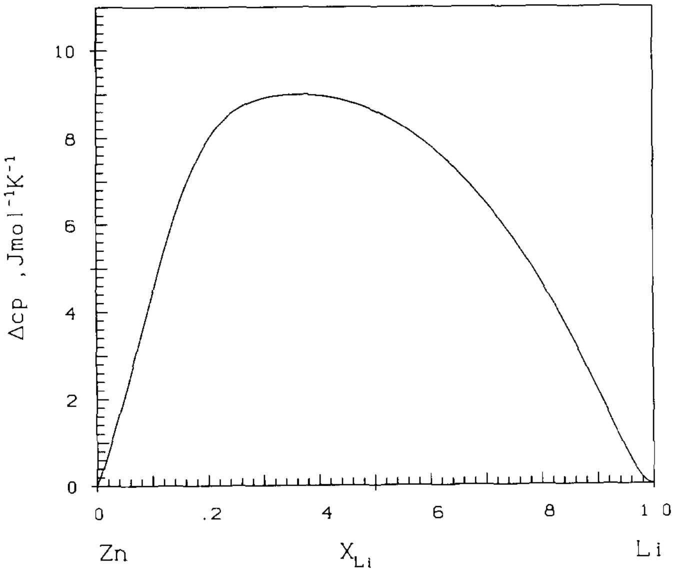

Fig. 6. Calculated excess specific heat of liquid Li–Zn alloys at 820 K.

mental uncertainties. The ΔH values calculated using eqn. (5) are compared in Fig. 1 with the experimental values and the results obtained using the association model. The results obtained using the Krupkowski method show small deviations from the experimental values for lithium-rich alloys. To describe the thermodynamic properties of liquid Li–Zn alloys by Krupkowski's method three model parameters are necessary compared with five for the association model. The prediction of ΔC_p is possible only with the association model. The result for ΔC_p at 820 K is given in Fig. 6. The maximum value is about 9 J mol^{-1} K^{-1} which is in the same range as Al–Li alloys [8]. For both of these systems the maximum values for ΔH are also about -12 kJ mol^{-1}.

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