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Temperature dependence of the thermodynamic functions of strongly interacting liquid alloys

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Received 18 December 1991, in final form 9 March 1992

Abstract. A model is proposed to obtain expressions for thermodynamic functions like the heat of mixing (H_M), excess specific heat (ΔC_P), volume of mixing (V_M) and isothermal compressibility (χ_T) of liquid binary alloys with a strong compound-forming tendency in order to cover a large range of temperature. This has been used to analyse the temperature dependence of the free energy of mixing (G_M), H_M and ΔC_P for liquid Li–Sn alloys. The specific heat of the liquid Li_7Sn_2 alloy has been determined experimentally by drop calorimetric heat content measurements and is found to support the theoretical value, which is based on EMF analysis. The results indicate self-coordination towards the Sn-rich end and strong hetero-coordination in the region $0.33 \leq c_{\text{Li}} \leq 1.0$, being maximum around Li_3Sn . The influence of the chemical short-range order (CSRO) on the concentration fluctuations, $S_{cc}(0)$, chemical diffusion, D , and order parameter, α_1 , has been considered. $S_{cc}(0)$ registers a dominant temperature effect in the self-coordinated region, whereas the effect of temperature on the diffusion coefficient is most visible in the hetero-coordinated region.

1. Introduction

To understand the energetics of liquid alloys, it is necessary to have a good understanding of the behaviour of various thermodynamic functions well above and well below the melting temperature. To extrapolate the thermodynamic data from one given region of temperature to another, the region of criticality in the neighbourhood of either phase separation or glass formation is particularly significant. It becomes difficult in many cases to take experimental measurements over a wide range of temperature with high precision. It is, therefore, of considerable interest to make such investigations in the framework of a theoretical model. We intend to propose a simple scheme and apply it to the liquid Li–Sn system.

The present interest in liquid Li–Sn alloys is twofold. First, the base working data are available from the experiments of Moser *et al* (1986). These authors have checked that the electromotive force (EMF) data and the calorimetric measurements are in good agreement with each other. Secondly, among the Li-based liquid alloys, Li–Sn happens to be one of the most strongly interacting liquid alloys. The heat of formation, H_M , is as low as $\simeq -40 \text{ kJ mol}^{-1}$ and is quite asymmetric as a function of concentration. The H_M versus c curve is triangular and the curve of the excess entropy of mixing is S-shaped.

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The associative tendency between unlike atoms in Li-Sn is strong and therefore we have used the association model here. It has been found to be very useful (for recent reviews see Sommer 1990, Singh 1987) to explain the deviations from ideal and regular solution behaviour for many binary liquid alloys. The model, in essence, assumes the formation of appropriate chemical complexes, $A_\mu B_\nu$ ($\mu A + \nu B = A_\mu B_\nu$; A and B are constituent elements, μ and ν are small integers), which are in chemical equilibrium with some left-over A and B atoms. The association model, in its general form (Jordan 1970, Bhatia and Hargrove 1974, Predel and Oehme 1974, McAlister and Crozier 1974, Sommer 1982, Bhatia and Singh 1982, Singh *et al* 1991), contains four energy parameters—the energy of formation of the complex (g) and the three interaction energies between the species A, B and $A_\mu B_\nu$ —for the evaluation of the free energy of mixing and the activity.

The present approach differs from earlier work in the sense that we need only the free energy of mixing at one concentration, which acts as a base datum. This has made it possible to extract the concentration-dependent values of the free energy of mixing (G_M), heat of mixing (H_M) and excess specific heat (ΔC_P). The temperature and concentration dependences of the concentration fluctuations, $S_{cc}(0)$, in the long-wavelength limit, the chemical diffusion coefficient, D , and the chemical short-range order (CSRO) parameters, α_1 , have also been evaluated. The results indicate self-coordination (like atoms pair as nearest neighbours) towards the Sn-rich end and strong hetero-coordination (unlike atoms pair) for $0.33 \leq c_{Li} \leq 1.0$.

From the thermodynamic point of view, the positive excess specific heat is the most important indicator of the existence of CSRO in liquid alloys. We have, therefore, determined it for liquid Li₇Sn₂ alloy by drop calorimetric experiments, which are in very good agreement with our model calculation based on EMF analysis. In section 2, the theoretical model is described briefly. The experimental determination of the excess specific heat is given in section 3. The results on the temperature dependence of H_M and ΔC_P are discussed in section 4. Concentration fluctuations and chemical diffusion find their place in section 5. A brief discussion on the CSRO parameter then follows in section 6 and we conclude in section 7.

2. Model description

Let the binary alloy contain in all N atoms, of which Nc_1 are A atoms and Nc_2 are B atoms. On the assumption of the existence of chemical complexes, $A_\mu B_\nu$, the binary alloy can be assumed to consist of n_1 individual A atoms, n_2 individual B atoms and n_3 complexes. From the conservation of atoms, therefore, one has

$$\begin{aligned} n_1 &= Nc_1 - \mu n_3 & n_2 &= Nc_2 - \nu n_3 \\ n &= n_1 + n_2 + n_3 = n_3(1 - \mu - \nu) + N. \end{aligned} \quad (1)$$

The free energy of mixing, G_M , of the binary alloy may be expressed as

$$G_M = G^{\text{alloy}} - Nc_1 G_1^0 - Nc_2 G_1^0 \quad (2)$$

where G_i^0 is the Gibbs function for the pure species i . Equations (1) and (2) taken together give

$$G_M = -n_3(\mu G_1^0 + \nu G_2^0 - G_3^0) + G^{\text{alloy}} - (n_1 G_1^0 + n_2 G_2^0 + n_3 G_3^0) \quad (3)$$

or, in a more convenient form,

$$G_M = -n_3g + G_T \quad (4)$$

with

$$g = \mu G_1^0 + \nu G_2^0 - G_3^0 \quad (5)$$

$$G_T = G^{\text{alloy}} - (n_1 G_1^0 + n_2 G_2^0 + n_3 G_3^0). \quad (6)$$

Here g represents the free energy of formation of the complex. By its logical implications, g may depend on temperature and pressure, i.e. $g \equiv g(T, P)$, but is independent of concentration. G_T denotes the free energy of mixing of the ternary mixture consisting of species A, B and $A_\mu B_\nu$. Considering A and B as monomers and $A_\mu B_\nu$ as a $(\mu + \nu)$ -mer, G_T can readily be expressed in a Flory-like expression (for example see Bhatia and Singh 1984):

$$G_T = k_B T \{ n_1 \ln(n_1/N) + n_2 \ln(n_2/N) + n_3 \ln[(\mu + \nu)n_3/N] \}. \quad (7)$$

Obviously, equation (7) conforms to a situation where A, B and $A_\mu B_\nu$ mix ideally. This is not a serious limitation because the strong interactions of the mixture are considered in essence via the formation of the complexes. We may recall that a similar approximation is found (Bhatia and Singh 1980) to yield a very encouraging result for other strongly interacting liquid alloys, namely Li-Pb and Na-Pb. For a given temperature (T) and pressure (P), the equilibrium values of n_3 can be obtained from the condition

$$(\partial G_M / \partial n_3)_{T, P, N, c} = 0. \quad (8)$$

Equations (4) and (8) yield

$$n_1^\mu n_2^\nu / n_3 = (\mu + \nu) N^{\mu + \nu - 1} \exp[-(\mu + \nu - 1)] \exp(-g/k_B T). \quad (9)$$

Equation (9) can be solved numerically to get n_3 for given values of μ, ν and g . For strongly interacting liquid alloys it is expected that $g/RT \gg 1.0$, which implies either $n_1 \rightarrow 0$ or $n_2 \rightarrow 0$. Then for the chemical composition, $c_1 = c_2 = \mu/(\mu + \nu)$, we have $n_1 = n_2 = 0$, $(\mu + \nu)n_3 = N$ and so $G_T = 0$; G_M can safely be expressed as

$$G_M/RT \simeq -n_3g/RT. \quad (10)$$

Equations (9) and (10) can be solved self-consistently to yield n_3 and g as a function of temperature with $G_M(T)$ as input data at the stoichiometric composition c_c . Once g is determined at c_c , G_M can be obtained as a function of concentration with the help of equations (4), (9) and (1).

The heat of mixing, H_M , becomes

$$H_M = G_M - T(\partial G_M / \partial T)_P. \quad (11)$$

On using equation (4), one gets

$$H_M = n_3 [T(\partial g / \partial T)_P - g]. \quad (12)$$

In getting equation (12), $\partial n_i/\partial T$ has been neglected because n_3 , for Li_3Sn , has been found to depend little on T in the range of temperature that interests us. The specific heat, ΔC_P , can thus be expressed as

$$\Delta C_P = (\partial H_M/\partial T)_P = n_3 T (\partial^2 g/\partial T^2)_P. \quad (13)$$

Likewise g , $(\partial g/\partial T)_P$ and $(\partial^2 g/\partial T^2)_P$ are also concentration-independent.

The temperature derivative of g can be obtained from G_M versus T data by making use of equations (9) and (10). Similarly if the base data G_M are available as a function of pressure around the stoichiometric composition, many other properties could be determined; for example, the volume of mixing, V_M ($V_M = V^{\text{alloy}} - c_1 V_1^0 - c_2 V_2^0$, V_1^0 is the volume of the pure element) is given by

$$V_M = (\partial G_M/\partial P)_{T,c} = (\partial G_M/\partial P)_{T,c,n_3}. \quad (14)$$

Hence with the help of equation (14), one has

$$V_M = -n_3 (\partial g/\partial P)_T. \quad (15)$$

The isothermal compressibility, χ_T , becomes

$$\chi_T = -(1/V)(\partial V/\partial P)_T \quad (16)$$

that is

$$\chi_T = c_1 V_1^f \chi_T^{1(o)} + c_2 V_2^f \chi_T^{2(o)} + (n_3/V^{\text{alloy}})(\partial^2 g/\partial P^2)_T \quad (17)$$

where $V_i^f (= V_i^0/V^{\text{alloy}})$ is the reduced volume and $\chi_T^{i(o)}$ is the isothermal compressibility of the pure element i . Liquid alloys, which do not experience any volume contraction or expansion on mixing (i.e. $\partial g/\partial P = \partial^2 g/\partial P^2 = 0$), have the compressibility

$$\chi_T = (c_1 \chi_T^{1(o)} V_1^0 + c_2 \chi_T^{2(o)} V_2^0) / (c_1 V_1^0 + c_2 V_2^0). \quad (18)$$

Equation (18) corresponds to compressibility of ideal alloys. It should be noticed that χ_T for ideal alloys is usually expressed in the literature as $\chi_T = c_1 \chi_T^{1(o)} + c_2 \chi_T^{2(o)}$, which only seems true for $V_1^0 = V_2^0$.

It is thus possible to provide a consistent interpretation of liquid alloys with strong compound-forming tendency in the light of many observable properties. It may be emphasized that, for want of the availability of $G_M \sim P, T$ base data, equations (12), (13), (15) and (17) can still be used to compute H_M , ΔC_P , V_M and χ_T respectively as a function of concentration where $(\partial g/\partial T)_P$, $(\partial^2 g/\partial T^2)_P$, $(\partial g/\partial P)_T$ and $(\partial^2 g/\partial P^2)_T$ should be treated as parameter. In that case these derivatives need to be fixed by the observed value of the respective function at any one given concentration.

3. Experimental determination of the excess specific heat

The specific heat of the liquid Li_7Sn_2 alloy has been determined by drop calorimetric heat content measurements. The experimental apparatus has already been described (Sommer *et al* 1980). It consists basically of a furnace for heating the samples up to the measurement temperature and a calorimeter operating at room temperature. The alloy was contained in a vacuum tightly closed molybdenum ampoule. For the calibration a sample container filled with tin, the heat content of which is well known (Barin and Knacke 1973), was measured together with the alloy sample at each temperature. The results for the heat content $H^T - H^{298}$ of Li_7Sn_2 alloy are given in table 1 and the temperature dependence is shown in figure 1. The melting enthalpy H^m obtained from heat content measurements is $H_{\text{Li}_7\text{Sn}_2}^m = 8.3 \pm 0.5 \text{ kJ mol}^{-1}$. The molar specific heats of liquid and solid alloys obtained from the temperature dependence of the heat content measurements are

$$C_P(\text{Li}_7\text{Sn}_2) = 34 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1} \quad 1056 \text{ K} \leq T \leq 1184 \text{ K} \quad (19)$$

$$C_P(\text{Li}_7\text{Sn}_2) = 33 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1} \quad 984 \text{ K} \leq T \leq 1030 \text{ K}.$$

Table 1. Heat content of the Li_7Sn_2 alloy.

Temp. (K)	$H^T - H^{298}$ (kJ mol ⁻¹)	Temp. (K)	$H^T - H^{298}$ (kJ mol ⁻¹)
984	20.07	1073	31.64
993	20.50	1083	32.31
1000	20.71	1086	32.12
1013	20.84	1091	31.31
1015	21.58	1100	32.37
1022	21.09	1105	33.16
1029	21.53	1113	32.72
1044	22.80	1115	32.90
1051	25.27	1123	33.46
1052	26.32	1128	32.86
1055	26.81	1138	33.34
1055	28.28	1148	34.17
1056	28.17	1158	34.37
1059	31.41	1170	35.06
1068	31.30	1184	35.10

Using C_P data for Li and Pb (Barin and Knacke 1973) the excess molar heat for the liquid Li_7Sn_2 alloy is

$$\Delta C_P = 5.2 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1} \quad 1056 \text{ K} \leq T \leq 1184 \text{ K}. \quad (20)$$

The melting enthalpy of Li_7Sn_2 shows a sharp increase of the heat content just below the melting point, which is very large owing to two-phase melting as a consequence of non-stoichiometry or impurities. This premelting effect could be caused by an increasing concentration of lattice defects. By making use of the relation

$$\Delta H_{\text{AB}}^f = c_A H_A^m + c_B H_B^m - H_{\text{AB}}^m + H_M \quad (21)$$

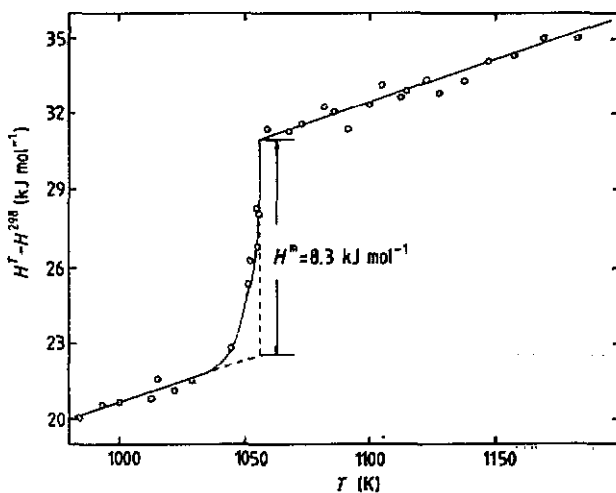


Figure 1. Temperature dependence of the heat content of Li_7Sn_2 .

valid at the melting temperature of the compound, the internal consistency of H^m , H_M and the heat of formation of the compound ΔH_{AB}^f obtained with different experimental techniques could be tested. For instance, with $H_M(\text{Li}_7\text{Sn}_2) = -40 \pm 2 \text{ kJ mol}^{-1}$, $H_{\text{Li}_7\text{Sn}_2}^m = 8.3 \pm 0.5 \text{ kJ mol}^{-1}$, $H_{\text{Li}}^m(1056 \text{ K}) = 4.1 \text{ kJ mol}^{-1}$ and $H_{\text{Sn}}^m(1056 \text{ K}) = 7 \text{ kJ mol}^{-1}$, one obtains $\Delta H_{\text{Li}_7\text{Sn}_2}^f(1056 \text{ K}) = -43.5 \pm 3 \text{ kJ mol}^{-1}$. The value for the solution enthalpy of Li_7Sn_2 obtained calorimetrically at 800 K is $10.7 \pm 0.5 \text{ kJ mol}^{-1}$ (Sommer *et al* 1982). With $-57.4 \pm 3.8 \text{ kJ mol}^{-1}$ for the partial enthalpy of lithium in tin at infinite dilution as obtained from the calorimetric measurements of Moser *et al* (1986), we get $\Delta H_{\text{Li}_7\text{Sn}_2}^f = -37.8 \pm 5$ at 298 K. Kubaschewski and Seith (1938) obtained $-40.2 \text{ kJ mol}^{-1}$ for the heat of formation of Li_7Sn_2 at room temperature. Considering the experimental uncertainties, the comparison of $\Delta H_{\text{Li}_7\text{Sn}_2}^f$ calculated with equation (21) and the value obtained by solution calorimetry shows the internal consistency of H^m , H_M and ΔH^f of the compound Li_7Sn_2 obtained with different experimental techniques.

4. Temperature dependence of G_M , H_M and ΔC_P

The theoretical expressions of section 2 have been applied here to evaluate G_M , H_M and ΔC_P as functions of concentration and temperature. The phase diagram (see figure 2) and the other properties, including the concentration fluctuations in the long-wavelength limit (see figure 6), indicate that the complex likely to exist in the liquid phase is Li_3Sn ($\mu = 3$, $\nu = 1$). The EMF data of Moser *et al* (1986) around the concentration $c_1 = c_c$ have been used as base data in equations (10) and (9) to determine g as a function of temperature. The value of g is found to decrease with increasing T (for example, $g = 128.506 \text{ kJ mol}^{-1}$ at 800 K and $115.857 \text{ kJ mol}^{-1}$ at 1200 K). The g versus T plot is shown in figure 3.

Thus, H_M and ΔC_P have been evaluated from equations (12) and (13) respectively. The required values of $(\partial g / \partial T)_P$ and $(\partial^2 g / \partial T^2)_P$ were obtained by computing g at small intervals by using equations (9) and (10) around the temperatures of the investigation (see table 2). The first derivative is negative and the magnitude

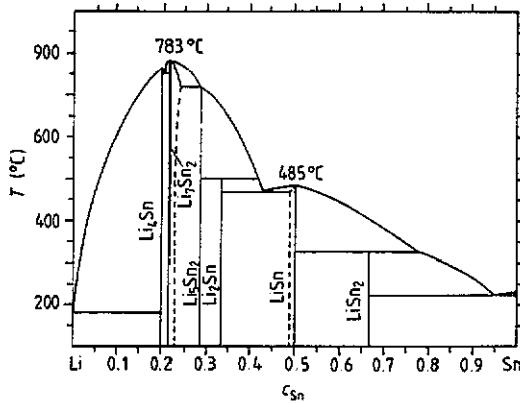


Figure 2. Phase diagram of Li-Sn (Massalski *et al* 1986).

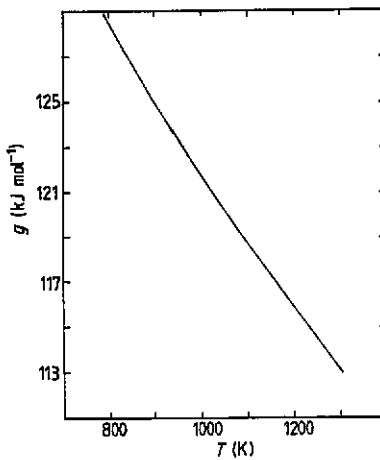


Figure 3. Temperature dependence of the formation energy (g) of the complex Li_3Sn .

decreases with increasing temperature, whereas $\partial^2 g / \partial T^2$ is positive and decreases at higher temperatures.

The values of G_M , H_M (see figure 4) and ΔC_P (see figure 5) computed at two different temperatures, $T = 900$ K and 1200 K, are plotted as functions of c_{Li} . The values of n_3 are also depicted in figure 4. G_M and H_M are compared with those obtained from calorimetric and EMF measurements by Moser *et al* (1986) at 900 K. The agreement between theory and experiment is satisfactory. Though the procedure outlined above is quite simple and does not involve any disposable parameter, most of the salient features of H_M and G_M are successfully exhibited. The magnitudes of H_M and G_M are found to decrease with increasing temperature. The effect of temperature is more distinct around the stoichiometric composition. Besides a tendency to smoothen the steep gradient, the positions of the minima in H_M and G_M shift with increasing temperature.

The computed values of ΔC_P at 900 and 1200 K are plotted in figure 5. It can be seen that ΔC_P is also quite asymmetric and exhibits a maximum around the

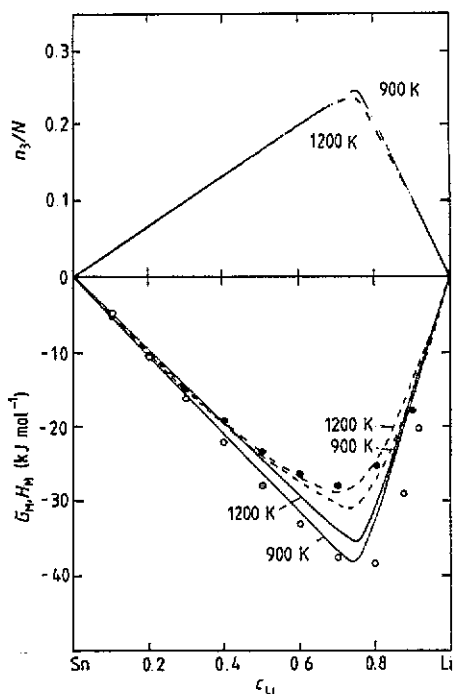


Figure 4. Free energy of mixing G_M (---, ●), heat of mixing H_M (—, ○) and number n_3 (— · —) of chemical complexes in Li-Sn alloys at $T = 900$ and 1200 K. The curves are calculated and points are taken from experiment (Moser *et al* 1986) at 900 K.

Table 2. Formation energies of the complex (Li_3Sn) and its temperature derivatives.

T (K)	g (kJ mol ⁻¹)	$(\partial g/\partial T)_P$ (kJ mol ⁻¹ K ⁻¹)	$(\partial^2 g/\partial T^2)_P$ (J mol ⁻¹ K ⁻²)
850	126.716	-0.0354	+0.0292
900	124.991	-0.0341	+0.0284
1000	121.734	-0.0317	+0.0224
1100	118.705	-0.0295	+0.0208
1200	115.857	-0.0279	+0.016

compound-forming concentration. It decreases with increasing temperature, at all concentrations, being largest in the vicinity of $c_{\text{Li}} \approx 0.75$. The effect of temperature on ΔC_P is more than that of H_M and G_M .

It may be noted that the theoretically determined value, i.e. $4.6 \text{ mol}^{-1} \text{ K}^{-1}$, of ΔC_P for Li_7Sn_2 from equation (13) is quite close to the value $5.2 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$ that has been determined directly from drop calorimetric heat content measurements as in section 3. This shows that the theoretical analysis of the thermodynamic function for Li-Sn based on EMF data and that on calorimetric measurements lead to a consistent result.

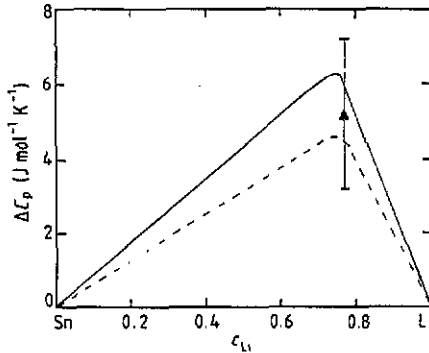


Figure 5. Excess specific heat (ΔC_p) for liquid Li-Sn alloys: calculated with equation (13) at 900 K (—) and 1200 K (---); (▲) experimental.

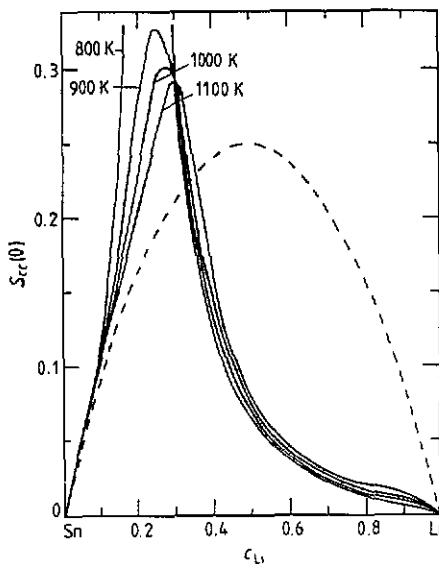


Figure 6. Concentration fluctuations, $S_{cc}(0)$, in liquid Li-Sn alloys at $T = 800, 900, 1000$ and 1100 K: (---) ideal values ($= c_1 c_2$).

5. Concentration fluctuations and chemical diffusion

Now we present the results on the temperature dependence of the long-wavelength limit of the concentration fluctuations, $S_{cc}(0)$, in the Li-Sn system. Since its inception by Bhatia and Thornton (1970), it has been widely used (for recent reviews see Chieux and Ruppertsberg 1980, Wagner 1985, Singh 1987) to study the nature of atomic order in binary liquid alloys. If, at a given concentration, $S_{cc}(0) \gg S_{cc}^{id}(0)$ ($S_{cc}^{id}(0) = c_1 c_2$), there is a tendency for segregation, and $S_{cc}(0) \ll S_{cc}^{id}(0)$ indicates order in the alloys. In principle, $S_{cc}(0)$ can be determined directly from small-angle diffraction experiments, but because of difficult experimental problems it has never been accomplished successfully. Contrary to this, it can be obtained thermodynamically

cally from the measured partial free energy, i.e.

$$S_{cc}(0, T) = (1 - c)a_{Li}(\partial a_{Li}/\partial c)_{T,P,N}^{-1} = (1 - c)\{(1/RT)(d/dc) \times [\bar{G}_{M,Li}(c, T)]\}^{-1} \quad (22)$$

for $c \equiv c_{Li}$, where $\bar{G}_{M,Li}(-RT \ln a_{Li})$ is the partial free energy of mixing of Li, i.e.

$$\begin{aligned} \bar{G}_{M,Li}(c, T) = & (-2319.4 + 1.837T)(1 - c)^2 + 10400.5 - 9.459T)(1 - c)^3 \\ & + (-19585.1 + 18.926T)(1 - c)^4 + (17123.6 - 16.921T)(1 - c)^5 \\ & + (-5681.59 + 5.615T)(1 - c)^6 \quad \text{kJ mol}^{-1}. \end{aligned} \quad (23)$$

Equation (23) follows from the work by Moser *et al* (1986). Values of $S_{cc}(0, T)$ have been evaluated at four temperatures ($T = 800, 900, 1000$ and 1100 K) and are plotted in figure 6. It indicates that the concentration fluctuations in Li-Sn alloys deviate largely from the ideal values and exhibit characteristic features as a function of both concentration and temperature. At the Sn-rich end ($0.67 \leq c_{Sn} \leq 1.0$), $S_{cc}(0)$ is greater than the ideal values, which indicates that like atoms, i.e. Li-Li and Sn-Sn, tend to pair as nearest neighbours. But in the region $0.33 \leq c_{Li} \leq 1.0$, $S_{cc}(0)$ is much smaller than $S_{cc}^{id}(0)$, i.e. there exists a strong hetero-coordination. Though $S_{cc}(0)$ of Li-Sn does not exhibit a distinctive minimum at any concentration, which is usually found in liquid alloys with strong compound-forming tendency (Bhatia and Singh 1984, Singh 1987), the maximal deviation from the ideal values has been found to occur around $c_{Li} \simeq 0.6$ and $S_{cc}(0)$ secures as minimum a value as 0.039 at 900 K.

The effect of temperature on $S_{cc}(0)$ is of particular interest and is visibly dominant in the region of segregation rather than the hetero-coordinated region. It decreases fast in the segregated region whereas in the hetero-coordination region it increases slightly with increasing temperature. Interestingly enough, the cross-over in the nature of variation of $S_{cc}(0)$ occurs around $c_{Li} \simeq 0.3$ where $S_{cc}(0)$ depends very little on temperature (for example at $c_{Li} = 0.3$, $S_{cc}(0) = 0.304, 0.291, 0.295$ and 0.307 at $T = 800, 900, 1000$ and 1100 K respectively). However, the position of the maximum of $S_{cc}(0)$ shifts towards larger contents of Li with increase of temperature.

The values of $S_{cc}(0, T)$ have been further used to investigate the chemical diffusion in Li-Sn liquid alloys, which is likely to play an important role in many technological and corrosion phenomena. The equivalence between $S_{cc}(0)$ and the diffusion coefficient, D , can be established with the help of Darken's equation. In terms of activity, equation (22) can be re-written as

$$\partial a_{Li}(c, T)/\partial c = (1 - c)a_{Li}(c, T)/S_{cc}(0, T). \quad (24)$$

Darken's equation, on the other hand, suggests

$$D_m = D_s d \ln a_{Li}/d \ln c_{Li} \quad (25)$$

with

$$D_s = c_{Li}D_{Sn} + c_{Sn}D_{Li}. \quad (26)$$

D is usually known as the interdiffusion coefficient, D_{Sn} and D_{Li} as the self-diffusion coefficients of Sn and Li respectively. From equations (24) and (25), one has

$$D_m(c, T) = D_s(c, T) S_{cc}^{\text{id}}(0) / S_{cc}(0, T) \quad (27)$$

or, more conveniently,

$$[D_m(c, T) - D_s(c, T)] / D_s(c, T) = [S_{cc}^{\text{id}}(0) - S_{cc}(0, T)] / S_{cc}(0, T). \quad (28)$$

For ideal mixing, $S_{cc}(0, T) \rightarrow S_{cc}^{\text{id}}(0)$, i.e. $D_m(c, T) \rightarrow D_s(c, T)$; for ordered alloys, $S_{cc}(0, T) < S_{cc}^{\text{id}}(0, T)$, i.e. $D_m(c, T) > D_s(c, T)$; and similarly for segregation $D_m(c, T) < D_s(c, T)$. The ratio $D_m(c, T) / D_s(c, T)$ computed as a function of concentration and temperature is shown in figure 7.

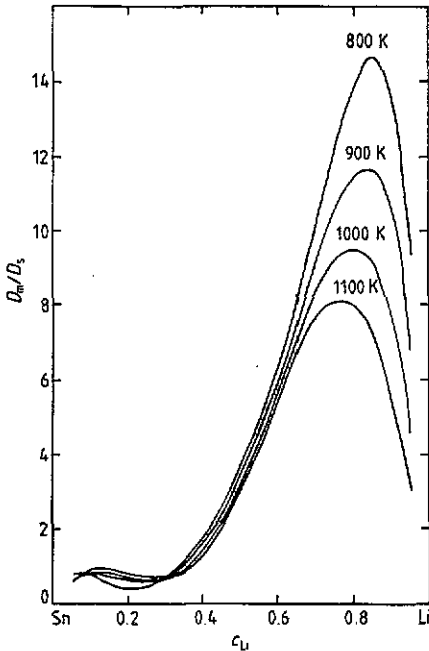


Figure 7. Ratio of the chemical diffusion, D_m/D_s , in liquid Li-Sn alloys at $T = 800, 900, 1000$ and 1100 K.

The plot of D_m/D_s exhibits a peak around the composition Li_3Sn . This might occur due to an enhanced value of D_m . With increasing temperature, the sharpness and the magnitude of the peak are reduced. As the temperature increases, the complexes dissociate and thereby D_m decreases. It is interesting to observe that the temperature effect on diffusion is more visible around the stoichiometric composition Li_3Sn than that on $S_{cc}(0)$.

6. Chemical short-range order parameter

From the foregoing discussion it is clear that strong hetero-coordination exists towards the Li-rich end, being maximum around Li_3Sn . With a view to quantifying the degree

of order, we propose to compute the chemical short-range order (CSRO) parameters (Cowley 1950, Warren 1969). For the nearest-neighbour sites, it can be defined as

$$\alpha_1 = 1 - P_{AB}/c_B \quad (29)$$

where P_{AB} is the conditional probability to find a B atom next to a given A atom, and c_B is the concentration of B atoms and is identical to c_2 in the notation of section 2. In terms of the number of bonds between unlike atoms (A-B), equation (29) can be written as

$$\alpha_1 = 1 - N_{AB}/Nz c_A c_B \quad (c_A \equiv c_1; c_B \equiv c_2) \quad (30)$$

where z is the coordination number and N_{AB} represents the number of bonds between unlike atoms that exists in the system. Based on quasi-lattice theory for compound-forming molten alloys, Bhatia and Singh (1982) worked out a simple expression for N_{AB} in terms of n_3 and, therefore, α_1 can be expressed as

$$\alpha_1 = \frac{(\mu + \nu - 1)n_3}{Nz c_1 c_2} \left(-\beta + \frac{z(c_2^2 \mu + c_1^2 \nu)}{\mu + \nu} + \frac{2\gamma n_3}{(N - \gamma n_3)} - \frac{[\mu - (\mu + \nu)c_1]^2}{(\mu + \nu)^2} \right) \quad (31)$$

with

$$\gamma = 2(\mu + \nu - 1)/z.$$

In (31) β takes into account the internal structure of the complexes. In the absence of specific knowledge on the internal structure, β acts as a parameter and has been suggested to be very close to unity. This is the maximum possible value that β can have and ensures that all the favoured bonds in the complex are bonds between unlike atoms.

Table 3. Chemical short-range order parameter (α_1) in liquid Li-Sn alloys.

c_{Li}	α_1		$\alpha_1^{(limiting)}$
	900 K	1200 K	
0.1	0.0261	0.0252	0.111
0.2	0.0006	0.0005	0.25
0.3	-0.0276	-0.0272	-0.428
0.4	-0.0596	-0.0587	-0.666
0.5	-0.0969	-0.0954	-1.000
0.6	-0.1429	-0.1406	-0.666
0.7	-0.2054	-0.2012	-0.428
0.8	-0.2322	-0.2322	-0.25
0.9	-0.1924	-0.1924	-0.111

The computed values of α_1 at 900 K and 1200 K are tabulated in table 3. For our calculation, we have taken $z = 10$. The limiting values of α_1 corresponding to

respective concentrations are also listed. From a simple probabilistic approach, one can easily show that α_1 lies in the range

$$\begin{aligned} -c_1/c_2 \leq \alpha_1 \leq 1 & \quad c_1 \leq \frac{1}{2} \\ -c_2/c_1 \leq \alpha_1 \leq 1 & \quad c_1 \geq \frac{1}{2}. \end{aligned} \quad (32)$$

At $c_1 = \frac{1}{2}$, one has $-1 \leq \alpha_1 \leq 1$. The maximum possible value, $\alpha_1^{\max} = 1$, suggests total segregation leading to phase separation, whereas $\alpha_1^{\min} = -1$ represents complete order of pairs of nearest-neighbour atoms in the A-B configurations. For random distribution of atoms $\alpha_1 = 0$.

It is interesting to observe that, though equation (31), in its simplest form, does not contain any energy parameter, it exhibits change of sign in the computed values of α_1 . At the Sn-rich end, α_1 is positive, i.e. segregation, and then it becomes negative, i.e. order. It may be emphasized that equation (31) has been derived quite independently from equation (22), but both the values of α_1 and $S_{cc}(0)$ lead to the same result. Also α_1 suggests that the maximum hetero-coordination occurs towards the Li-rich end, which is in agreement with results obtained from neutron diffraction measurements (Alblas *et al* 1984). At $c_{Li} = 0.9$, the computed value of α_1 , i.e. -0.1924 , is lower than the permitted value, i.e. -0.111 . We may recall that the theoretical H_M also exhibits deviation around the same concentration. This may happen because one of the interaction energies, say between left-over Li atoms and the complexes, which has been neglected here, is playing an important role in this region. Another possible reason is the use of a Flory-like expression, see equation (7), which is only true for $z \rightarrow \infty$. Incorporation of finite z in equation (7) and hence in equation (9) is likely to improve the shortcomings.

7. Summary and conclusion

In the present paper, we have used a simple thermodynamic model to predict the concentration dependence of various thermodynamic functions like free energy of mixing, heat of mixing, excess specific heat, volume of mixing and compressibility of liquid alloys with strong compound-forming tendency over a wide range of temperature. This has made it possible to extract a consistent interpretation of the temperature, pressure and concentration dependences of many other thermodynamic functions from a given free energy of mixing at only one c . We have applied it to liquid Li-Sn alloys to investigate G_M , H_M and ΔC_P as functions of c and T . The investigation implies a strong hetero-coordination in the melt towards the Li-rich end, being maximum around Li_3Sn .

Since the positive excess specific heat is the most important indicator of the existence of CSRO in liquid alloys, we have measured it directly for Li_7Sn_2 alloy by a drop calorimetric experiment. Within the experimental error, the calorimetric result is in good accord with the theoretical value obtained on the basis of EMF analysis.

Results on concentration fluctuations, $S_{cc}(0)$, which are very useful to infer the nature of atomic order in liquid alloys, have been provided over a wide range temperature ($T = 800$ to 1100 K). It indicates self-coordination towards the Sn-rich end and strong hetero-coordination for $0.33 \leq c_{Li} \leq 1.0$, being maximum around $c_{Li} \approx 0.6$. The value of $S_{cc}(0)$ of Li-Sn undergoes a dominant temperature effect in the

self-coordinated region where it decreases fast to attain the random value ($= c_1 c_2$) with increasing T , above the melting temperature. Contrary to this, $S_{cc}(0)$ increases slightly with increasing T in the hetero-coordinated region.

Darken's equation on chemical diffusion has been used to express the latter in terms of $S_{cc}(0)$. The computed values of the chemical diffusion coefficient exhibit anomalous behaviour as a function of c and T around the stoichiometric concentration Li_3Sn . There is an indication of an ample increment in the values of mutual diffusion coefficients D_m around stoichiometry. The temperature effect on diffusion is more visible around the compound-forming concentration Li_3Sn than that on $S_{cc}(0)$.

The degree of order in liquid Li-Sn alloys has been examined with the help of the CSRO parameter (α_1), which is calculated as a function of c and T . Like $S_{cc}(0)$, α_1 also indicates weak segregation in a narrow band of concentration towards the Sn-rich end and strong hetero-coordination for larger contents of Li. The temperature effect is found to be only small as regards the atomic arrangement of atoms in the nearest-neighbour shell.

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