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Calculation of the heat capacity of liquid Pb/Li, Na, K alloys according to the HPH formalism

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Abstract. Measured excess heat capacities ΔC_p of the liquid alloys Pb/Li, Na, K are compared with values obtained from the entropies of mixing ΔS which were calculated according to the formalism of Hafner, Pasturel and Hicter (HPH). Input parameters are the entropies of the pure components, the molar volumes, the enthalpies of mixing at the liquidus temperature, the heat capacities, and the variation of these quantities with temperature and composition. The HPH formalism and the consequences of the above mentioned comparison are discussed.

1. Introduction

For binary liquid alloys of Pb/Li (Saar and Ruppertsberg 1987a), Pb/Na (Ruppertsberg and Jost 1989) and Pb/K (Saar and Ruppertsberg 1988) we determined complete diagrams for the variation of the heat capacity C_p with composition $0 \leq x \leq 1$ and temperature $T_1 < T < 1300$ K. T_1 is the liquidus temperature. In all three cases we observed strong deviations from the ideal $C_p^{\text{id}}(x)$ behaviour which is given by the Neumann–Koop rule. In general $\Delta C_p = C_p - C_p^{\text{id}}$ was found to be positive with a maximum value at a special composition which we call x_m . The individual $\Delta C_p(x, T)$ curves of the three systems look quite different and the alteration of the curves is remarkably discontinuous in going from Pb/Li to Pb/Na and to Pb/K. For the first system we observed a maximum relative deviation of $\Delta C_p/C_p^{\text{id}} = 0.75$ at $x_m = 20$ at. % Pb. This value was obtained close to T_1 and drops rapidly to $\Delta C_p/C_p^{\text{id}} = 0.45$ within a temperature range of 100 K, beyond which only a minor further variation was observed until the highest investigated temperature of $T_1 + 280$ K. A ΔC_p of approximately the same magnitude was also observed by Sommer (1988) who investigated alloys with $x = 20$ and 50 at. % Pb. For Pb/Na we found a much smaller deviation of only $\Delta C_p/C_p^{\text{id}} = 0.2$ at about $x_m = 30$ at. % Pb. No drop of C_p with T was found. Rather a small increase was observed for the alloys containing between 10 and 95 at. % Pb. The most spectacular deviation of $\Delta C_p/C_p^{\text{id}} = 2.1$ at $x_m = 0.5$ occurs at T_1 in Pb/K. The C_p first decreases rapidly with rising temperature but then becomes flatter beyond $T_1 + 100$ K with $\Delta C_p/C_p^{\text{id}}$ values of about 0.7. A very similar composition dependence was observed by Saboungi *et al* (1986) for the concentration range of 0–70 at. % Pb. They explain the anomalous behaviour by the formation of clusters in the melt which rapidly dissociate with increasing temperature

(Johnson and Saboungi 1987), and they (Saboungi *et al* 1987) find a support for this assumption in the unusual amplitude and position of a prepeak in the total structure factor observed with neutron diffraction. There was some discussion concerning the exact size (Reijers *et al* 1987) and the interpretation (Hafner 1989) of this prepeak but there is no doubt that the structure of Pb/K is no longer hard-sphere like but shows, depending on composition, a greater or lesser preference for the formation of anion clusters.

For Pb/Li we (Saar and Ruppertsberg 1987a) proposed another explanation for the anomalous temperature dependence of $\Delta C_p(x_m)$, based on the assumption of the existence of chemical short-range order (CSRO) which is superimposed on a random dense-packed, hard-sphere structure (RDPHS). The latter is known to be a good starting point for describing most liquid metals and many alloys. The assumption that Pb/Li belongs to this group of alloys is supported by the results of neutron diffraction investigations (Ruppertsberg and Reiter 1982; Ruppertsberg and Schirmacher 1984) and of computer-simulation experiments, performed by Jacucci *et al* (1984). According to these observations the global arrangement of the Li and Pb ions in the melt is RDPHS-like and close to substitutional. A superimposed CSRO leads to a preference for unlike nearest neighbours. At the composition Li_4Pb , which corresponds to x_m , lead ions are completely surrounded by lithium ions and the number of Li–Li nearest neighbours is reduced compared with a random distribution. The term ‘CSRO’ in this context is analogous to ‘short-range order’ (SRO) in crystalline disordered substitutional alloys. SRO yields modulations of the Laue diffuse scattering (LDS) which are found, just to cite one of the best known examples, in the disordered high-temperature FCC CuAu phase. The modulations become sharper with decreasing temperature because the spatial correlations between the corresponding concentration fluctuations become longer ranged. On the formation of long-range order these modulations eventually transform into the superlattice peaks. Reiter *et al* (1977) observed superlattice peaks at low temperature in the α -phase of FCC Ag/Li which disappear on heating and are substituted by broad modulations of the LDS including an especially pronounced ‘prepeak’ in front of the (111) reflection. On melting the Bragg peaks transform into the broad undulations characteristic of liquid structures, but the prepeak which is characteristic of SRO in the solid phase and of CSRO in the liquid phase remained almost unaffected. The same was observed on melting Mg/Li (Ruppertsberg *et al* 1980).

Referring again to Pb/Li, for neighbouring atoms the CSRO is most pronounced at x_m . At this composition and at T_1 it turns out to be especially long-ranged. The corresponding sharp prepeak broadens rapidly with increasing temperature, which indicates that the range of the order decreases at the same rate. We assumed (Saar and Ruppertsberg 1987a) that these effects are responsible for the large excess value of $C_p(x_m)$ and its rapid initial drop on heating. However, a quantitative description of the total $\Delta C_p(x, T)$ behaviour is still lacking.

A formalism for describing quantitatively the behaviour of a system of equal-size hard spheres which interact by means of Yukawa potentials was proposed by Hafner, Pasturel and Hicter (1984a, b, 1985a, b) (hereafter referred to as HPH) and quite successfully applied to a large number of binary compound-forming liquid alloys. Recently the model was extended by Hafner and Jank (1988) to the case of segregating systems.

In the present paper we will use the experimentally obtained ΔC_p values amongst other quantities, for testing special aspects of the HPH formalism.

2. Formalism

According to HPH the Gibbs free energy of mixing of a liquid binary alloy is given by the following expression:

$$\begin{aligned}\Delta G &= \Delta G_{\text{el}} + \Delta G_{\text{HS}} + \Delta G_{\text{ord}} = \Delta H - T\Delta S \\ \Delta G &= \Delta H_{\text{el}} - T\Delta S_{\text{el}} - T\Delta S_{\text{HS}} + \Delta H_{\text{ord}} - T\Delta S_{\text{ord}}\end{aligned}\quad (1)$$

The electronic term ΔG_{el} may be calculated according to the Pines and Nozières (1966) formalism. The Mansoori equation (see for example Young 1977) yields the hard-sphere contribution

$$\Delta S_{\text{HS}} = \Delta S_{\text{id}} + S_{\eta} + S_{\sigma} \quad (2)$$

as a sum of the ideal mixing term, a term arising from the variation of packing η , and the diameter mismatch term which is proportional to $(\sigma_1 - \sigma_2)^2$. The squared difference of the hard-sphere diameters, ΔG_{ord} in (1) being due to chemical ordering. The calculation of ΔG_{ord} according to HPH is possible for substitutional alloys for which $\sigma_1 = \sigma_2 = \sigma$. The authors *postulated* that σ is about the same for the two pure components and does not change on mixing. η may then be calculated from the molar volume. Strong negative excess volumes, which are typical of the alloys studied in this paper, yield large η -values. Hafner (1985) also proposed a simple rule for calculating the volume contraction on mixing sp-bonded metals. Good understanding of this phenomenon would be important for a satisfactory description of these materials. However, for testing the HPH formalism it seems better to use the experimentally observed volume contractions as an input parameter. The same is done with the enthalpy of mixing ΔH from which the ordering enthalpy is calculated

$$\Delta H_{\text{ord}} = \Delta H - \Delta H_{\text{el}} \quad (3)$$

by subtracting the electronic term. We calculated ΔH_{ord} for different temperatures by taking $\Delta H(T_i)$ values from the literature and using our experimentally obtained ΔC_p -values. An important step in the HPH formalism is the calculation of ΔS_{ord} from ΔH_{ord} . This is possible in the framework of the mean spherical approximation (MSA) and for Yukawa-type interactions. It is the validity of this step which, together with the influence of the hard-sphere contributions, is tested in the present paper in a way proposed by HPH. We determined ΔS , equation (1), at two different temperatures and recalculated $\Delta C_p = T(\partial \Delta S / \partial T)_p$ or

$$\Delta C_p = [\Delta S(T_1) - \Delta S(T_2)](T_1 + T_2)/2(T_1 - T_2). \quad (4)$$

ΔC_p obtained in this way is a mean value for the temperature range chosen.

The next equations will outline in more detail the way to proceed from ΔH_{ord} to ΔS_{ord} :

$$\varepsilon = -x_1 x_2 (Q_1 - Q_2)^2 \exp(-z)/\sigma \quad (5)$$

is the potential at contact between two spheres with diameter σ . Q_1 and Q_2 are the charges. $z = \kappa \cdot \sigma$ and κ is the inverse screening length. The ordering enthalpy turns out to be

$$\Delta H_{\text{ord}} = -\varepsilon\omega/2 \quad (6)$$

and the following relation exists between ε , ω , η , z and $\beta = 1/k_B T$:

$$12\beta\varepsilon\eta = \omega[z - \omega/(2 \exp(z))]/\{1 + \omega[1 - \exp(-z)]/2z\}^4. \quad (7)$$

ω may thus be obtained from the equations (6) and (7) if ΔH_{ord} is known. ΔS_{ord} may then be calculated from the following equations:

$$\Delta S_{\text{ord}} = k_B[f(\omega) - f(0)]/2\eta \quad (8)$$

with

$$f(\omega) = -(a_1 + a_2\omega + a_3\omega^2)/[72b^2(1 + b\omega)^3]$$

$$a_1 = z\{2/[\exp(z) - 1] - 1\} \quad a_2 = -3[1 - 3 \exp(-z)]/2$$

$$a_3 = \exp(-z)[1 - \exp(-z)]/4z \quad b = [1 - \exp(-z)]/2z.$$

The following figures will illustrate the practical application of this formalism. Figure 1 gives $-\beta\eta\Delta H_{\text{ord}}$ as a function of ω and was obtained from equations (6) and (7). Its meaning is similar to figure 1 in Waisman (1973), where it was pointed out that only the branches starting at $\omega = 0$ are physically meaningful. The author related the maximum at about $\omega = 2z$ to the critical point of a liquid-liquid miscibility gap. A more complete study of this branch of the curve was recently published by Hafner and Jank (1988).

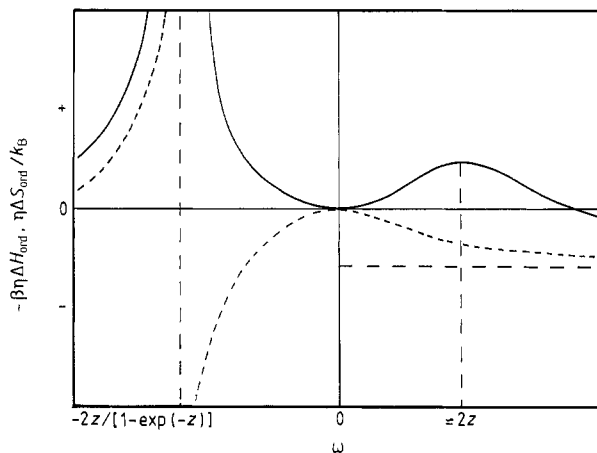


Figure 1. Schematic diagrams of $-\beta\eta\Delta H_{\text{ord}}$ versus ω (full curves) and $\eta\Delta S_{\text{ord}}/k_B$ (broken curves, $z > 1$) calculated according to equations (6) to (8).

It is because β and η are both positive, that ΔH_{ord} from figure 1 turns out to be negative. This confirms our earlier statement (Ruppertsberg 1988) deduced from the behaviour of a simplified version of ΔH_{ord} . Because in our case ε , equation (5), is negative ω , equation (6) also comes out to be negative and for the present discussion only the branch of the full drawn curve between $\omega = 0$ and $\omega = -2z/[1 - \exp(-z)]$ has to be taken into account.

In principle we now proceeded in the following way: the given values of T , η and ΔH_{ord} yield the ordinate value of the full drawn curve in figure 1 from which ω is obtained, as well as $\eta\Delta S_{\text{ord}}/k_B$ calculated according to equation (8) (given as broken curves in

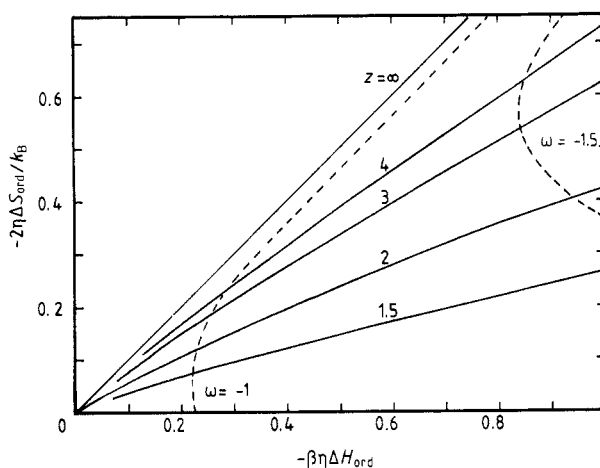


Figure 2. Diagram relating ΔS_{ord} to ΔH_{ord} according to equations (6) to (8) and calculated for different values of z (full curves). The broken curves connect the points with $\omega = -1.0$ and -1.5 , respectively.

figure 1). For relating ΔS_{ord} quantitatively to ΔH_{ord} (which is done in figure 2) one has to take the screening into account. For complete screening, i.e. $z = \infty$, one obtains the simple proportionality

$$2\eta\Delta S_{\text{ord}}^{\infty}/k = \beta\eta\Delta H^{\infty} \quad (9)$$

which corresponds to the steepest of the full drawn curves shown in figure 2. The signification of equation (9) will be discussed later. For liquid Li_4Pb and Li_7Ag_3 we (Ruppersberg and Schirmacher 1984) observed z -values of about 3 and 6, respectively. In this region of typical metallic screening ΔS_{ord} for a given ΔH_{ord} is only about 20–30% smaller than for $z = \infty$ and it is quite insensitive to small variations of z . According to HPH a reasonable choice for practical purposes is $z = 3.14$ (π).

The curve for $z = 1$ in figure 2 turns out to be almost identical with the abscissa. This strange behaviour is related to stepwise fundamental changes of the different branches of the broken curve in figure 1 which occur if z is reduced below 1. For z smaller than about 0.9 the whole broken curve has finally become inverted. Altogether this indicates that equation (8) loses its physical meaning if the screening becomes significantly smaller than that for metallic phases. The broken lines in figure 2 connect the points which have the same value of ω . The $\omega = -1$ curve starts at the bottom of the diagrams at about $z = 1$ and ends at the top with $z = 16.7$.

3. Results

We attempt to find out to what extent the HPH formalism describes correctly the thermodynamic behaviour or correlates correctly different properties of the compound-forming systems under investigation. According to this formalism the different properties of mixing are composed from electronic, hard-sphere (HS) and ordering terms. Only the evaluation of the last-mentioned contribution is restricted to systems for which $\sigma_1 = \sigma_2$. In order to obtain the most realistic description we will not enforce this condition in

Table 1. Properties of the pure elements. The first temperature given for the different elements is the melting point.

| T (K) | S (J K ⁻¹) | V (cm ³ mol ⁻¹) | σ (Å) | $10^3 \eta$ | T (K) | S (J K ⁻¹) | V (cm ³ mol ⁻¹) | σ (Å) | $10^3 \eta$ |
|------------|-----------------------------|---|-----------------|-------------|------------|-----------------------------|---|-----------------|-------------|
| Lithium | | | | | Lead | | | | |
| 454 | 46.90 | 13.77 | 2.65 | 424 | 601 | 92.22 | 19.44 | 3.02 | 448 |
| 1000 | 70.13 | 15.29 | 2.47 | 309 | 700 | 96.88 | 19.69 | 3.00 | 430 |
| 1050 | 71.51 | 15.47 | 2.46 | 301 | 750 | 98.90 | 19.81 | 2.98 | 422 |
| 1150 | 74.14 | 15.86 | 2.43 | 285 | 848 | 102.67 | 20.07 | 2.96 | 406 |
| 1250 | 76.54 | 16.27 | 2.41 | 270 | 900 | 104.43 | 20.20 | 2.94 | 398 |
| Sodium | | | | | 1000 | 107.55 | 20.47 | 2.92 | 383 |
| 371 | 66.63 | 24.77 | 3.21 | 421 | 1050 | 108.94 | 20.61 | 2.91 | 377 |
| 700 | 84.00 | 26.94 | 3.03 | 324 | 1100 | 110.34 | 20.75 | 2.90 | 370 |
| 750 | 85.94 | 27.42 | 3.01 | 314 | 1150 | 111.61 | 20.89 | 2.89 | 364 |
| Potassium | | | | | 1250 | 114.02 | 21.18 | 2.87 | 352 |
| 336 | 75.36 | 47.34 | 3.99 | 422 | | | | | |
| 848 | 103.72 | 55.08 | 3.59 | 265 | | | | | |
| 900 | 105.47 | 56.15 | 3.56 | 253 | | | | | |
| 1100 | 111.61 | 60.68 | 3.42 | 207 | | | | | |

calculating the HS part. The electronic term is not influenced by the choice of the HS parameters.

To obtain $\Delta S_{\text{HS}}(x, T)$ from the Mansoori equation one has to know $\sigma_1(x, T)$, $\sigma_2(x, T)$ and $\eta(x, T)$. We calculated these data from the experimentally obtained molar volumes $V(x, T)$ and from the $\sigma(T)$ and $\eta(T)$ values of the pure elements. According to the Gibbs–Bogoliubov variational method, the σ of the pure components was chosen in such a way that the estimates of entropy for the real system contain no contribution from the thermal variation of σ . This yields for metals (see Young 1977): $S = S_{\text{HS}} + S_{\text{el}} = S_{\text{gas}} + S_{\eta} + S_{\text{el}}$. We took the entropy values given in table 1 from the literature (Barin and Knacke 1973), and obtained η from the equation $S_{\eta}/k = -\eta(4 - 3\eta)/(1 - \eta)^2$. σ was then calculated according to $\sigma^3 = 6(V/N)\eta/\pi$. $\sigma(T)$ and $\eta(T)$ of the pure elements are given in table 1. These data differ somewhat from the values obtained from optimum fits of the structure factors: e.g., for liquid lithium, we (Ruppertsberg 1987) obtained at 454 K $\sigma_{\text{Li}} = 2.82$ Å and $d\eta/dT$ turned out to be -2.3×10^{-4} K⁻¹ instead of about 1.7×10^{-4} K⁻¹ calculated from table 1.

For calculating ΔS_{HS} of the mixture we studied two different cases:

(i) σ_1 and σ_2 were assumed to be independent on composition. The packing fractions were obtained from the relation

$$\eta(x, T) = N\pi(x_1\sigma_1(T)^3 + x_2\sigma_2(T)^3)/6V(x, T) \quad (10)$$

and are plotted in figure 3. The resulting $\Delta C_{\text{p}}^{\text{pack}}(x)$ values are given in figures 5 to 7 below for the temperatures indicated in the relevant figure captions. T_1 and T_2 in equation (4) were chosen to be 25 K below and above these temperatures, respectively.

(ii) $\eta(x, T)$ was assumed to vary linearly with composition. According to the classical idea of the chemical compression, the volume contraction was related to a shrinking of the diameter of the alkali-metal ions (figure 3), whereas the diameter of lead was kept constant. $\Delta C_{\text{p}}^{\text{pack}}(x)$ obtained in this way turned out to be much smaller than for case (i).

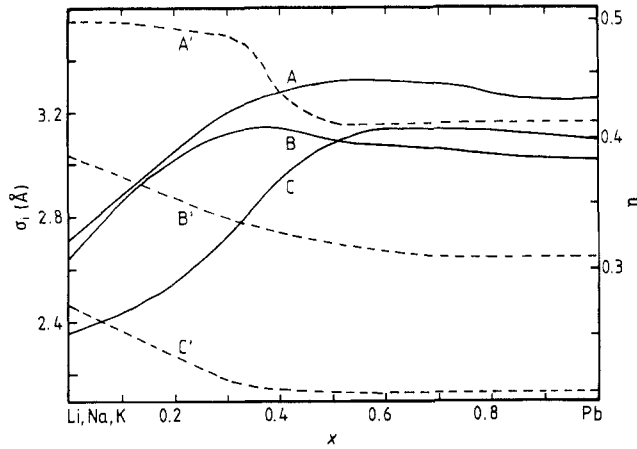


Figure 3. Variation of the hard-sphere parameter with composition. $\eta(x)$ (full curves) calculated assuming invariant σ (table 1) according to case (i) $\eta_{\text{Pb/Na}}$ at 700 K (curve A), $\eta_{\text{Pb/Li}}$ at 1000 K (curve B) and $\eta_{\text{Pb/K}}$ at 900 K (curve C). $\sigma(x)$ (broken curves) of the alkali-metal atoms calculated assuming linear variation of η (table 1) with x according to case (ii) σ_{K} (curve A'), σ_{Na} (curve B') and σ_{Li} (curve C'). The σ - and η -values are given for the same temperature.

The enthalpy of mixing of the free electron gas was calculated according to Pines and Nozières (1966). The corresponding equations given by HPH contain the molar volumes of the pure components and of the mixture and, in addition, the charges Z_i of the ions. For the alkali-metal ions we chose $Z = 1$. With $Z_{\text{Pb}} = 4$ equation (3) yields positive ΔH_{ord} -values at the lead rich side of the Pb/Na, K alloys, which is impossible. Such a behaviour was also observed for several alloy systems by HPH who postulated that ΔH_{ord} vanishes at these compositions. According to Hafner (1989) this behaviour is due to a failure of the simple Pines–Nozières formalism in these cases. We finally chose $Z_{\text{Pb}} = 3.2$ for Pb/Na, K which yields negative ΔH_{ord} values for all compositions and does not substantially change the $\Delta C_{\text{P}}^{\text{ord}}$ -values calculated from ΔS_{ord} in the composition range where its determination was possible using $Z = 4$. In principle, $\Delta C_{\text{P}}^{\text{ord}}$ increases with decreasing absolute values of ΔH_{ord} , assuming all other parameters to be unchanged. This is due to the bending of the $\beta\eta\Delta H_{\text{ord}}$ versus $2\eta\Delta S_{\text{ord}}/k_{\text{B}}$ curves given in figure 2. The electronic heat capacities calculated from the variation of ΔH_{el} with temperature are plotted in the figures 5 to 7 below. The $\Delta C_{\text{P}}^{\text{ord}}(x)$ given as full drawn curves in figure 4 was obtained from the temperature variation of ΔH_{ord} calculated according to equation (3). The corresponding ΔH values were taken from Predel and Oehme (1979) for Pb/Li, from the compilation of Hultgren *et al* (1973) for Pb/Na and from Saboungi *et al* (1986) for Pb/K. The variation of ΔH with T was calculated using our $C_{\text{P}}(x, T)$ data.

ΔS_{ord} was calculated from the equations (6) to (8) which do not contain σ_1 and σ_2 explicitly. These equations, however, were obtained for substitutional RDPHS systems with a superimposed CSRO related to Yukawa interactions. These assumptions include the condition $\sigma_1 = \sigma_2$. However, the formalism was shown (HPH) to yield quite satisfactory results even if these conditions are not exactly fulfilled, and we study in the present paper its formal application for the above-mentioned cases (i) and (ii) by inserting the corresponding $\eta(T, x)$ -values into equations (7) and (8). ΔS_{ord} which we calculated for $z = 3.14$ turned out to be almost unaffected from the choice of $\eta(x)$

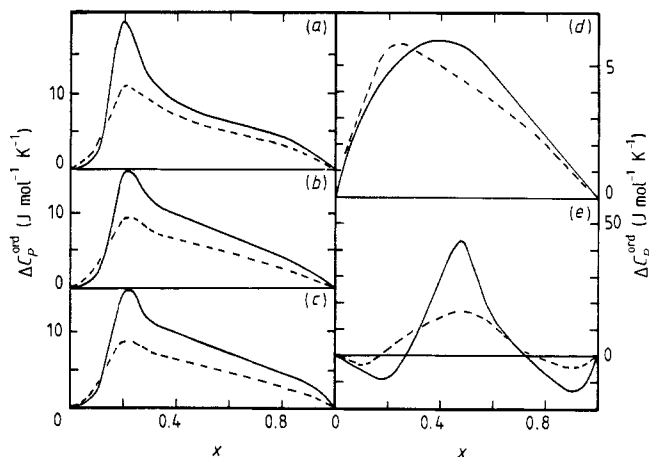


Figure 4. Variation of ΔC_p^{ord} with composition calculated from $\Delta H_{\text{ord}}(x, T)$ (full curves) and from $\Delta S_{\text{ord}}(x, T)$ (broken curves). (a) Pb/Li at 1025 K, (b) Pb/Li at 1100 K, (c) Pb/Li at 1200 K, (d) Pb/Na at 725 K, (e) Pb/K at 875 K.

according to (i) or (ii), and also the corresponding values of ΔC_p^{ord} calculated from equation (4) differed only by some percent at maximum. The $\Delta C_p^{\text{ord}}(x)$ curves obtained from the entropy data (i) are given in figures 4 to 7 as broken curves. In figures 5 to 7 the total ΔC_p values calculated according to (i) and the ΔC_p curves obtained from the experiments are both plotted.

4. Discussion

For a given value of z , ΔS_{ord} is related to ΔH_{ord} by the only slightly bent curves in figure 2. Nevertheless a comparison of the original heat capacity calculated from ΔH_{ord} (ΔC_p^{Hord}) with the values obtained from ΔS_{ord} (ΔC_p^{Sord}) is not trivial. The curves in figure 4 demonstrate that ΔC_p^{Sord} may be larger or smaller than ΔC_p^{Hord} or may even have a different sign. This is due to the fact that η , $d\eta/dT$, T and ΔT also enter into equations (4) and (6) to (8) for calculating ΔC_p^{Sord} . Qualitatively, the agreement between ΔC_p^{Hord} and ΔC_p^{Sord} is quite satisfactory including the temperature variation of these quantities which is given in figure 4 for the case of liquid Pb/Li. Quantitatively, the agreement is best for Pb/Na. We do not feel able to decide whether this is related to the almost perfect matching of the hard-sphere diameters in this case (table 1) or to the relatively small ΔC_p of Pb/Na. Finally we have the impression that there should be a more direct way to check the reliability of the scheme for calculating ΔS_{ord} from ΔH_{ord} : the condition $\Delta C_p^{\text{Sord}} = \Delta C_p^{\text{Hord}}$ introduced into equation (9) yields $\Delta H_{\text{ord}}^{\infty} = A/T$ and ΔC_p^{Sord} becomes $-\Delta H_{\text{ord}}^{\infty}/T$. Only if this equation is fulfilled will correct values for $\Delta S_{\text{ord}}^{\infty}(T)$ be obtained. It should be possible to find analogous relations between ΔC_p^{ord} and ΔH_{ord} for finite z . Eventually one should use more accurate values of z and take their temperature variation into account. The latter was observed by Ruppertsberg and Schirmacher (1984).

Figures 5 to 7 give the experimental $\Delta C_p(x)$ curves together with the calculated total values and their different components. ΔC_p^{id} calculated for the gas term was always found to be very small and is not shown in the figures. The electronic term is also small but, especially in the case of Pb/Na, far from negligible. The packing term obtained for

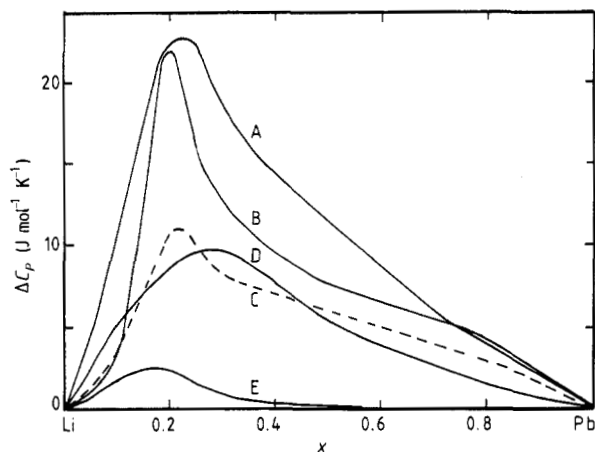


Figure 5. Heat capacity data for liquid Pb/Li at 1025 K. ΔC_p^{ord} was calculated from ΔS_{ord} . $\Delta C_p^{\text{calc}} = \Delta C_p^{\text{el}} + \Delta C_p^{\text{pack}} + \Delta C_p^{\text{ord}} + \Delta C_p^{\text{id}}$. The last term is small and is not given in the figure. Curve A, ΔC_p^{calc} ; curve B, ΔC_p^{exp} ; curve C, ΔC_p^{ord} ; curve D, ΔC_p^{pack} ; curve E, ΔC_p^{el} .

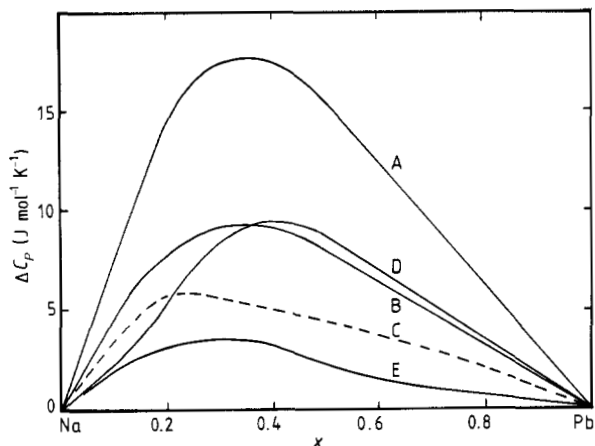


Figure 6. Heat capacity data for liquid Pb/Na at 725 K. ΔC_p^{ord} was calculated from ΔS_{ord} . $\Delta C_p^{\text{calc}} = \Delta C_p^{\text{el}} + \Delta C_p^{\text{pack}} + \Delta C_p^{\text{ord}} + \Delta C_p^{\text{id}}$. The last term is small and is not given in the figure. Curves labelled as in figure 5.

case (i) with the assumption of invariant σ -values is quite pronounced. It is as strong or even stronger (Pb/Na) than the contribution of chemical ordering. In the case of Pb/Na it shifts the peak of the calculated total ΔC curve considerably.

Pb/Na should be the best candidate for applying the HPH formalism. It gave indeed the best agreement between the ΔC_p^{ord} values calculated from ΔH_{ord} and ΔS_{ord} . The total calculated ΔC_p , however, is much too large. The contrary is true of the Pb/Li curves: ΔC_p^{ord} is too small but the maximum value of the total calculated ΔC_p agrees almost exactly with the experimental value. The formal reason for these discrepancies is quite evident: according to equation (3) the experimentally obtained heat capacity is identical to ΔC_p^{Hord} plus the corresponding electronic term. A hard-sphere contribution is not provided. If, on the other hand, ΔC_p^{ord} is identical to ΔC_p^{Hord} , as it should be, then equation (1) yields an erroneous result for ΔC_p whenever ΔC_p^{HS} is other than zero, because this HS contribution has to be added to obtain the total ΔC_p . We (Saar and Ruppertsberg 1987b) had a similar problem when we calculated ΔS_{HS} of the weakly interacting liquid Ba/Li alloys starting from temperature-dependent HS parameter

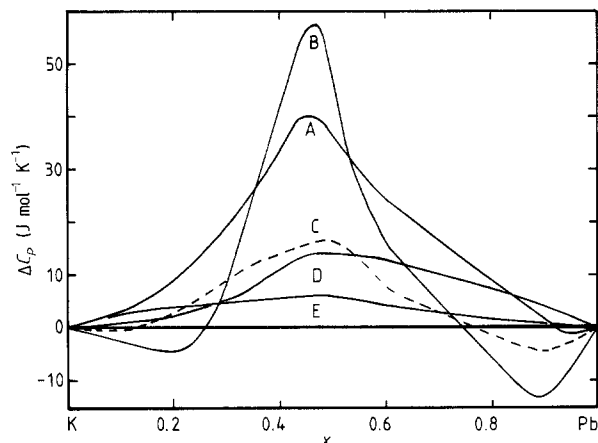


Figure 7. Heat capacity for liquid Pb/K at 875 K. ΔC_p^{ord} was calculated from ΔS_{ord} . $\Delta C_p^{\text{calc}} = \Delta C_p^{\text{el}} + \Delta C_p^{\text{pack}} + \Delta C_p^{\text{ord}} + \Delta C_p^{\text{id}}$. The last term is small and not given in the figure. Curves labelled as in figure 5.

obtained from diffraction data. We finally learned that an athermal behaviour of S_{HS} results if the HS parameters of the pure components are deduced from the entropy (as we did in this paper). The same is true for ΔS_{HS} if in addition $\eta(x)$ is assumed to be linear in x . For liquid Ba/Li this is a plausible assumption. One possible solution for the present case (Pb/Li, Na, K) would thus be to replace the assumption of invariant σ (called '(i)' before) by '(ii)', i.e. linear variation of η , which yields an HS behaviour that is indeed close to athermal. The diameter of the alkali-metal ions is found in this case to be reduced by about 10% if mixed with lead (see figure 3). The variation with composition corresponds to the scheme of 'chemical compression' only in the cases of Pb/Li, Na and looks more complex for Pb/K. The calculated total ΔC_p^{calc} curves given in the figures 5 to 7 will be changed considerably.

5. Conclusions

The HPH formalism is the only existing one which is proposed for relating electronic properties, particle interactions, structure and thermodynamic properties for a large variety of liquid alloys. Given the complexity of the problem the formalism is necessarily based on the very simplifying assumptions from which, for example the condition $\sigma_1 = \sigma_2$ is strictly fulfilled only in very exceptional cases. On the other hand, especially in the field of liquids, there are several examples of theories which have found a much wider field of practical and very useful applications than originally thought. Therefore it seems important to us to clarify the importance of the different ingredients of the HPH model, and to check their practical application.

We are convinced that the introduction of ΔH_{ord} was a very important step for the understanding of liquid alloys in general, independent of the rest of the HPH formalism, and applicable also for alloys which are not of the substitutional type. The calculation of ΔH_{ord} in the framework of HPH should be improved by more realistic equations for the electronic part of the enthalpy of mixing. An effect of central importance for strongly interacting alloys is the volume contraction. More precise theoretical predictions would be helpful. An essential step for obtaining thermodynamic properties is the calculation of ΔS_{ord} from ΔH_{ord} . The corresponding equations look quite complex, but in practice

they yield quite simple correlations as we have shown in this paper. One has to find out to what extent this fits into the world of thermodynamics.

A classical and well established ingredient for describing simple liquids is the hard-sphere model. However, we have the impression that something may go wrong with this part of the HPH formalism, at least if one tries to calculate heat capacities. There seem to be restrictions on the choice of the composition dependence of HS parameters and their variation with temperature which we have not understood.

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