

DETERMINATION OF THE HEAT CAPACITY OF LIQUID ALLOYS ACCORDING TO THE  
 $(\partial p/\partial T)_S$  PROCEDURE: Pb/Na

H. RUPPERSBERG and J. JOST

FB Ingenieurwissenschaften, Universität des Saarlandes, D-6600 Saarbrücken,  
W-Germany

SUMMARY

After having studied the molar heat capacities  $C_p$  and the density  $\rho$  of liquid Pb/Li and Pb/K alloys and their variations with composition  $x$  and temperature  $T$  we now present the results for Pb/Na which is another system with a strong tendency towards compound formation.  $C_p$  is calculated from  $\rho(x, T)$  and from the adiabatic variation of  $T$  with the pressure  $p$ . We outline the corresponding experimental procedures.

INTRODUCTION

From neutron diffraction data of liquid  $\text{Li}_4\text{Pb}$  we (Ref. 1) calculated the curves  $\rho_{\text{CC}}(r)$  and  $\omega(r)$ . The former describes the variation of chemical short-range order (CSRO) with the interatomic distance  $r$  and the latter corresponds to the interaction potential.  $\omega(r)$  was obtained by using a formalism of unknown reliability at that time. A combination of both quantities allowed us to calculate the ordering enthalpy,  $\Delta H_{\text{ord}}$ , which was introduced by Hafner, Pasturel and Hicter ("HPH", Ref. 2) and corresponds to the enthalpy difference between the chemically ordered and the disordered state, all other structural and electronic parameters being kept constant. To give a simple example for the signification of  $\Delta H_{\text{ord}}$  we consider a substitutional alloy in which the atoms have  $Z$  nearest neighbours. Its enthalpy of mixing  $\Delta H$  is given by  $\Delta H = -x_1 x_2 Z \omega$  if, according to the model of conformal solutions, a composition independent interchange energy  $\omega$  between nearest neighbours and random distribution of the atoms are postulated. Evidently, the latter is not realistic and if one allows for CSRO by introducing the Warren Cowley CSRO-parameter  $\alpha = 1 - Z_{12}/(x_2 Z)$  an additional  $\Delta H_{\text{ord}}$ -term appears:  $\Delta H_{\text{ord}} = x_1 x_2 Z \omega \alpha$ . The total enthalpy of mixing thus becomes  $\Delta H = -x_1 x_2 Z \omega (1-\alpha)$  (see Ref. 3). Analogous expressions, based on the Flory-Huggins equation, are obtained for mixtures of atoms with unequal size (Ref. 4).

At 995 K which is just above the liquidus temperature  $T_m$  of  $\text{Li}_4\text{Pb}$  we

(Ref. 1) obtained  $\Delta H_{\text{ord}} = -16.5$  KJ/mol which corresponds to more than one half of the maximum enthalpy of mixing (table 1). From the temperature variation of the neutron diffraction data we calculated  $\Delta C_P^{\text{ord}} = 30$  J/mol/K, which is of the same magnitude as the ideal heat capacity  $C_P^{\text{id}} = 32$  J/mol/K obtained from Neumann Kopp's law. To check the reliability of this calculation we determined the molar volume  $V(x, T)$  as well as the adiabatic variation  $\Delta T$  of the temperature which occurs if the pressure is changed by  $\Delta p$ : It will be shown below that these quantities allow the calculation of  $C_P$ . We first studied liquid Pb/Li alloys (Ref. 5) and then Pb/K (Ref. 6).  $\Delta V/V^{\text{id}}(x)$  and  $C_P(x)$  are given in Figs. 3 and 5, respectively, for  $T$  close to the highest  $T_m$  in the systems.  $C_P$  is also plotted at 150 K above this temperature. The value of  $C_P$  obtained from the neutron diffraction data of liquid  $\text{Li}_4\text{Pb}$  is given as a triangle in Fig. 5 and is seen to be really of the correct order of magnitude. The curves in Figs. 3 and 5 are strongly anomalous with respect to composition and  $C_P$  is seen to vary drastically with temperature. The compositions at which the strongest anomalies occur are different in both systems. The same is true of other properties some examples of which are given in Table 1. It was therefore interesting to

Table 1

Extreme values of the enthalpy of mixing,  $\Delta H$ , the excess stability function  $\Delta E$  (Ref. 7) and the resistivity (Ref. 8). The corresponding composition (at% Pb) and the temperature are given in parenthesis.

Alloy	$-\Delta H$ KJ/mol	$\Delta E$ KJ/mol	R $\mu\Omega\text{cm}$
Pb/Li	28.2(23;1000 K) (Ref. )	965(18;1000 K)	450(22;1000 K)
Pb/Na	17.3(30;698 K) (Ref. 10)	245(20;723 K) 190(50;723 K)	450(22;698 K)
Pb/K	19.7(52;848 K) (Ref. 7)	250(52;879 K)	920(49;853 K)

study in the same way liquid Pb/Na alloys. Some volume data published by Hesson et al. (Ref. 11) and by McAlister (Ref. 12) existed already and the corresponding  $\Delta V/V_1$  values are given in Fig. 3 as triangles. Saboungi et al. (Ref. 13) determined  $C_P(T)$  of liquid  $\text{Pb}_{\text{B}}\text{Na}_{\text{B}}$ . Their data are given in Fig. 4 as a dashed line. Matsunaga et al. (Ref. 14) calculated  $\Delta C_P(x)$  at 700 K from EMF data and at 650 K from the extrapolation of these values. Their

results are given in Fig. 6 as dotted (650 K) and dashed (700 K) curves. The authors give an interpretation in terms of compound formation. A discussion in terms of the HPH formalism of the whole set of  $C_p$  data including the results for Pb/Na of the present paper will be given in another publication by Ruppertsberg and Saar.

#### EXPERIMENTAL PROCEDURES AND RESULTS

Lewis and Randall (Ref. 15) proposed the following equation for calculating the heat capacity:

$$C_p = - M \cdot T (\partial \rho / \partial T)_p \cdot (\partial p / \partial T)_s / \rho^2$$

$M$  is the molecular weight to which  $C_p$  is referred. The signification of the other terms was explained above. To our knowledge this relation was only used twice for investigating liquid metals, namely by Dixon and Rodebush (Ref. 16) in the late twenties and more recently by Boehler et al. (Ref. 17).

For the determination of  $(\partial p / \partial T)_s$  we measured the variation  $\Delta T$  on changing the pressure by  $\Delta p$ . About 40 ml of the melt were contained in the vessel outlined in figure 1, made from low-carbon steel and equipped in its centre with a sealed-in thermocouple. The vessel was placed in the middle of a furnace and connected with pressurizing and depressurizing tubes and valves. Condensation of metal vapours was reduced by operating an additional heating

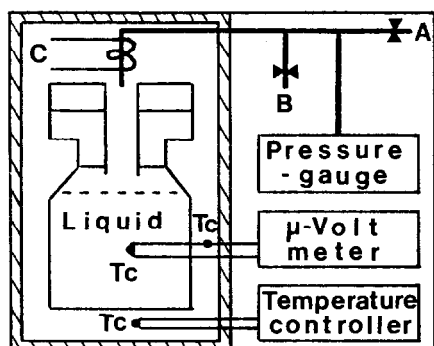


Fig. 1: Experimental set up:  
A: Argon inlet;  
B: Argon outlet;  
C: Additional heating coil;  
Tc: Thermocouples;  
hatched area: furnace.

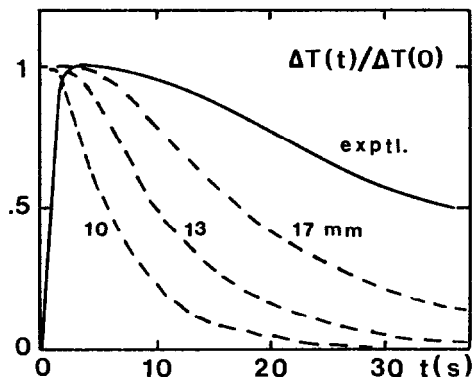


Fig. 2: Relative temperature variation with time after pressurizing. Dashed curves are calculated for the given container radii. The full-drawn curve was obtained from experiment.

coil just above the vessel. The whole system which is outlined in Fig 1 was operated in a dry-box in an atmosphere of circulated and purified argon. The maximum temperature we obtained was 1300 K at a maximum pressure of 20 bar. The latter was measured with a standardized quartz-spiral manometer (Texas Instruments). The corresponding  $\Delta T$  was of the order of several 0.01 K yielding a tension of the internal thermocouple of several  $\mu$  Volts. These were recorded with a  $\mu$  voltmeter (Keithley). The equation of heat transport yields the  $\Delta T(t)/\Delta T(0)$  curves which are shown in Fig. 2 for metallic heat conductivity and different values of vessel radii. The container was assumed to remain at the original temperature. An experimental curve given in the same figure is smeared out at small times essentially due to the time constant of the  $\mu$ V-meter. Because the theoretical curves start with a horizontal slope we took the maximum value of  $\Delta T(t)$  which was observed after several seconds for calculating  $(\Delta p/\Delta T)$ . It was possible to stabilize the thermostat so that its temperature drift during the time of registration  $\Delta T(t)$  was negligible. The reduced slope of the experimental curve for longer times is related to the loose thermal coupling of the outside thermocouple. Reaching a new temperature and its stabilizing is a very time-consuming procedure and will be improved in the future by computer control. However, it was already possible to registrate  $(\Delta p/\Delta T)$  values for much smaller  $T$ -steps than is possible with most other procedures for  $C_p$  determination of liquid metals. We will try to achieve the same temperature resolution as Schürmann and Parks (Ref. 18) who studied  $C_p$  close to the critical temperature of the miscibility gap of Hg/Ga in steps of  $\Delta T \approx 0.01$  K. But the pulse technique of these authors did not allow the heat contents of the liquid specimen and the container to be separated.

Contrary to the observations with Pb/Li and Pb/K, the values of  $T \cdot (\Delta p/\Delta T)$  for Pb/Na were almost independent of temperature. If plotted against composition, the deviation from the ideal is much smaller than for the other two alloy systems and no clearly visible inflections points occur as was the case for Pb/Li,K. The relative reproducibility after repeating a measurement for a given temperature was  $\pm 1.5$  %. Repeated measurements and a linear least-square fit through the points resulting for different temperatures yield relative errors related to random deviations of  $\pm 0.8$  % (standard deviation). The density was measured in the same dry-box using the maximum bubble pressure apparatus as described by Ruppertsberg and Speicher (Ref. 19). Linear regressions of the  $\rho(T)$  curves yielded  $(\partial\rho/\partial T)_p$ . Table 2 gives the compositions, the temperature ranges investigated,  $T_m$ ,  $\rho$  at  $T_m$  and  $(\partial\rho/\partial T)_p$ . The errors given were obtained in the same way as described above.

$\Delta V/V^{id}$  is shown in Fig. 3.

Table 2

Density  $\rho$  at the liquidus temperature  $T_m$  and its variation with temperature  $(\partial\rho/\partial T)_p$  of liquid Pb/Na alloys. Accuracy of  $\rho$  and  $(\partial\rho/\partial T)_p$ :  $\pm 0.5$  and  $\pm 5\%$ , respectively.

Composition at% Pb	T-range investigated K	$T_m$ K	$\rho$ g/cm <sup>3</sup>	$-(\partial\rho/\partial T)$ 10 <sup>4</sup> g/cm <sup>3</sup> /K
0	380 - 800	369.5	0.927	2.25
5	570 - 1035	550	1.305	2.85
10	620 - 1115	600	1.735	4.95
20	660 - 1130	659	2.705	6.3
31	685 - 1090	677	3.93	8.8
35	670 - 1065	665	4.34	10.0
41	630 - 1115	606	5.08	11.5
50	660 - 1120	645	5.95	11.5
62	605 - 1115	573	7.22	11.7
72	630 - 1120	593	8.13	12.7
80	620 - 1115	580	8.90	12.7
100	600 - 1300	600	10.66	13.5

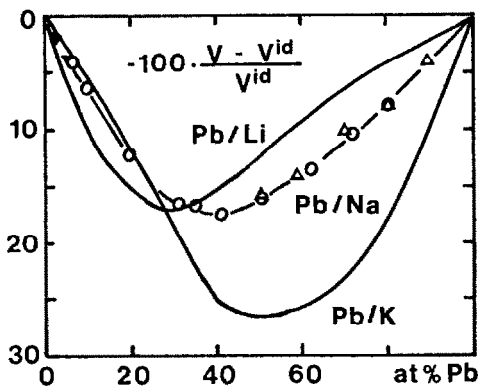


Fig. 3: Relative volume contraction of Pb/Li, Na, K at 1000, 700, and 900 K, respectively.

○: this work,  
 △: Hesson et al. (Ref. 11),  
 ▽: McAlister (Ref. 12).

The  $C_p(T)$  curves obtained for the different compositions are plotted in Fig. 4. Their ordinate scales are shifted by  $Z$  which is given together with the compositions in the same figure. To demonstrate the influence of the random  $(\Delta\rho/\Delta T)_s$ -errors we give the points calculated from the individual results at the corresponding temperature together with a full drawn line resulting from a linear fit. For calculating  $C_p$  we assumed linear variation of  $\rho$  with  $T$  which is not necessarily the case. Uncertainties of  $(\partial\rho/\partial T)_p$  are the most important source of error.

Concerning the absolute error, we were able to reproduce  $C_p$  given in the literature for mercury within 0.5 %. The results obtained at higher temperatures are certainly worse but difficult to evaluate because there are no high precision  $C_p$  data available.

$\Delta C_p$  versus  $x$  is given in Fig. 6 for  $T = 700$  K. It is almost independent of temperature.

## DISCUSSION

Some years ago Bergman and Komarek (Ref. 20) pointed out that despite its fundamental significance very little is known about the heat capacity of liquid alloys and its variation with composition and temperature. In the meantime it became clear that even a strongly anomalous behaviour of  $C_p(x, T)$  for which these authors presented a few examples is far from exceptional. Thus, it seems to be important to obtain more information about this property. Our results obtained for Pb/Li,K (Ref. 5 and 6), for Li/Ca (unpublished) and the present work demonstrate that the calculation of heat capacities from experimental  $\rho(T)$  and  $(\partial\rho/\partial T)$  data is a very valuable method for evaluating complete  $C_p(x, T)$  diagrams. It seems especially useful for studying strong temperature variations of  $C_p$ .

Actually the accuracy of the  $C_p$  data obtained by the method of Lewis and Randall is restricted by the experimental errors of  $(\partial\rho/\partial T)$ . It would be hard to detect  $C_p(T)$  anomalies which are related to a non-linear behaviour of  $\rho(T)$ . The strong variations of  $C_p$  with  $T$  which we observed were indeed contained in the  $(\Delta\rho/\Delta T)$ -term. This is different for the deviations of  $C_p(x)$  from the Neumann Kopp law. These are related to irregularities in all three quantities  $\rho$ ,  $(\partial\rho/\partial T)$  and  $(\Delta\rho/\Delta T)$ .

It seems disadvantageous that  $\rho(T)$  has to be determined in addition to  $(\Delta\rho/\Delta T)$  for calculating  $C_p$ . However, what we said above about the lack of  $C_p$  values is also true of  $\rho(x, T)$ . This is especially inconvenient because the density often has to be inserted into the equations for calculating special properties from the corresponding experimental data as for example for calculating the compressibility from the velocity of sound. Precise  $\rho(x, T)$  values are also necessary for theoretical investigations of liquid alloys as was pointed out again recently by Lai (Ref. 21) who studied the relation between the excess entropy and the electrical resistivity of liquid Pb/Na starting from first-principles nonlocal pseudopotentials.

The results which we observed for Pb/Na are not especially spectacular. Compared with Pb/Li,K  $C_p(x)$  of Pb/Na, Fig. 5, deviates only moderately

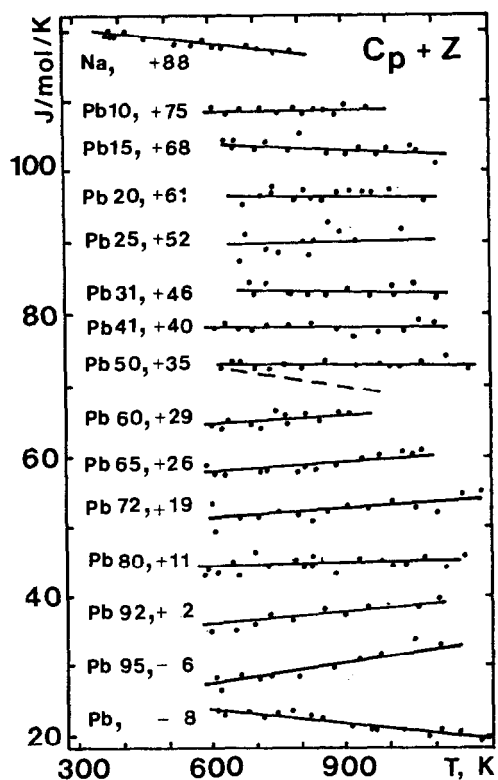


Fig. 4:  $C_p$  ( $T$ ) of Pb/Na. The ordinate scales are shifted by  $Z$  which is the number given following the composition. The dashed line was obtained by Saboungi et al. (Ref. 13).

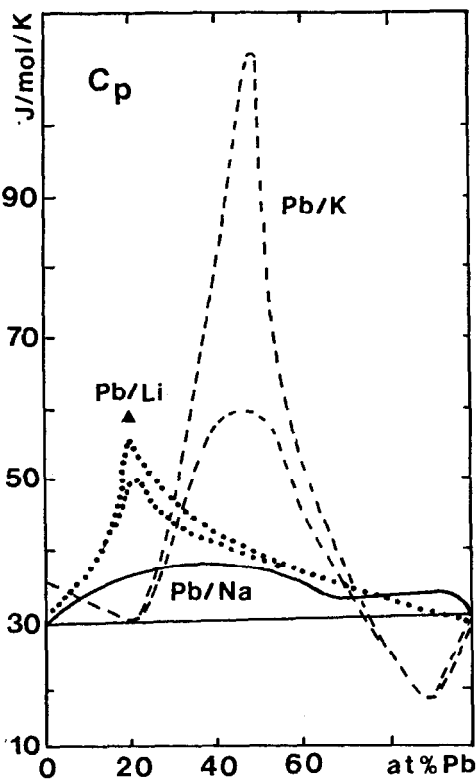


Fig. 5:  $C_p$  ( $x$ ). Full drawn curve: Pb/Na at 700 K. Dotted curves: Pb/Li (Ref. 5) at 1000 K and 1150 K, respectively. Triangle: value calculated from the neutron diffraction data (Ref. 1). Dashed curves: Pb/K (Ref. 6) at 845 K and 1000 K, respectively.

from the ideal behaviour. Remarkable is the complete absence of special effects in  $C_p$  ( $T$ ), Fig. 4, close to the melting points which we observed even in the almost ideal Ca/Li system (not published). The general shape of the  $\Delta C_p$  ( $x$ ) curve, Fig. 6, agrees quite well with the values published by Matsunaga et al. (Ref. 14). However, the peak which they observed at about 25 at% Pb is much larger and sharper and in this composition range they observed a much stronger variation of  $\Delta C_p$  with temperature. We have no indication of a second peak occurring at lower temperatures. At 700 K our  $C_p$  (50 at%) agrees almost perfectly with the value published by Saboungi et

al. (Ref. 13). Inspection of Fig. 4 shows that the slope ( $dC_p/dT$ ) observed by these authors is somewhat larger than our value. However, the corresponding deviation might easily be within the error limits of both experiments.

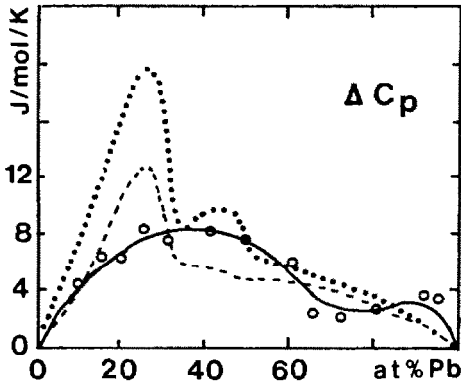


Fig. 6:  $\Delta C_p(x)$  of Pb/Na. Full drawn curve and circles: this work, 700 K. Dashed and dotted curves: Matsumaga et al. (Ref. 14), 700 and 650 K, respectively.

The behaviour of Pb/Na is spectacular only in so far as  $C_p(x, T)$  looks much more ideal than in the case of liquid binary mixtures of lead with other alkali metals. The corresponding plots for Pb/Li, K are given in Fig. 5. A strongly anomalous temperature variation for equiatomic Pb/Rb, Cs, similar to Pb/K, was recently observed by Saboungi et al. (Ref. 13).

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