Thermochimica Acta, 44 (1981) 385—390
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

THERMODYNAMIC ANALYSIS OF BINARY METAL SYSTEMS BY DIFFERENTIAL THERMAL ANALYSIS

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(Received 2 October 1980)

Different methods are used to determine the thermodynamic activities of components in binary and multi-component metal systems [1—3]. These methods have certain advantages and disadvantages, depending on the system being investigated as well as on the purpose of the investigations being carried out.

Dobovišek [4] has pointed out the possibility of using differential thermal analysis as a method for determining the thermodynamic quantities in binary metal systems. Fruitful research activity has been developed at the University of Ljubljana which has given remarkable results [5—8].

In this paper, the author has tried to make a contribution towards improving the use of DTA as a method for the thermodynamic analysis of binary metal systems, using the results achieved in this area by Dobovišek and his associates. The Pb—Sn system, which has already been investigated by Dobovišek [4] and other researchers [9], is chosen as an example in order to be able to compare the results obtained.

EXPERIMENTAL

DTA was used for experimental investigation and experiments were carried out on apparatus previously described [10]. The sample heating rate in all cases was 8.5°C min^{-1}, and all experiments were carried out in an atmosphere of air.

Samples were prepared such that the required tin mass was melted beforehand at the bottom of a beaker within which a protective tube was fixed for the thermocouple. To the same tube a lead ring was fixed which had a corresponding mass in order to provide, after melting, an alloy of the required composition. In all cases two meltings were carried out in accordance with the procedure for this type of determination [11]. Calcinised alumina was used as reference material.

RESULTS AND DISCUSSION

It is known that the following relation exists between the area of the DTA peak and the heat of reaction [12]

$$m\,\Delta H_T^0 = gK_s \int \Delta T\,\mathrm{d}t \qquad (1)$$

where m, ΔH_T^0, gK_s and $\int \Delta T \mathrm{d}t$ are sample mass, reaction heat, calibration constant and area of the peak, respectively.

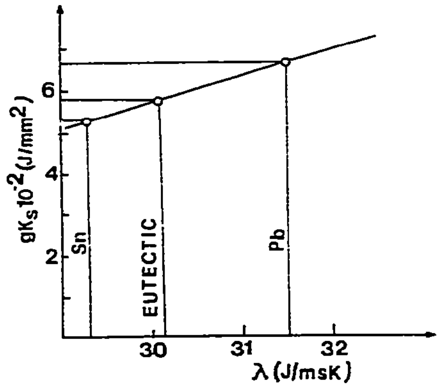
By recording the relationship of the peak area and sample mass for the pure metals, Pb and Sn, as well as for their eutectic, it is possible to determine the calibration constant of the apparatus, gK_s, which represents the equivalence factor between the peak area and spent or liberated heat which is registered on the DTA curve by the corresponding exothermic or endothermic peak. In order to eliminate the influence of the geometric constant g in the calibration constant gK_s [13], the sample volume was 0.2 cm^3 in subsequent investigations.

Živković [13] has shown that gK_s in a linear function of the conductivity coefficient of sample heat, and pointed out the need for corrections of values for gK_s for each concrete composition of the system investigated. Figure 1 shows the relationship of gK_s as a function of the heat conductivity coefficient, where it is obvious that the foregoing conclusion is valid.

If the calculated value of gK_s is shown as a function of the system composition (Fig. 2), it may be seen that there also exists a linear relationship. This, offers the possibility that, based upon the given composition of the system investigated, the true value for gK_s may be determined directly and more simply, which has not been mentioned in the literature.

Therefore a new method of experimental investigation is proposed for the determination of the thermodynamic quantities for metal systems by DTA which is sufficiently cheap and quick compared with other methods that may be used for the same purpose.

Verification of the proposed method for evaluating DTA results was carried out on the Pb—Sn system which has already been investigated by DTA, and the results processed such that the calibration constant gK_s was calcu-



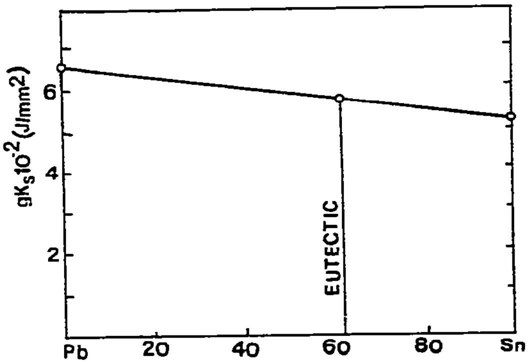


Fig. 1. Relationship of gK_s with the coefficient of thermal conductivity of the sample.

Fig. 2. Relationship of gK_s with the composition of the Pb—Sn system.

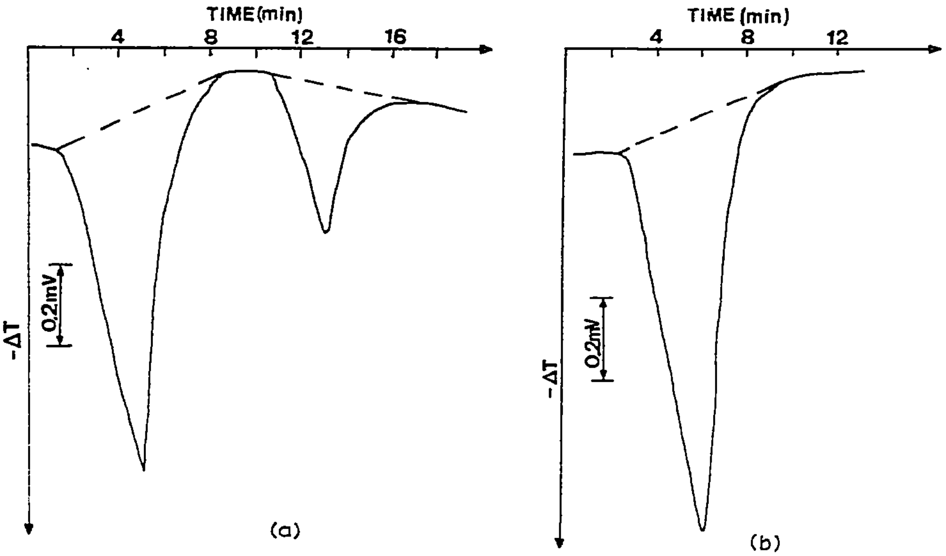


Fig. 3. DTA curves for the alloy of eutectic composition: (a) first melting; (b) second melting.

lated as a mean value for pure metals and also investigated by measuring electromotor forces in the melted system.

Determination of ΔH_{liq} *and* ΔH_{sol}

During the first melting of the sample, tin melts first, followed by lead which causes two peaks to appear on the DTA curve. The second peak on the DTA curve corresponds to the melting of lead and the heat of mixing of lead and tin in a molten state. For all samples the second melting effects obtained on the DTA curve characterize the melting of the eutectic and of the solid solution. Based on these results the heat of mixing in the solid and

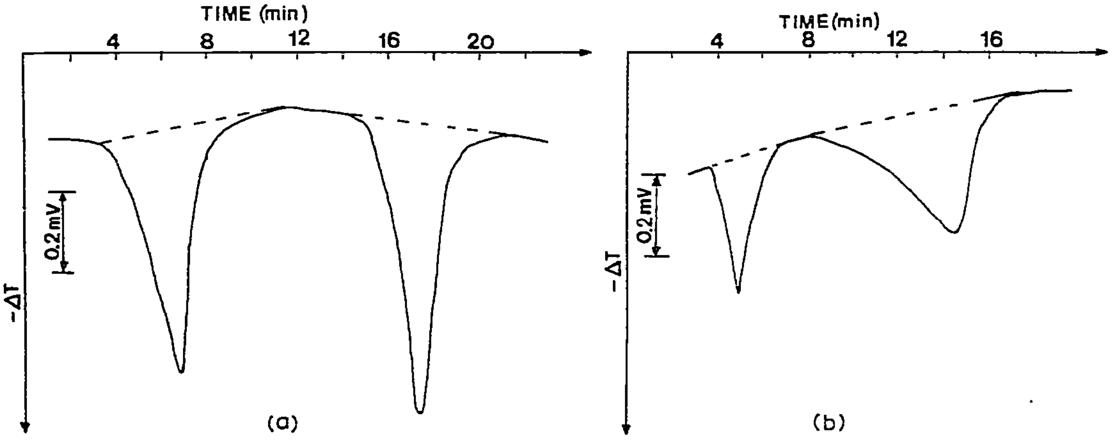


Fig. 4. DTA diagrams for the alloy with mole contribution of lead of 0.7095: (a) first melting; (b) second melting.

liquid states was determined. Figures 3 and 4 show the corresponding DTA diagrams for the alloy of eutectic composition and the alloy with a mole contribution of lead of 0.7095, respectively.

The heat which is required for the melting of pure metals (the first melting) amounts to

$$\Delta H_{\mathrm{I}} = X_{\mathrm{A}} L_{\mathrm{A}} + (1 - X_{\mathrm{A}}) L_{\mathrm{B}} + \Delta H_{\mathrm{liq}} \tag{2}$$

and the heat required for melting the alloy (the second melting)

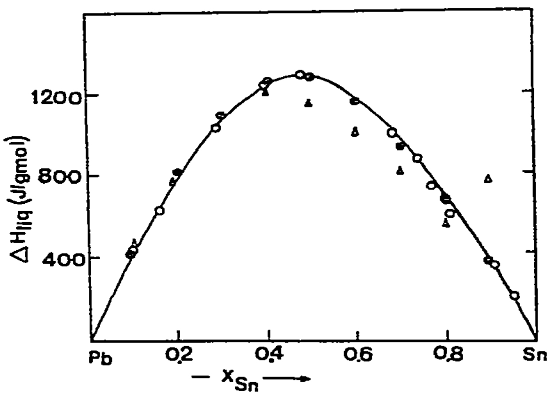
$$\Delta H_{\mathrm{II}} = X_{\mathrm{A}} L_{\mathrm{A}} + (1 - X_{\mathrm{A}}) L_{\mathrm{B}} + \Delta H_{\mathrm{liq}} - \Delta H_{\mathrm{sol}} \tag{3}$$

The difference between eqns. (2) and (3) gives the heat of mixing in the solid state

$$\Delta H_{\mathrm{sol}} = \Delta H_{\mathrm{I}} - \Delta H_{\mathrm{II}} \tag{4}$$

where X_{A}, L_{A}, ΔH_{liq} and ΔH_{sol} are the mole contribution of component A, melting heat of component A, mixing heat in liquid state and mixing heat in solid state, respectively.

In this way, using the determined relationship of gK_{s} as a function of system composition (Fig. 2), values for ΔH_{liq} and ΔH_{sol} were calculated, and the values obtained as a function of system composition are shown in Figs. 5 and 6, respectively. These results were compared with those of Elliot and Chipman [9] and Dobovišek and Smajić [5]. From this comparison it may be seen that agreement of the results obtained for ΔH_{liq} with those of Elliot and Chipman is perfect, and that with the results of Dobovišek and Smajić it is very close, especially on the tin side. This is so because the value determined for gK_{s} in ref. 5 was calculated as a mean value for pure metals, which is closer to the gK_{s} constant for lead. By comparing results for ΔH_{sol} with literature values [5] it may be seen that the dispersion of the results of the preceding investigation is larger for the same reasons as for ΔH_{liq}.



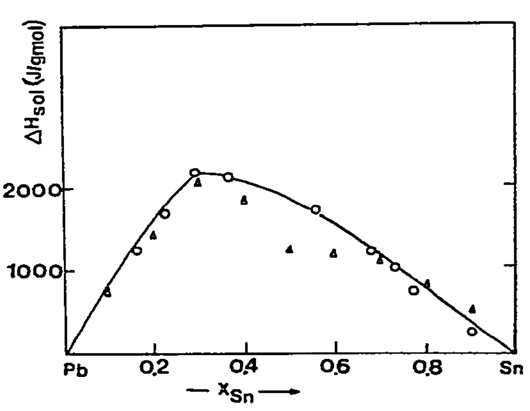


Fig. 5. Relationship of ΔH_{liq} with the composition of the Pb—Sn system. ○, This study; ●, Elliot and Chipman [9]; △, Dobovišek and Smajić [5].

Fig. 6. Relationship ΔH_{sol} with the composition of the Pb—Sn system. ○, This study; △, Dobovišek and Smajić [5].

Determination of activities

The activity values of the components of the binary system investigated were determined by Planck potential, such that the value for the enthalpy mixing of the components was determined experimentally and the enthalpy value calculated for the case of ideal solutions

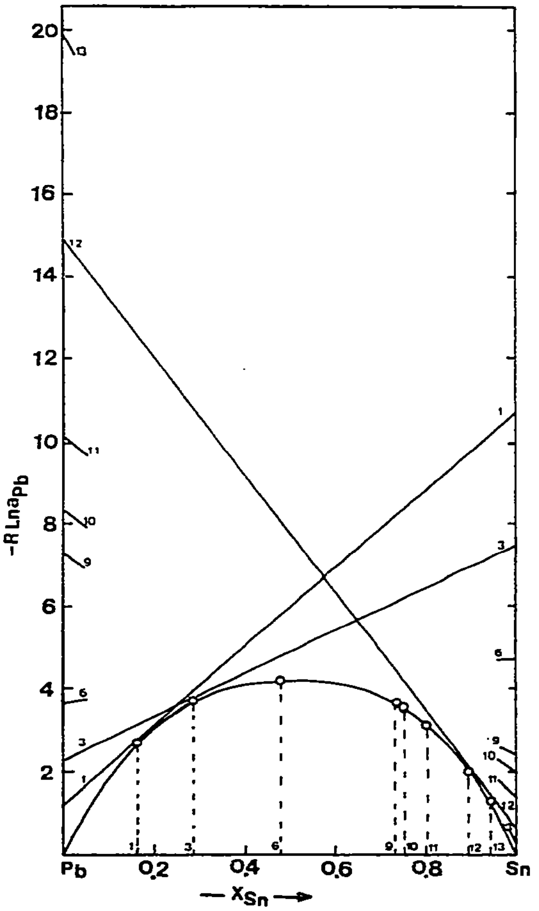
$$\Delta S^{\mathrm{id}} = -R(X_1 \ln X_1 + X_2 \ln X_2) \tag{5}$$

where X is the mole contribution of the component.

Values of Planck potential were calculated as follows

$$P_{X,T} = \Delta S_{X,T} - \frac{\Delta H_{X,T}}{T} \tag{6}$$

Figure 7 shows a graphic representation of the Planck potential in relation to concentration. Intersects $-R\ln a_{\mathrm{Pb},X,T}$ and $-R\ln a_{\mathrm{Sn},X,T}$ were determined



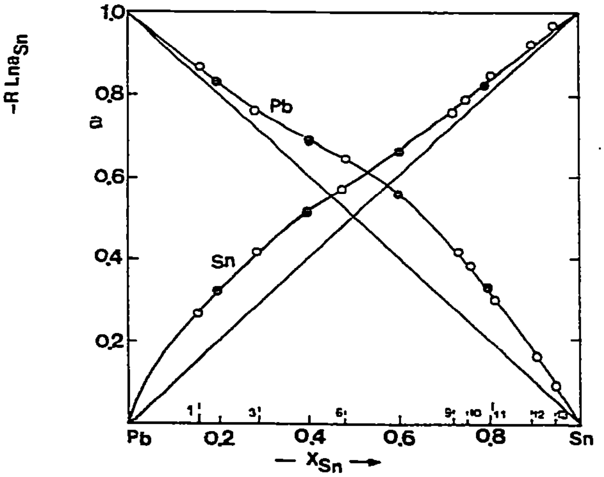


Fig. 7. Graphic representation of the Planck potential in relation to concentration at 773 K.

Fig. 8. Activities as a function of the composition of the Pb—Sn system at 773 K. ○, This study; ●, Elliot and Chipman [9].

by drawing the tangents on the Planck potential curve. Based on these values, the components' activities at 773 K were calculated. Results obtained for activities as a function of the Pb—Sn system are shown in Fig. 8, where at the same time they are compared with results of Elliot and Chipman [9].

Calculated values of the components' activities at 773 K in the Pb—Sn system, using the proposed method for evaluating DTA results, are in good agreement with results quoted in the literature [9] which were obtained by precise electrochemical measurement. This is proof that the proposed method for calculation of the gK_s constant in the investigation of binary systems is correct and that, as such, it may be recommended for further investigations in this area.

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