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APPLICATION OF THE SETARAM HIGH TEMPERATURE CALORIMETER FOR DETERMINATION OF MIXING ENTHALPIES OF LIQUID ALLOYS

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ABSTRACT

The suitability of the SETARAM high temperature calorimeter for the determination of mixing enthalpies of liquid metallic alloy systems has been investigated. Several methods of calibration were investigated as well as the dependence of the calibration factor on total mass in the crucible and volume of the crucible occupied. The results indicate that calibration with an inert substance, such as tungsten or molybdenum, during the course of the mixing experiments is the optimal procedure. Heats of mixing for liquid Au–Sn and Cu–Sn alloys were determined at 1380 K and 1440 K, respectively, and compared with literature values. The agreement of the values obtained here and those in the literature is satisfactory.

INTRODUCTION

Interest in the determination of the thermodynamics of mixing in the liquid state at high temperature has increased in the past several years. This has been due, on the one hand, to increased emphasis on the calculation and optimization of ternary and higher order systems from binary data, necessitating the generation of additional binary data, and, on the other hand, to increased interest in the structure of liquid metallic alloys and the factors influencing these structures.

As pointed out by Predel et al.[1], the measurement of mixing enthalpies for liquid alloys at high temperature is difficult and the available calorimeter types are limited. For this reason, it was decided to examine the suitability of the SETARAM high temperature calorimeter for the determination of mixing enthalpies of liquid metallic alloy systems.

EXPERIMENTAL EQUIPMENT

The calorimeter used in this work was a commercial calorimeter of the differential type manufactured by SETARAM in Lyon, France. A complete description is available from SETARAM and it has also been described and applied to the determination of partial enthalpies by Gaune-Escard and Bros[2]. Thus only a brief description will be given here. The calorimeter is a vertical type and the two segments of the differential thermopile sit vertically one above the other within the constant temperature zone of the furnace. Each thermopile is composed of 18 Pt–30% Rh/Pt–6% Rh thermoelements. The working crucible is inserted in the upper thermopile while the lower thermopile contains an empty reference crucible used to maintain a reasonable thermal balance in the system. Samples are added to the system through an Al_2O_3 tube which also acts as an outlet tube for a protective gas such as argon. Temperature is measured by a Pt–30% Rh/Pt–6% Rh thermocouple positioned next to the working crucible and is recorded on a 2-channel strip-chart recorder along with the differential output from the thermopile. The system is also equipped with an electronic integrator for the differential output which provides a digital count of the area under the ΔT–t (differential temperature–time) curve as a function of time (t).

EXPERIMENTAL PROCEDURE AND RESULTS

Calibration

In order to successfully use any calorimeter to determine mixing enthalpies, the system must be calibrated with a known heat effect. The most convenient heat effect and that most commonly used is the heat content of a pure metal between room temperature (or the initial sample temperature) and the temperature of the calorimeter. In this case, the total area under the ΔT–t curve is directly proportional to the total heat content and the proportionality factor is the calibration factor. This energy conversion factor, ε, is given by

$$\varepsilon = Q_{\text{total}} \Big/ \int_0^\infty \Delta T \mathrm{d}t \qquad (1)$$

where Q_{total} is the total heat effect and

$$\int_0^\infty \Delta T \mathrm{d}t$$

is the area under the ΔT–t curve. The factor ε contains such parameters as the system heat capacity and the heat transfer coefficients for the total calorimeter system. Since most calorimeter systems are generally massive, ε is not normally a function of either the total mass of liquid in the system or the total volume of liquid. However, in the SETARAM calorimeter, the total available crucible volume is only 0.7 cm^3 corresponding to a nominal mass for most liquid metals of about 5 g. Thus the first step in this investigation was to determine whether the energy conversion factor, ε, was constant or whether it was a function of the fraction of available volume occupied, expressed in mm of depth of liquid, or the liquid mass.

In order to carry this work out, an empty crucible was placed in the calorimeter and the system brought to a constant temperature above the melting point of the calibrating substance, which was either tin or copper for the initial experiments. At this point, 20 successive additions of samples of the calibrating substance, each weighing 0.250 g, were made into the calorimeter. The total area for each addition was determined from the integrator reading (corrected for any baseline shift) and the energy conversion factor calculated for each addition using the heat content data given by Hultgren et al.[3]. The energy conversion factors were calculated both as a function of mass and as a function of volume occupied, using the liquid density data given by Allen[4]. Typical results of some of these experiments are shown in Figs. 1 and 2. Figure 1 shows the energy conversion factor, ε, as a function of mass for five different experiments with Sn as the calibrating substance while Fig. 2 shows the same data plotted as a function of the height of liquid in the crucible. The temperature for each experiment was about 1350 K. The lines through the data points are the calculated least-square fit to the experimental data points. From these two figures, it is obvious that the energy conversion factor, ε, depends on both the mass in the crucible and the bath height. Moreover, the functional relationship is not the same from one series of additions to another. It is not surprising that this occurs since the upper thermopile only contacts the crucible in a region close to the maximum height of the liquid bath and the heat transfer process between crucible and thermopile, and therefore the energy conversion factor, depends upon the position of the crucible within the thermopile. Thus a day-to-day variation in the calibration must occur.

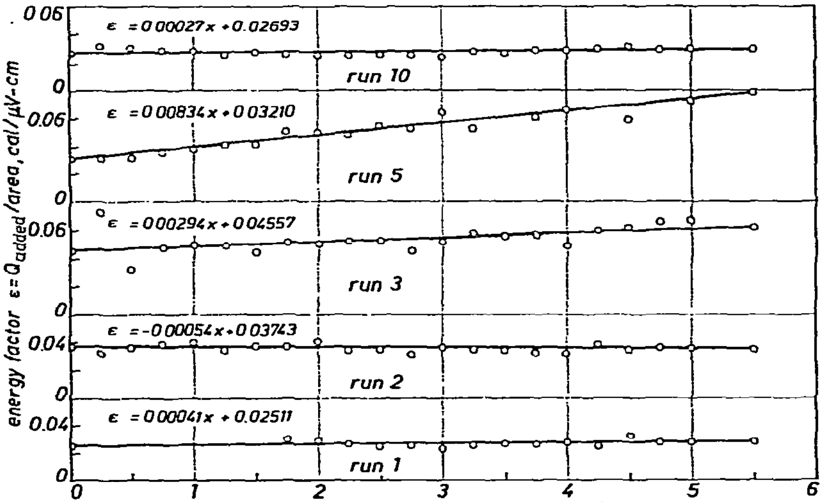

Fig. 1. Energy conversion factor as a function of mass for tin additions from room temperature to 1350 K.

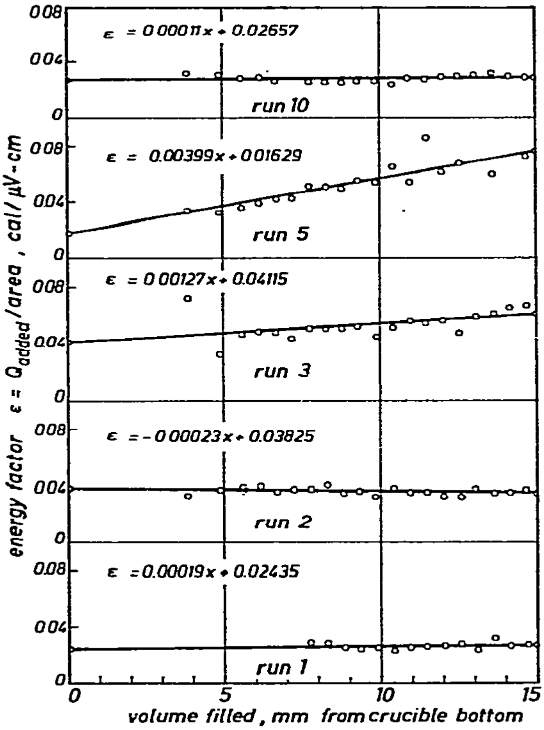

Fig. 2. Energy conversion factor as a function of liquid depth for tin additions from room temperature to 1350 K.

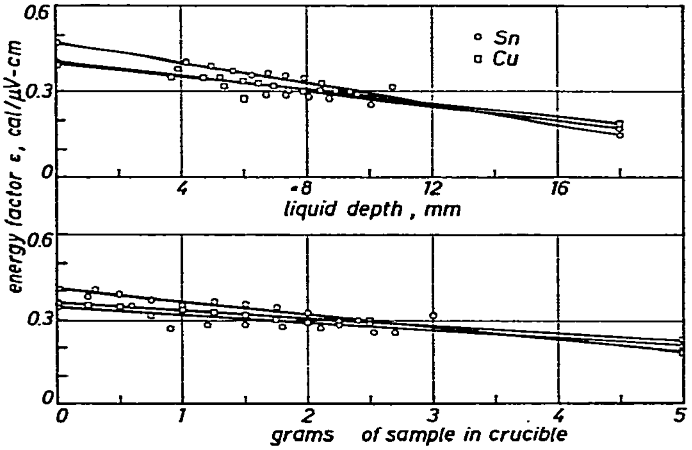

Fig. 3. Initial calibration during measurement for Cu–Sn alloys, $T = 1440$ K (same crucible for each run).

As a result of the above work, a second method of calibration was investigated. Since it appeared to be impossible to use a pre-determined calibration factor for determination of the mixing enthalpies and since the energy factor appeared to be a linear function of mass and volume, it was decided to make an initial calibration for each run. The least-squares line was then extrapolated to the mass or volume corre-

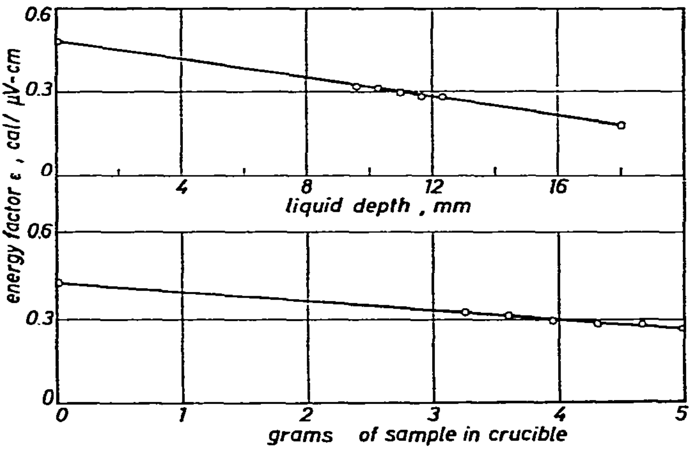

Fig. 4. Typical calibration with tungsten in between sample additions (Cu–Sn system 1440 K).

sponding to that present after an alloy addition. This extrapolated value for the energy conversion factor was then used to calculate the thermal effect associated with the addition of the second alloy component, the first component being the calibration material. Figure 3 shows some typical curves for this calibration technique measured during the determination of the mixing enthalpies for liquid Cu–Sn alloys. It is of interest to note that the curves are not the same even though all three experiments were carried out using the same crucible. This is another indication that the position of the crucible in the thermopile is of considerable importance. Even though this technique proved quite satisfactory for Au–Sn alloys, it was somewhat less than satisfactory for Cu–Sn alloys and, as a result, a third technique was investigated.

The third technique involved calibration with an inert substance such as tungsten or molybdenum and proved to be the most satisfactory. Small samples of W or Mo were added to the liquid bath after each two alloy sample additions. The least-squares fit to a straight line was calculated and the energy factors determined by extrapolation for the first two sample additions and by interpolation between two calibration points for the remaining sample additions. An example of this calibration technique is shown in Fig. 4 for the Cu–Sn system. It should be pointed out that the volume used for tungsten is the atomic volume at room temperature. As can be seen in Fig. 4, the energy factor is linear with both mass and volume and it is obvious that an interpolation between two points should provide a considerably better calibration factor than extrapolation from lower volumes or masses. It is also apparent from Figs. 1 and 2 that the first 10 points can have a slope differing slightly from that of the second 10 points and thus the second calibration technique described above may not be satisfactory in all cases. It should also be pointed out that, in some cases, reaction can occur between the bath and W or Mo. Metallographic examination showed this did not occur in this case.

Enthalpies of mixing

In order to test the above calibration methods and to determine the applicability of the SETARAM calorimeter to the measurement of mixing enthalpies at high temperature, several experiments were run on the Au–Sn and Cu–Sn systems. Since the procedure for determination of the mixing enthalpies is the same regardless of the calibration procedure, this will be discussed first.

If the addition of n_1 moles of an element A at T_1 to an alloy bath, at T_2, containing n_2 moles of element A and n_3 moles of element B is considered, then the following equation can be written.

$$n_1 \mathrm{A}(T_1) + \text{alloy } 1\,(T_2) \rightarrow \text{alloy } 2\,(T_2) \qquad (2)$$

where alloy 2 contains $(n_1 + n_2)$ moles of component A and n_3 moles of component B. The measured enthalpy change, ΔH^{meas}, accompanying the above mixing process is given by

$$\Delta H^{\mathrm{meas}} = H_{\mathrm{alloy}\ 2}(T_2) - H_{\mathrm{alloy}\ 1}(T_2) - n_1 H^0_{\mathrm{A}}(T_1) \qquad (3)$$

where $H_{\mathrm{alloy}\ 1,2}$ represents the enthalpy of the alloy of the given composition and H°_{A} is the enthalpy of pure A at T_1. Further, $H^{\circ}_{\mathrm{A}}(T_1)$ can be expressed by

$$H^0_{\mathrm{A}}(T_1) = H^0_{\mathrm{A}}(T_2) - \Delta H^{\mathrm{A}}_{T_1 \rightarrow T_2} \qquad (4)$$

where $\Delta H^{\mathrm{A}}_{T_1 \rightarrow T_2}$ is the heat content of A between T_1 and T_2.

Substitution of eqn. (4) into eqn. (3) yields the isothermal heat effect for the mixing of n_1 moles of component A and $(n_2 + n_3)$ moles of alloy 1 to form alloy 2.

$$\Delta H^{\mathrm{meas}} = H_{\mathrm{alloy}\ 2} - H_{\mathrm{alloy}\ 1} - n_1\,(H^0_{\mathrm{A}}(T_2) - \Delta H^{\mathrm{A}}_{T_1 \rightarrow T_2}) \qquad (5)$$

If alloy 1 is formed from n_2 moles of pure A and n_3 moles of pure B, then $\mathrm{H}_{\mathrm{alloy}\ 1}$ is given by

$$H_{\mathrm{alloy}\ 1} = \Delta H_1 + n_2 H^0_{\mathrm{A}} + n_3 H^0_{\mathrm{B}} \qquad (6)$$

where ΔH_1 is the isothermal enthalpy effect for the formation of alloy 1 from pure A and pure B. Substitution of this into eqn. (5) and simplifying gives

$$\Delta H_{\mathrm{alloy}\ 2} = \Delta H_{\mathrm{alloy}\ 1} + \Delta H^{\mathrm{meas}} - n_1\,\Delta H^{\mathrm{A}}_{T_1 \rightarrow T_2} \qquad (7)$$

This can be written in general for the $(i + 1)$th measurement in a series as

$$\Delta H_{i+1} = \Delta H_i + \Delta H^{\mathrm{meas}}_{i+1} - n_1\,\Delta H^{\mathrm{A}}_{T_1 \rightarrow T_2} \qquad (8)$$

Obviously, in order to apply eqn. (8), ΔH_i must be known. The best starting point is from a pure metal bath so that $\Delta H_i = 0$ and the heat effect for the first alloy addition is given by

$$\Delta H_1 = \Delta H^{\mathrm{meas}}_1 - n_1\,\Delta H^{\mathrm{A}}_{T_1 \rightarrow T_2} \qquad (9)$$

Succeeding heat effects are calculated from the previous value, the measured heat effect and the heat content. The mixing enthalpy for the alloy is then determined by dividing the calculated isothermal heat effect by the total number of moles in the alloy system.

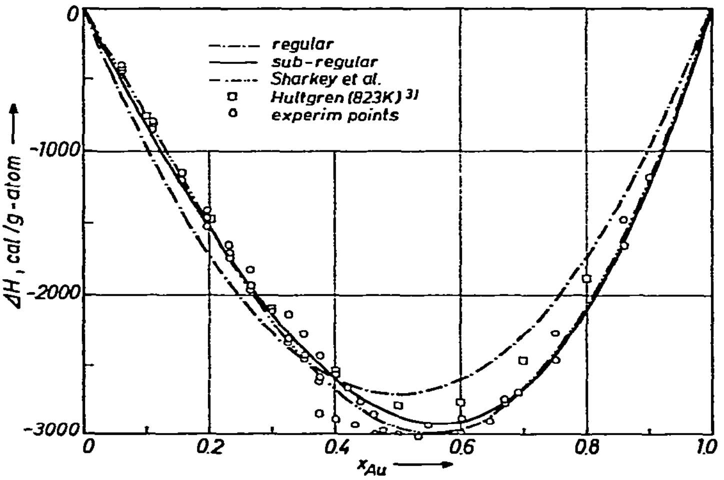

Fig. 5. Mixing enthalpy for Au–Sn at 1380 K.

The Au–Sn alloy system was investigated using the initial calibration technique. Ten samples of gold or tin each weighing 0.25 g were successively added to the crucible and then 10 samples of tin or gold, respectively, were added in succession to the liquid metal bath. The calibration effects were evaluated and the extrapolated values were used to calculate the measured heat effects for alloying from

$$\Delta H^{\rm meas} = \varepsilon \left[\int_0^\infty \Delta T \mathrm{d}T \right]_{\text{alloy addition}} \tag{10}$$

More than 50 experimental points were measured in this way and the results are shown in Fig. 5 along with the values reported by Hultgren et al.[5]. It should be pointed out that since the energy factor, ε, is calculated on both a mass basis and a volume basis, the resulting $\Delta H^{\rm mix}$ values can also be determined on a mass basis or a volume basis. The volume-based calculation obviously assumes an ideal volume since limited data are available at high temperatures for mixing volume changes. That there is very little difference between these two methods of calculation is shown in Table 1 where $\Delta H^{\rm mix}$ values calculated from both weight and volume calibrations are listed. All the experimental points in Fig. 3 are based on the weight calibration.

The data were also fit with 3 different models in an attempt to obtain a valid analytical expression relating $\Delta H^{\rm mix}$ and mole fraction. Both the sub-regular model[6] and the modified quasi-chemical model of Sharkey et al.[7] adequately represent the experimental data, whereas the regular solution model is unsatisfactory. From the sub-regular model, $\Delta H^{\rm mix}$ is given by

$$\Delta H^{\rm mix} = -\ 8253\ x_{\rm Au}x_{\rm Sn}^2 - 14595\ x_{\rm Au}^2x_{\rm Sn}\ (\text{cal/g at}) \tag{11}$$

and from the modified quasi-chemical model by

$$\Delta H^{\rm mix} = -\ 7301\ x_{\rm Au}x_{\rm Sn}^2 - 13120\ x_{\rm Au}^2x_{\rm Sn} - 6066\ x_{\rm Au}^2x_{\rm Sn}^2\ (\text{cal/g at}) \tag{12}$$

TABLE 1

COMPARISON OF ΔH^{mix} EVALUATED FROM MASS AND VOLUME CALIBRATIONS FOR Au–Sn

x_{Sn}	$-\Delta H^{\mathrm{mix}}$ *(mass)* *(cal/g at)*	$-\Delta H^{\mathrm{mix}}$ *(volume)* *(cal/g at)*
0.142	1651	1646
0.249	2436	2434
0.332	2742	2745
0.399	2864	2877
0.453	2908	2929
0.499	2995	3022
0.537	2986	3019
0.570	2924	2962
0.599	2875	2918
0.624	2836	2885
0.648	2454	2466
0.675	2308	2318
0.703	2138	2146
0.734	1974	1980
0.768	1741	1745
0.806	1518	1520
0.847	1210	1212
0.892	855	857
0.943	458	458

As can be seen from Fig. 3, the agreement between the literature values and the values reported here is quite good on the tin-rich side and satisfactory on the gold-rich side. The maximum deviation is about 200 cal/g at with the exception of 4 points around $x_{\mathrm{Au}} = 0.4$.

The Cu–Sn system was initially investigated using the calibration extrapolation technique. This proved quite unsatisfactory for this system. The results were very non-reproducible and very scattered. As a result, the inert calibration technique was

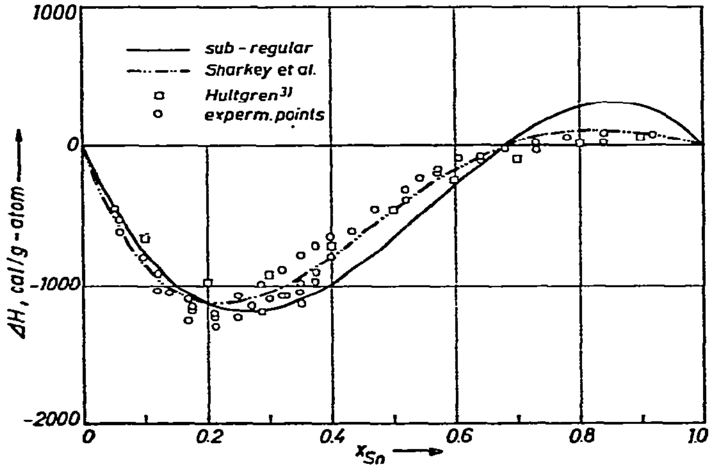

Fig. 6. Mixing enthalpy for Cu–Sn at 1440 K.

TABLE 2

COMPARISON OF ΔH^{mix} EVALUATED FROM MASS AND VOLUME CALIBRATIONS FOR Cu–Sn

x_{Sn}	$-\Delta H^{\mathrm{mix}}$ *(mass)* *(cal/g at)*	$-\Delta H^{\mathrm{mix}}$ *(volume)* *(cal/g at)*
0.05	441	442
0.097	794	794
0.138	1050	1051
0.176	1161	1164
0.211	1203	1210
0.243	1183	1194
0.273	1144	1160
0.300	1095	1118
0.325	1075	1104
0.349	1053	1089

used and proved to be quite satisfactory. Again, over 50 data points were measured and the results are shown in Fig. 6. For this system, a bath of 2 g of Cu or Sn was added initially to the crucible and ten samples weighing 0.2 g each of either Sn or Cu were added in succession to form the alloy. After every 2 alloy element addition, a calibration was made with a 0.2 g sample of tungsten. As pointed out previously, no reaction with W occurred in this system. A typical calibration curve is shown in Fig. 4. Again, very little difference occurred between ΔH^{mix} values calculated from mass and volume calibrations as shown in Table 2 and the experimental points in Fig. 6 are calculated on a mass calibration basis.

The data reported here differ somewhat from that of Hultgren et al.[5], being about 100 cal/g at more negative on the Cu-rich side and about 100 cal/g at more positive on the Sn-rich side. The agreement with the more recent results of Takeuchi et al.[8] is considerably better. Even though no values are given in the paper, data from a plot of ΔH^{mix} vs. x_{Sn} yield a value for ΔH^{mix} ($x_{\mathrm{Sn}} \approx 0.2$) of -1070 cal/g at which agrees quite well with the present results.

As in the Au-Sn system, the data were fit with two different analytical models. Because of the S-shape of the ΔH^{mix}–x_{Sn} curve it is obvious that the regular solution model does not apply to this system. The modified quasi-chemical model of Sharkey et al.[7] gives the best analytical fit to the experimental data and ΔH^{mix} is adequately expressed by

$$\Delta H^{\mathrm{mix}} = -11952\, x_{\mathrm{Sn}} x_{\mathrm{Cu}}^2 + 922\, x_{\mathrm{Sn}}^2 x_{\mathrm{Cu}} + 14373\, x_{\mathrm{Cu}}^2 x_{\mathrm{Sn}}^2 \text{ (cal/g at)} \tag{13}$$

The equivalent expression based on the sub-regular model is

$$\Delta H^{\mathrm{mix}} = -9989\, x_{\mathrm{Sn}} x_{\mathrm{Cu}}^2 + 4619\, x_{\mathrm{Sn}}^2 x_{\mathrm{Cu}} \text{ (cal/g at)} \tag{14}$$

SUMMARY AND CONCLUSIONS

Three different calibration techniques were tried with the SETARAM calorimeter and mixing enthalpies for the Au–Sn and Cu–Sn systems were measured using two of these techniques. Based on the results, it is concluded that the inert material calibration technique yields satisfactory results for measurement of high-temperature mixing enthalpies for liquid metallic alloys.

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