Journal of Thermal Analysis, Vol. 35 (1989) 2447–2460

MEASUREMENT OF ENTHALPIC PARAMETERS USING A DIFFERENTIAL CALORIMETRIC METHOD: APPLICATION TO In–Bi ALLOYS

C. Bichara, C. Bergman and *J. C. Mathieu*

CENTRE DE THERMODYNAMIQUE ET DE MICROCALORIMÉTRIE — C.N.R.S.
26, RUE DU 141$^{\text{eme}}$ R.I.A. — 13003 — MARSEILLE, FRANCE

(Received December 8, 1988)

An attempt is made to develop a calorimetric method by taking full advantage of the differential possibilities offered by the Tian–Calvet calorimeter. This method is intended to measure the enthalpic parameter, defined as the limiting value (dilute solutions) of the derivative of the partial enthalpy of mixing with respect to the concentration, in liquid In–Bi alloys. The results, although rather scattered, exhibit a systematic discrepancy when compared with those obtained by the classical direct reaction calorimetry method with the same calorimeter. They are in better agreement with the values estimated from simple thermodynamic models.

The purpose of this paper is to describe a calorimetric method intended for measurement of the enthalpic parameter of liquid alloys. Its first application is made to In–Bi melts. For a binary alloy (AB), the enthalpic parameter (η_A^A) is defined as

$$\eta_A^A = \lim_{x_A \to 0} \left(\frac{\partial \Delta h_A}{\partial x_A} \right) \tag{1}$$

where Δh_A is the partial enthalpy of mixing of A in B.

This enthalpic parameter is a measure of the mutual interaction of two A atoms in a dilute solution of A in B: it is the second term (in x_A^2) of a Taylor expansion of the enthalpy of mixing as a function of the concentration [1]. It is also the second derivative of the output of the calorimeter with respect to the concentration. Clearly, the calorimetric experiment must have extreme precision if one wishes to obtain a significant value of η_A^A.

In the past, direct reaction calorimetry (D.R.C.) has been used to measure the partial enthalpy of mixing and its limiting value for dilute solutions (Δh_A^∞). From these measurements, one could in principle obtain a value of η_A^A, but the lack of accuracy excludes significant results. In some cases [2], even the sign of the measured value of η_A^A seems to be questionable.

Nevertheless, it is possible to estimate this parameter by means of thermodynamic models. If a regular solution model [3] is used with Bragg–Williams (B.W.) or quasichemical (Q.C.) approximation, the enthalpic parameter takes the values

$$\eta^{A}_{A\,\mathrm{B.W.}} = -2\Delta h^{\infty}_{A} \tag{2}$$

or

$$\eta^{A}_{A\,\mathrm{Q.C.}} = -2\Delta h^{\infty}_{A} \exp\left(\frac{2\Delta h^{\infty}_{A}}{zRT}\right) \tag{3}$$

where z is the average number of first neighbours, T is the temperature and R is the gas constant.

Description of the methods

1) Direct reaction calorimetry

The principle of the method [4] is to drop small quantities (n_i) of element A into a melt, initially of pure B, in the laboratory cell of the calorimeter. From these experiments, one obtains the integral molar heat of formation of the alloy (A_xB_{1-x}):

$$\Delta h^{f}(x_j) = \frac{\sum\limits_{i=1}^{j} \Delta H_i}{n_B + \sum\limits_{i=1}^{j} n_i} \tag{4}$$

where ΔH_i is the variation of the enthalpy during the i-th addition. Provided that the quantities of A added to the liquid melt are sufficiently small, the partial molar enthalpy of formation of component A is:

$$\Delta h_A(x_i) = \frac{\Delta H_i}{n_i} \tag{5}$$

With a linear regression procedure, this method yields the quantities Δh^{∞}_{A} and η^{A}_{A}.

2) Differential calorimetry

The method is derived from that proposed by Deneuville et al. [5] to measure the enthalpy of the order–disorder transformation in the gold–copper system. The basic idea is to measure directly, for each drop, the quantity $\frac{\partial \Delta h_A}{\partial x_A}$ approximated by the difference between the two partial molar heats of mixing (Δh^{1}_{A} and Δh^{2}_{A}) produced simultaneously in each cell (1 and 2) of the Tian–Calvet calorimeter at the concentrations x_A^1 and x_A^2. Following Deneuville et al. [5], when simultaneous heat effects (Q_1 and Q_2) are produced in both cells of the calorimeter, the basic equation is

$$\delta_S = \frac{Q_1}{K_1} - \frac{Q_2}{K_2} \tag{6}$$

where δ_S is the area of the thermal curve recorded during the experiment, and K_1 and K_2 are the calibration constants of the cells of the calorimeter.

This equation is valid provided that the heat effects are not too important, so that each cell can be considered to be thermally independent from the other.

i) Calibration method

The calorimeter is calibrated under the same conditions as the actual experiment by dropping simultaneously two samples of A (masses m_1 and m_2; molar mass M_A; heat content between room temperature and the temperature of the cells Q_A) into liquid A contained in each cell. Following Eq. (6), one obtains, after each drop:

$$\frac{m_1^i}{m_2^i} = K_1 \frac{\delta_S{}^i M_A}{m_2^i Q_A} + \frac{K_1}{K_2} \tag{7}$$

A linear regression procedure allows calculation of K_1 and $\frac{K_1}{K_2}$. As will be discussed further, the utmost precision is required for $\frac{K_1}{K_2}$.

ii) Principle of the experiment

The principle of the experiment is to measure the heat effect produced by the heating of two samples of A, whose masses (m_1 and m_2) have been carefully chosen, and their dissolution in two liquid baths of alloy A_xB_{1-x} whose compositions (x_1 and x_2) are slightly different. This operation is repeated many times: for each step, the difference between the partial molar heats of mixing at the concentrations x_1 and x_2 is calculated, and, if it is assumed that $\frac{\partial \Delta h_A}{\partial x_A}$ is constant within a certain range of concentration ($0 \leqslant x_A \leqslant x_{\max}$), the enthalpic parameter is obtained as

$$\eta_A^A = \lim_{x \to 0} \left(\frac{\partial \Delta h_A}{\partial x_A} \right) \simeq \frac{\Delta h_A(x_1) - \Delta h_A(x_2)}{x_1 - x_2} \tag{8}$$

For the i-th addition, the chemical reactions in the cells are

Cell 1:

$$n_1^i A_{(\mathrm{sol},T_0)} + \left(n_1^B + n_1^0 + \sum_{j=1}^{i-1} n_1^j \right) \mathrm{AB}_{(\mathrm{liq},x_1^{i-1},T)} \dashrightarrow \dashrightarrow \left(n_1^B + n_1^0 + \sum_{j=1}^{i} n_1^j \right) \mathrm{AB}_{(\mathrm{liq},x_1^i,T)} \tag{9}$$

Cell 2:

$$n_2^i \mathrm{A}_{(\mathrm{sol},T_0)} + \left(n_2^B + \sum_{j=1}^{i-1} n_2^j \right) \mathrm{AB}_{(\mathrm{liq},x_2^{i-1},T)} \dashrightarrow \dashrightarrow \left(n_2^B + \sum_{j=1}^{i} n_2^j \right) \mathrm{AB}_{(\mathrm{liq},x_2^i,T)} \tag{10}$$

where n_1^B and n_2^B are the numbers of moles of B in the crucibles,
n_1^i and n_2^i are the numbers of moles of A added at the i-th drop,
n_1^0 is the initial number of moles of A in cell 1, and
x_α^i is the mole fraction of A in cell α after the i-th drop.

The heat balance equations are as follows:

Cell 1:

$$Q_1^i = \left(n_1^B + n_1^0 + \sum_{j=1}^{i} n_1^j \right) \Delta h^f_{(x_1^i,T)} - - \left(n_1^B + n_1^0 + \sum_{j=1}^{i-1} n_1^j \right) \Delta h^f_{(x_1^{i-1},T)} + n_1^i Q_A \tag{11}$$

Cell 2:

$$Q_2^i = \left(n_2^B + \sum_{j=1}^{i} n_2^j \right) \Delta h^f_{(x_2^i,T)} - - \left(n_1^B + \sum_{j=1}^{i-1} n_2^j \right) \Delta h^f_{(x_2^{i-1},T)} + n_2^i Q_A \tag{12}$$

Taking into account the definition of the partial enthalpy of mixing (Eq. (5)), these two equations give

$$Q_1^i = n_1^i \Delta h_A(y_1^i) + n_1^i Q_A \tag{13}$$

$$Q_2^i = n_2^i \Delta h_A(y_2^i) + n_2^i Q_A \tag{14}$$

which, combined with Eq. (6), are the basic equations governing the experiment.

From these, we obtain

$$\left(\frac{\partial \Delta h_A}{\partial x}\right) = \frac{\left(\frac{K_1 \delta_{S^i}}{n_1^i} - \left(1 - \frac{K_1 n_2^i}{K_2 n_1^i}\right)(\Delta h_A(y_2^i) + Q_A)\right)}{(y_1^i - y_2^i)} \tag{15}$$

Except for the usual simplification, which consists in attributing the value of Δh_A to the average concentration $\left(y_\alpha^i = \frac{(x_\alpha^i + x_\alpha^{i-1})}{2}\right)$ between two drops, Eq. (15) is exact. We nevertheless need an approximation to calculate the term $(\Delta h_A(y_2^i))$. It seems reasonable to write

$$\Delta h_A(y_2^i) = \Delta h_A^\infty + p y_2^i \tag{16}$$

where p is the average of the measured values of $\frac{\partial \Delta h_A}{\partial x}$. This requires an iterative calculation, whose convergence is that much faster that the quantities n_1^i and n_2^i are chosen to minimize the term $1 - \frac{K_1 n_2^i}{K_2 n_1^i}$.

Looking at Eq. (15), one can easily understand that the crucial points are as follows:

— A very accurate knowledge of the calibration constants. The relative precision for $\frac{K_1}{K_2}$ was found to be of the order of $1 \sim 2 \cdot 10^{-3}$.

— A careful choice of the quantities n_1^0, n_1^i and n_2^i. In the actual experiment, they were chosen so that $x_\alpha^i - x_\alpha^{i-1} \approx 0.01$ and that the term $\left(1 - \frac{K_1 n_2^i}{K_2 n_1^i}\right)$ would be minimal for each drop (approximately $5 \cdot 10^{-3}$). This use of the calorimeter, where one tries to minimize the apparent heat effect recorded, requires extreme precision in the weighing.

Experimental considerations

1) Apparatus

The calorimeter used is a Tian–Calvet calorimeter [6], operating in the temperature range 300–600 K. The introduction of the samples, the data logging and the treatment are controlled automatically by a microcomputer and suitable electronic and mechanical devices. The output signal of the calorimeter is amplified by a Keithley 150B amplifier, working in the 100 μV range, converted to a numerical signal and then read by a Commodore 3000 microcomputer. The mechanical introductor and the electronic interfaces have been constructed in the laboratory. The weighing of the samples (Koch–Light, 99.999% purity), a crucial point of the experiment, is made with a Mettler UM 3 microbalance: the absolute error in the weighing is less than ± 20 μg for the liquid bath, and less than ± 5 μg for the samples of A.

2) Integration of the thermal curves

The electric output signal of the calorimeter is integrated numerically. The shape of the thermal curves produced by the simultaneous heat effects in each cell of the calorimeter is rather variable, with no systematic trend being observed: the baselines before and after the experiment are generally different, and a correction is made in the following way:

$$\delta_S = \int_{T_i}^{T_f} f(t)\,\mathrm{d}t - \int_{T_i}^{T_f} \left((M_i - M_f)\, e^{\frac{-t}{\tau}} + M_f \right) \mathrm{d}t \tag{17}$$

where $f(t)$ is the output signal of the calorimeter,
τ is the time constant of the calorimeter, and
M_i and M_f are the values of the initial and final baselines.

3) Error analysis on the measurement of the enthalpic parameter

A rigorous error analysis on the values of the enthalpic parameter given by Eq. (15) is difficult. It is therefore more appropriate to study the effects of variation in the important parameters, which are

— the area of the thermograms (δ_{S^i}),
— the quantities n_1^i and n_2^i, and
— the calibration constants K_1 and K_2.

The absolute error in the integration, estimated by the integration of blank effects, is of the order of $\pm 5 \cdot 10^{-6}$ V · s, which represents a relative error of ± 5%. Such a relative variation involves an absolute variation in the values of the enthalpic parameter which is always less than ± 500 J/mol.

The errors in the quantities n_α^i interfere in two ways:

— in the term $\left(1 - \dfrac{K_1 n_2^i}{K_2 n_1^i}\right)$, but the relative error $\dfrac{\delta(m_1/m_2)}{(m_1/m_2)}$ is about $2 \cdot 10^{-4}$, which is much smaller than $\dfrac{\delta(K_1/K_2)}{(K_1/K_2)}$ $(1 \sim 2 \cdot 10^{-3})$;

— in the mole fractions in the denominator of Eq. (15), but the errors in the numerator are much more important.

The most important effect is the error in $\dfrac{K_1}{K_2}$: indeed, this term is multiplied by

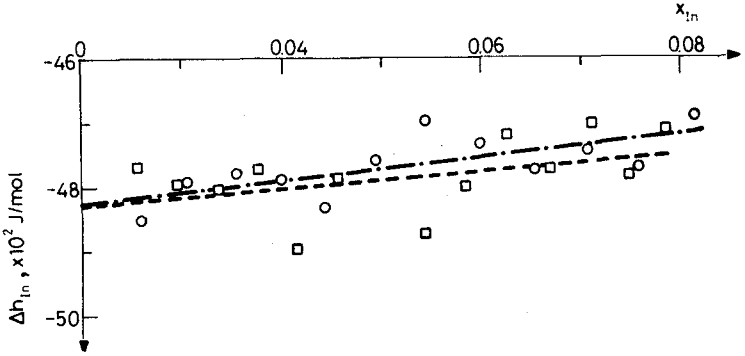

Fig. 1 Partial molar enthalpy of mixing of indium, Δh_{In}, vs. mole fraction x_{In} at 562 K, obtained by direct reaction calorimetry ○ series 1; □ series 2

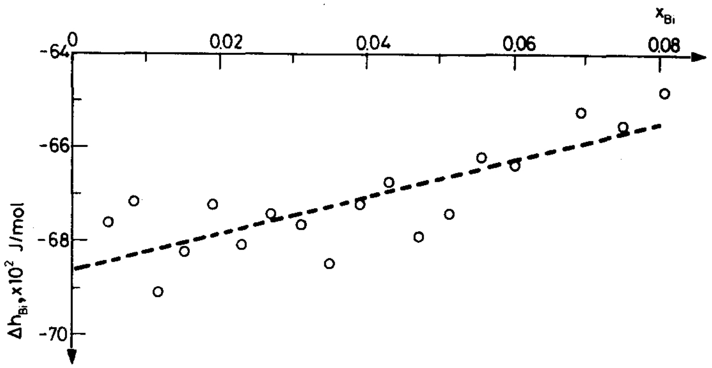

Fig. 2 Partial molar enthalpy of mixing of bismuth, Δh_{Bi}, vs. mole fraction x_{Bi} at 562 K, obtained by direct reaction calorimetry

$(h_A(y_2^i)+Q_A)$, which is of the order of 5000 J/mol in the system we studied. Small variations in $\frac{K_1}{K_2}$ (± 1%) involve a strong effect on the average value of the slope of the partial enthalpy of mixing (± 1000 J/mol). This is probably the reason why our results are rather scattered.

Results on the In–Bi system

1) Direct reaction calorimetry

Prior to the differential method, we measured Δh_{In}^{∞}, Δh_{Bi}^{∞}, η_{In}^{In} and η_{Bi}^{Bi} in liquid In–Bi alloy by means of direct reaction calorimetry at 562 K. The results, corresponding to Figs 1 and 2, are

	$\Delta h^{\infty}_{\mathrm{In}}$, J/mol	$\eta^{\mathrm{In}}_{\mathrm{In}}$, J/mol
Series 1	-4823 ± 150	856 ± 570
Series 2	-4825 ± 150	1153 ± 400
	$\Delta h^{\infty}_{\mathrm{Bi}}$, J/mol	$\eta^{\mathrm{Bi}}_{\mathrm{Bi}}$, J/mol
	-6865 ± 200	3900 ± 750

The following tabulation presents some results from the literature:

Authors	Temperature	$\Delta h^{\infty}_{\mathrm{In}}$, J/mol	$\Delta h^{\infty}_{\mathrm{Bi}}$, J/mol
Wittig and Muller [7]	623 K	-6200	-6400
Robinson and Bever [8]	623 K	-5925 ± 150	—
Robinson and Leach [9]	623 K	-5774 ± 85	—

Our results are somewhat different from those in the literature. In particular, they indicate a greater asymmetry of the thermodynamic properties with respect to the composition. It should be noted that the results of Wittig et al. [7] were extrapolated to dilute solutions in such a way that their asymmetry was lowered.

2) Differential calorimetry

Figure 3 is the calibration curve of the calorimeter, corresponding to Eq. (7). The values of the calibration constant are

$$K_1 = 61.208 \pm 0.630 \text{ W/V},$$

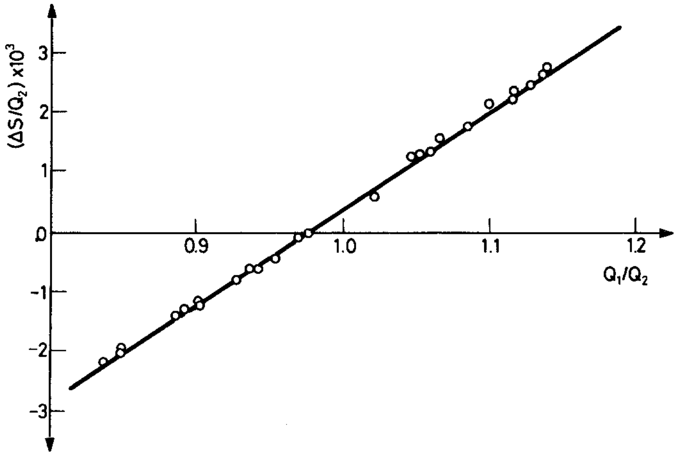

Fig. 3 Calibration curve of the calorimeter at 562 K in the differential method, according to Eq. (7)

Table 1 Values of $\eta_{\mathrm{In}}^{\mathrm{In}} = \left(\frac{\partial \Delta h_{\mathrm{In}}}{\partial x_{\mathrm{In}}}\right) = \left(\frac{\delta h}{\delta x}\right)$ obtained by differential calorimetry

Series 1

x_{In}	δh	δx	$\left(\frac{\delta h}{\delta x}\right)$
.01938	52.6	.00952	5910
.02877	60.4	.00919	6576
.03720	17.9	.00889	2014
.04114	32.8	.00856	3835
.05583	43.3	.00823	5263
.06507	27.5	.00790	3476

Series 2

x_{In}	δh	δx	$\left(\frac{\delta h}{\delta x}\right)$
.02258	37.1	.00669	5552
.03183	−48.2	.00642	−7502
.03941	31.5	.00621	5075
.04782	6.3	.00598	1056
.05646	42.0	.00575	7300
.06511	32.9	.00550	5980
.07346	39.5	.00525	7529
.08092	1.7	.00504	336
.08760	17.8	.00488	3650

Series 3

x_{In}	δh	δx	$\left(\frac{\delta h}{\delta x}\right)$
.01263	46.1	.01174	3925
.02083	81.3	.01107	7343
.02937	29.3	.01065	2756
.03809	30.8	.01046	2951
.04763	6.3	.01017	616
.05834	70.2	.00954	7357
.07000	84.5	.00886	9532
.08091	− 2.5	.00832	− 306
.08901	12.3	.00788	1567
.09593	19.1	.00758	2512
.10345	39.8	.00733	5432
.11165	44.1	.00707	6244

Table 2 Values of $\eta_{\mathrm{Bi}}^{\mathrm{Bi}} = \left(\frac{\partial \Delta h_{\mathrm{Bi}}}{\partial x_{\mathrm{Bi}}}\right) = \left(\frac{\delta h}{\delta x}\right)$ obtained by differential calorimetry

Series 1

x_{Bi}	δh	δx	$\left(\frac{\delta h}{\delta x}\right)$
.00722	− 57.3	.01068	− 5026
.01145	122.6	.01052	11650
.01558	53.2	.01037	5133
.02030	− 47.5	.01020	− 4654
.02542	14.4	.01000	1437
.03074	175.2	.00980	17879
.03574	− 6.5	.00959	− 673
.04282	18.5	.00801	2304
.05248	27.4	.00759	3611

Series 2

x_{Bi}	δh	δx	$\left(\frac{\delta h}{\delta x}\right)$
.00876	10.4	.01031	1012
.01523	27.6	.01010	2732
.02042	−113.9	.00996	−11437
.02629	29.1	.00976	2980
.03120	84.4	.00956	8823
.03500	82.8	.00932	8876
.03990	161.7	.00917	17633
.04469	−114.9	.00902	−12742
.04893	142.3	.00825	17244
.05374	127.7	.00715	17850

and

$$\frac{K_1}{K_2} = 0.98268 \pm 0.00125$$

Table 1 presents the detailed results of the measurements of $\frac{\partial \Delta h_{\mathrm{In}}}{\partial x}$. Table 2 gives those relative to $\frac{\partial \Delta h_{\mathrm{Bi}}}{\partial x}$. These values are scattered. This is not so surprising if it is remembered that they correspond to the second derivative of the output of the calorimeter. If we start from these values, however, and recalculate the partial enthalpies of mixing (they are plotted in Figs 4 and 5) and, from there by linear regression, calculate the mean value of the enthalpic parameter, we obtain:

	Δh^{∞}_{In}, J/mol	η^{In}_{In}, J/mol
Series 1	−4787	4365
Series 2	−4860	3862
Series 3	−4816	4102
	Δh^{∞}_{Bi}, J/mol	η^{Bi}_{Bi}, J/mol
Series 1	−6917	4250
Series 2	−6957	5060

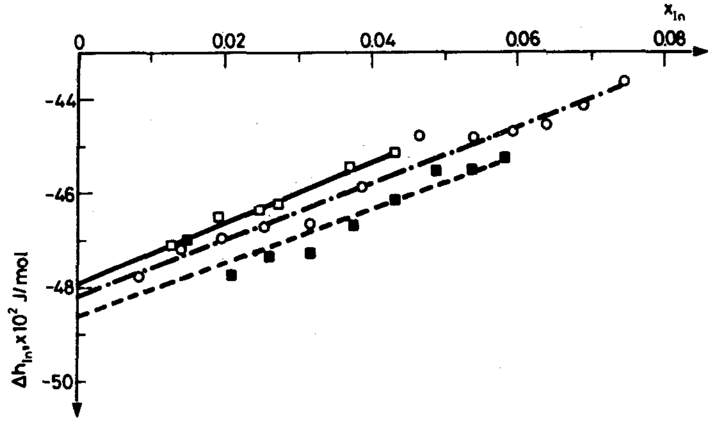

Fig. 4 Partial molar enthalpy of mixing of indium, Δh_{In}, *vs.* mole fraction x_{In} at 562 K, obtained by differential calorimetry. □ series 1; ■ series 2; ○ series 3

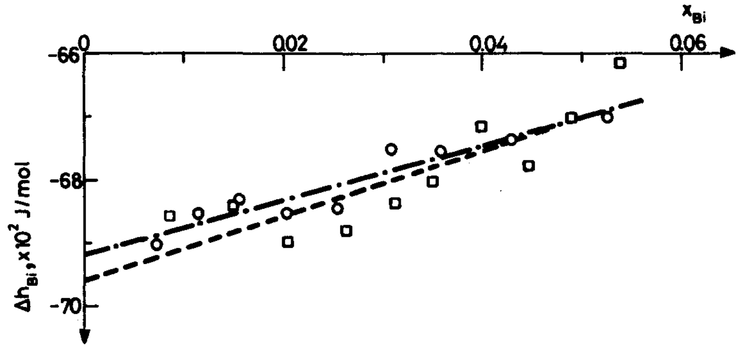

Fig. 5 Partial molar enthalpy of mixing of bismuth, Δh_{Bi}, *vs.* mole fraction x_{Bi} at 562 K, obtained by differential calorimetry. ○ series 1; □ series 2

An error analysis on these values is rather difficult since the values of Δh_A obtained by the differential method are strongly correlated: indeed, the i-th value depends on the $(i-1)$ previous ones. This clearly causes a larger error in the value of Δh_A^∞, as can be seen from our results. Direct reaction calorimetry seems better suited to measure that quantity. In contrast, direct reaction calorimetry is known to yield unreliable values of η_A^A. The differential method we have investigated yields values of η_A^A which, although still scattered, are significantly different from those obtained with the direct reaction calorimetry method. The reason for this discrepancy is not clear, but one might think of some kind of systematic error, which is avoided in direct measurements of η_A^A by means of the differential method. The only possible way to assess these results is to compare them with the values estimated from various thermodynamic models.

3) Estimations from thermodynamic models

Besides the classical regular solution model (Eqs (2) and (3)), which assumes that thermodynamic properties are symmetrical with respect to the concentration, other models can be used:

— The sub-regular solution model [10], which assumes a random distribution of the atoms and asymmetry such that

$$\eta_A^A = 2(\Delta h_B^\infty - \Delta h_A^\infty) \tag{18}$$

— The surrounded atom model [11], in the quasichemical approximation, which gives

$$\eta_A^A = -zRT(2\Phi_{z-1}\ln(\Phi_{z-1}) + (z-1)\Phi_2\ln(\Phi_2)) \tag{19}$$

where Φ_{z-1} and Φ_2 can be calculated from Δh_A^∞ and Δh_B^∞.

The quasichemical models require a knowledge of z (coordination number). Following the X-ray diffraction results of Bek, Nold and Steeb [12], we take the average value $z = 9$ in liquid In–Bi melts.

Finally, taking our experimental values ($\Delta h_{\mathrm{In}}^\infty = -4825$ J/mol and $\Delta h_{\mathrm{Bi}}^\infty = -6865$ J/mol), with the models cited above we obtain

Approximation	$\eta_{\mathrm{In}}^{\mathrm{In}}$, J/mol	$\eta_{\mathrm{Bi}}^{\mathrm{Bi}}$, J/mol
Regular solution (B.W.)	9652	13730
Regular solution (Q.C.)	7672	9908
Sub-regular solution	5570	17810
Surrounded atom (Q.C.)	5381	16083
Our results (D.R.C.)	1000	3900
Our results (differential method)	4100	4650

These estimations suggest that the differential calorimetric method we propose yields better values of the enthalpic parameter.

Conclusion

This paper presents an attempt to measure directly the enthalpic parameters in liquid In–Bi melts. The method we propose takes full advantage of the differential capacity of the Tian–Calvet calorimeter. The method mostly relies on a careful choice of the quantities of reactants, so that the calorimeter is used as a zero detector. It requires a very accurate weighing of the samples and a very accurate calibration of the calorimeter. The second point is the crucial point and probably the most difficult to achieve, since small variations in the calibration constants of the calorimeter may occur between the calibration and the actual experiment. Direct reaction calorimetry yields accurate values of the partial enthalpies of mixing at infinite dilution, whereas the differential calorimetric method seems better suited for determining the enthalpic parameters. In any case, for the measurement of the latter, the two methods yield significantly different values. Although rather scattered, those obtained by the differential method are in better agreement with the estimations of various thermodynamic models.

The reason for this discrepancy between the methods is not clear. It should be interesting to apply these methods to other, more energetic systems, in order to clarify this point.

References

1 C. N. Wagner, Thermodynamics of alloys, Addison–Wesley, Reading (MA, USA), 1952.
2 C. Chatillon-Colinet, J.-L. Deneuville, J. C. Mathieu and E. Bonnier, J. Chim. Phys., 7–8 (1975) 878–84.
3 E. A. Guggenheim, Mixtures, Oxford, Clarendon, 1952.
4 T. Kang and R. Castanet, J. Less-common Met., 51 (1977) 125–35.
5 J.-L. Deneuville, D. Gratias, C. Chatillon-Colinet and J.-C. Mathieu, High Temp. High Press, 9 (1977) 445–52.
6 E. Calvet and H. Prat, Recents Progrès en Microcalorimétrim, Paris, Masson, 1958.
7 F. E. Wittig and E. Muller, Z. Phys. Chem., 21 (1959) 47–73.
8 P. M. Robinson and M. B. Bever, Trans. Met. Soc. A.I.M.E., 233 (1965) 1908–9.
9 P. M. Robinson and J. S. Leach, Trans. Met. Soc. A.I.M.E., 236 (1966) 818–21.
10 H. K. Hardy, Acta Met., 1 (1953) 202.
11 J.-C. Mathieu, F. Durand and E. Bonnier, J. Chim. Phys., 11–12 (1965) 1289–303.
12 R. Bek, E. Nold and S. Steeb, Z. Naturforsch. A, 36 (1980) 150–3.

Zusammenfassung — Es wurde der Versuch unternommen, ein kalorimetrisches Verfahren zu entwickeln, das die Vorteile der Differentiation beim Tian–Calvet-Kalorimeter voll ausnutzt. Mittels dieser Methode sollte unter Berücksichtigung der Konzentration an flüssigen In–Bi Legierungen ein Enthalpieparameter gemessen werden, der als Grenzwert (verdünnte Lösung) der Ableitung der partiellen Mischungsenthalpie definiert wurde. Die Ergebnisse zeigen trotz größerer Streuung eine systematische Abweichung von den Werten, die auf demselben Kalorimeter mit dem klassischen DRC-Verfahren erhalten wurden und befinden sich in besserer Übereinstimmung mit den Werten, die auf der Basis einfacher thermodynamischer Modelle geschätzt wurden.

Резюме — Предпринята попытка разработать калориметрический метод с учетом преимуществ различных возможностей, предоставляемых калориметром Тиана–Калвета. Метод предназначен для измерения энтальпийного параметра, определяемого как предельное значение (разбавленные растворы) производной парциальной энтальпии смешения от концентрации для жидких сплавов индий-висмут. Полученные результаты, имеющие определенный разброс, показывают систематические различия по сравнению с таковыми, полученными классическим методом прямой реакционной калориметрии на том же самом калориметре. Все же они лучше согласуются со значениями, установленными на основе простых термодинамических моделей.