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A RE-EXAMINATION OF THE HEAT OF FUSION OF INDIUM

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ABSTRACT

The currently accepted value of the heat of fusion, ΔH, of indium is shown to be of doubtful accuracy so that indium is an unsuitable calibrant in differential scanning calorimetry. ΔH has been redetermined using a DSC calibrated with alumina, a technique which is shown to reproduce enthalpy changes in a variety of materials with an accuracy of $\pm 1\%$. The heat of fusion of indium is 3.35 kJ g-at^{-1} (29.2 J g^{-1}).

INTRODUCTION

A differential scanning calorimeter (DSC) must be calibrated if it is to measure enthalpy changes quantitatively. Modern instruments are capable of $\pm 1\%$ reproducibility on a routine basis and it is therefore essential to use a calibrant whose thermodynamic properties are known to at least a few tenths of a per cent if reproducibility is to be equated with accuracy. Most workers have used indium (specifically, the heat of fusion, ΔH) for this purpose. A high purity form is readily available, is easily handled, and has desirable baseline properties and the metal would be an ideal calibrant if ΔH were accurately known. The results of Celsen et al.[1] are used for ΔH, but unfortunately it is difficult to define the errors in their technique so that in this respect indium is an unsatisfactory standard. In addition, although in this laboratory we normally use α-alumina as a calibrant because enthalpy data are available which are accurate to a few tenths of a per cent, occasional comparative experiments with indium have revealed consistent differences between calibration constants based on the two materials. Since the results for alumina have been confirmed by many independent investigations re-examination of the data for indium is clearly needed.

This paper reports the result of such an investigation. The normal DSC procedure has been reversed and the heat of fusion of indium determined using a calorimeter which has been calibrated with synthetic sapphire[2] cross-checked against several other thermodynamically well-defined materials. The value obtained for ΔH is 3.35 ± 0.03 kJ g-at^{-1} (29.2 ± 0.3 J g^{-1}), 2.5% higher than the normally accepted figure.

EXPERIMENTAL

Perkin-Elmer calorimeters, Models DSC-1B and DSC-2, were used, great care being taken in their calibration and in assessing the overall accuracy of the results. All experiments were designed to measure the total enthalpy change $H(T_2)-H(T_1)$ when the calorimeter temperature was raised from one steady value, T_1, to another, T_2. An area proportional to $H(T_2)-H(T_1)$ was obtained by subtracting the DSC curve for the empty calorimeter from that for the loaded instrument. The latter contained either calibrant, for which $H(T_2)-H(T_1)$ and hence the area-to-enthalpy conversion factor, F, was known, or indium (melting temperature T_m, $T_1 < T_m < T_2$). Since only total enthalpy changes were required, thermal lag in the dynamic part of the experiment was unimportant and no correction was made for the apparent increase in the temperature of indium before melting was complete. Details of the isothermal temperature calibration, experimental procedure, and methods of computation have been described earlier[2,3].

As it is difficult to estimate experimental errors in this type of calorimetry the most realistic approach is to compare results obtained by this and other techniques for a variety of materials. Using α-alumina (Agate Products Ltd., preliminary experiments had shown that discs from this source were indistinguishable in the context of this paper from the National Bureau of Standards Standard Reference Material No. 720) as calibrant[4,5], enthalpy changes were determined for the following: benzoic acid[6] (B.D.H. calorimetric standard), tungsten carbide and indium oxide (samples supplied by Dr. J. F. Martin of this laboratory after examination by adiabatic calorimetry), polystyrene[7,8] (N.B.S. S.R.M. Nos. 705 and 706) and indium[9] (Koch-Light 99.9999%). A wide range of temperature was used, individual runs covering from 20 to 60 K.

RESULTS

Results were obtained over a period of more than two years. During this time not only did day-to-day operation require a wide range of instrumental settings, certain of which affected the conversion factor, F, but also the DSC-1B was replaced by a DSC-2. Under these circumstances absolute values of F are of little help in assessing instrumental performance. A better criterion, and the one adopted here, was to compare enthalpy changes measured in the DSC, using α-alumina as the calibrant, with values reported in the literature. No significant differences were found between the two calorimeters even though the DSC-2 has considerably better baseline reproducibility, this last confirms the validity of the computer treatment which allows for mismatches between "Full" and "Empty" baselines[2].

Figure 1 shows the ratio of "DSC" to "literature" enthalpy changes described above.

Results for the fusion of indium as a function of heating rate and temperature range are given in Table 1. The overall enthalpy change $H(T_2)-H(T_1)$ was con-

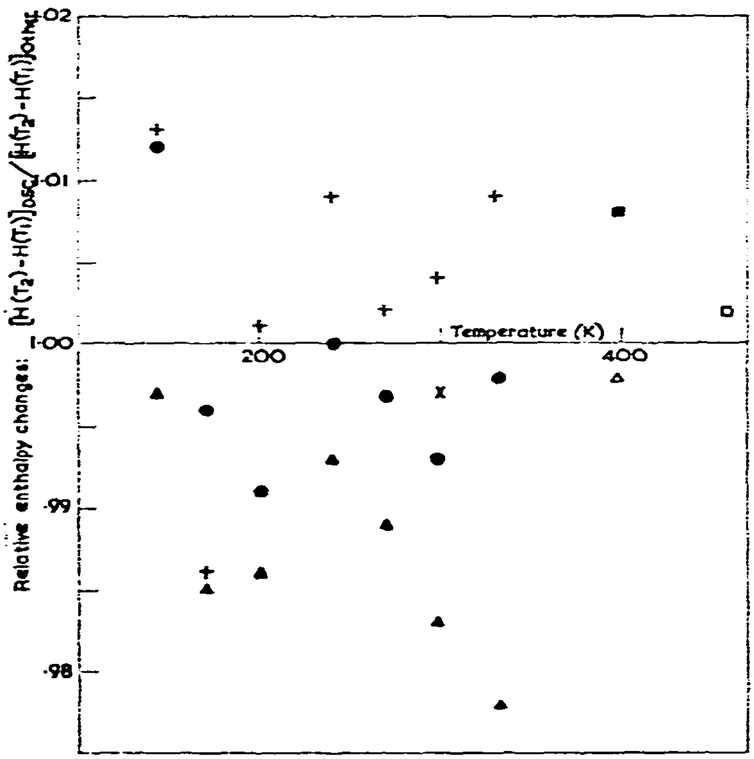

Fig. 1. Enthalpy changes $H(T_2)-H(T_1)$. DSC values (alumina calibrant) relative to other values: ●, benzoic acid[6]; ▲, polystyrene (N.B.S. 705)[7]; △, polystyrene (N.B.S. 706)[8]; ■ and □, indium solid and liquid[9]; +, tungsten carbide and ×, indium oxide (both adiabatic calorimetry, unpublished results from Dr. J. F. Martin of this laboratory).

TABLE 1

ENTHALPY CHANGES IN INDIUM

Factor, F ($J\ V^{-1}\ sec^{-1}$)	*Heating rate* ($K\ min^{-1}$)	T_1 (*K*)	T_2 (*K*)	$H(T_2)-H(T_1)$ (kJ g-at^{-1})	ΔH (*429.8 K*) (kJ g-at.$^{-1}$)
424.1	0.625	427.7	431.7	3.48	3.36
423.5	2.5	425.8	432.6	3.52	3.32
422.8	5	424.8	434.6	3.59	3.31
422.9	10	419.9	439.5	3.91	3.34
422.2	20	419.9	439.5	3.90	3.33

verted to the heat of fusion, ΔH, using the equations given by Hultgren et al.[9] for $H(T_2)-H(T_m)$ and $H(T_m)-H(T_1)$ with $T_m = 429.8$ K. These equations were also used to calculate the "literature" values for the solid and molten indium (over the ranges 375–425, 435–485 K, respectively) shown in Fig. 1. In the fusion experiments the absolute values of F shown in Table 1 are important because instrumental settings were kept constant so their reproducibility provides another assessment of calorimeter performance (the apparent change of F with heating rate is fortuitous, it normally has a random variation). The series of experiments forming Table 1 was repeated twice, once with a similar weight of indium (10 mg) and once with a considerably larger sample (60 mg). The arithmetic mean of the fifteen results was 3.35 kJ g-at^{-1} with a standard deviation of ± 0.03 kJ g-at^{-1} (29.2 ± 0.3 J g^{-1}).

DISCUSSION

Calibration and accuracy

There have been many investigations of the thermodynamic properties of α-alumina and existing data have been carefully reviewed by Ditmars and Douglas[4] who show that errors in $H(T_2) - H(T_1)$ are, at most, a few tenths of 1%. When this well-characterised material is used to calibrate a DSC, it is clear from Fig. 1 that enthalpy changes in other materials, which have a wide range of physical properties, can be determined with an accuracy of ± 1%. The results for the N.B.S. polystyrene No. 705 probably refer to real differences between samples. It was originally thought that the as-received boules of S.R.M. 705 would provide a suitable "sub-standard" but with any polymer, thermal history must be known with certainty if measurements are to be made in the solid state. In this connection it is noteworthy that in S.R.M. 706, for which our results are in excellent agreement with published values in the molten state, there is a 1% change in $H(350\text{ K}) - H(290\text{ K})$ on annealing[8]. Duplicate experiments confirm that our results for S.R.M. 705 are about 1% lower than those of Chang and Bestul[7]. All the results shown in Fig. 1 refer to individual experiments, rather than mean values, since it is important to know what limits of accuracy can be ascribed to a single run. Clearly ± 1% encompasses all uncertainties except at the lowest temperatures where there are uncertainties in the area conversion factor, F, because T_1 and T_2 are ill-defined owing to the lack of suitable melting- or transition-temperature standards. In addition there is exceptional curvature in the specific heat behaviour of α-alumina and the two effects combine to decrease the overall accuracy (benzoic acid is a better calibrant in this range).

No data from fusion or phase changes appear in Fig. 1. Specific heats are generally not greatly affected by small amounts of impurities and results for nominally similar materials can be compared with some confidence (ideally, identical samples, as with our In_2O_3 and WC, should be compared by DSC and an independent technique). Melting and phase changes are very susceptible to impurities, they are also generally "integrating" processes in the sense that they cover a finite temperature range and hence include a $c_p \Delta T$ contribution. Purity is frequently not mentioned in literature reports on ΔH_m and it may also be unclear how ΔH_m has been extracted from the experimentally observed quantity. Certain well-defined organic compounds, such as benzoic acid, are unsuitable because they have a high vapour pressure at their melting point. Pure metals are readily available, but a study of existing heats of fusion[10] reveals an unacceptably broad spectrum of values. It is for these reasons that we have confined our investigation of instrumental performance to a comparison of simple enthalpy changes of the $c_p \Delta T$ type.

The heat of fusion of indium

Recent values of ΔH are shown in Table 2. Calibration of a DSC with indium has hitherto seen the almost universal use of Oelsen et al.'s data[1]. Reference to the original publications[1,11] shows that a single filling of the calorimeter was used, the standard deviation given being a measure of the reproducibility of repeat experiments on this particular filling. Other metals were more extensively investigated using two or three independent loadings of the calorimeter and here variations of 2–3% were common. Similar figures are found in the later work[12] with a modified calorimeter and it must be concluded that 2–3% represents the reproducibility of this type of calorimeter. No purity was quoted for the indium but it may be significant that Roth et al.[20] obtained a very similar heat of fusion with a sample in which premelting was observed 1.7 K below T_m, the corresponding figure for our sample was 0.2 K.

TABLE 2

HEAT OF FUSION OF INDIUM

ΔH (*kJ g-at.*$^{-1}$)	*Reference*	*Technique*
3.26	Oelsen et al.[1,11]	Heating/cooling curves
3.18	Oelsen[12]	Heating/cooling curves
3.37	Predel[13]	DTA (electrical calibration)
3.34	Alpaut and Heumann[14]	DTA (electrical calibration)
3.35	Mochkovskii and Vecher[15]	DTA
3.30	Reznitskii et al.[16]	DTA
3.31	Malaspina et al.[17]	Calvet
3.26	Brennan and Gray[18]	DSC
3.13[a]	Flynn[19]	DSC
3.35	This work	DSC

[a] = 0.96 × 3.26, assuming ref. 1 was used to calculate the indium factor, $F(\mathrm{In}) = 1.04\,F(\mathrm{Al_2O_3})$

It is a matter of concern that three almost identical sets of DSC experiments (all using alumina as a calibrant) have given results which differ by several per cent (Table 2). There should be no ambiguities in the data treatment; our own results were reduced to ΔH using equations[9], the accuracy of which is confirmed both by the independence of ΔH on the overall temperature interval, Table 1, and by the agreement with our results, shown in Fig. 1, for $H(T_2) - H(T_1)$ in both the solid and liquid states; the other DSC results used a baseline technique to extract ΔH and this is a valid procedure, since the specific heat of the solid and liquid are virtually identical at T_m—one of the reasons why indium is such a popular calibrant.

Evidence supporting our result is given by the data of Table 2 which have been obtained by quite independent techniques. Collectively, these can leave little doubt that the heat of fusion of indium is 2–3% higher than the 1955 reports suggest and we believe they confirm our value of 3.35 ± 0.03 kJ g-at^{-1} (29.2 ± 0.3 J g^{-1}).

CONCLUSIONS

Calibration of a differential scanning calorimeter with alumina enables enthalpy changes to be determined with an accuracy of ±1%. Using a calorimeter calibrated in this way the heat of fusion of indium is shown to be 2.5% higher than the normally accepted value. Materially, indium is an excellent *potential* calibrant but quantitative data for a *true* calibrant should be confirmed, if possible, by independent techniques and we would prefer to see the present results backed by the precision of, say, adiabatic calorimetry before recommending the general use of indium.

As it is, alumina is a better defined and more versatile calibrant covering, as it does, the whole temperature range of the DSC.

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REFERENCES

1 W. Oelsen, O. Oelsen and D. Thiel, *Z. Metallk.*, 46 (1955) 555.
2 M. J. Richardson, *J. Polym. Sci. C*, 38 (1972) 251.
3 K. C. Mills and M. J. Richardson, *Thermochim. Acta*, 6 (1973) 427.
4 D. A. Ditmars and T. B. Douglas, *J. Res. Nat. Bur. Stand.*, 75A (1971) 401.
5 G. T. Furukawa, T. B. Douglas, R. E. McKoskey and G. T. King, *J. Res. Nat. Bur. Stand.*, 57 (1956) 67.
6 G. T. Furukawa, R. E. McKoskey and G. T. King, *J. Res. Nat. Bur. Stand.*, 47 (1951) 256.
7 S. S. Chang and A. B. Bestul, *J. Polym. Sci. A2*, 6 (1968) 849.
8 F. E. Karasz, H. E. Blair and J. M. O'Reilly, *J. Phys. Chem.*, 69 (1965) 2657.
9 R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys*, Wiley, New York, 1963.
10 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelly and D. G. Wagman, *Selected Values of the Thermodynamic Properties of the Elements*, American Society of Metals, Metals Park, Ohio, 1973.
11 W. Oelsen, K. H. Rieskamp and O. Oelsen, *Arch. Eisenhut.*, 26 (1955) 253.
12 W. Oelsen, *Arch. Eisenhut.*, 28 (1957) 1.
13 B. Predel, *Z. Metallk.*, 55 (1964) 97.
14 O. Alpaut and Th. Heumann, *Acta Met.*, 13 (1965) 543.
15 L. A. Mechkovskii and A. A. Vecher, *Russ. J. Phys. Chem.*, 43 (1969) 751.
16 L. A. Reznitskii, V. A. Kholler and S. E. Filippova, *Russ. J. Phys. Chem.*, 44 (1970) 299.
17 L. Malaspina, R. Gigli and V. Piacente, *Rev. Int. Hautes Temp. Refract.*, 8 (1971) 211.
18 W. P. Brennan and A. P. Gray, *Thermal Analysis Applications Study No. 9*, Perkin-Elmer Corp., Norwalk, Conn., 1973.
19 J. H. Flynn, *Thermochim. Acta*, 8 (1974) 69.
20 W. A. Roth, I. Meyer and H. Zeumer, *Z. Anorg. Chem.*, 214 (1933) 309.