Thermochimica Acta, 88 (1985) 199—204
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

LATENT HEAT MEASUREMENT BY DSC WITH SAPPHIRE AS STANDARD MATERIAL

Yoshio Takahashi

Electrotechnical Laboratory, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

ABSTRACT

A new method for measuring heats of transition and fusion is proposed. In the method, specific heat capacity of sapphire is used to measure temperature dependence of the proportionality coefficient between the peak area and the heat. Thus, the accuracy of the measurement is independent on the accuracy of other standard materials with known heat of transition or fusion, such as indium and tin which are used in the conventional method. But the accuracy depends on the high accuracy of the specific heat capacity of stable sapphire, so that it is improved remarkably, and the new method has other several advantages over the conventional method.

INTRODUCTION

DSC of both types of power compensation and heat flux is extensively applied to measurement of heats of transition and fusion. In a conventional method, standard materials with known heat of transition or fusion, such as indium, tin, lead, zinc and so on, have been used for calibration of the proportionality coefficient between the peak area of DSC curves and the heat to be measured (refs. 1 and 2). However, we should use as many standard materials as possible in the temperature range of measurement, taking into accounts of temperature dependence of the proportionality coefficient (ref 1), and the accuracy of the measurement by this method is limited by the accuracy of the heat of transition or fusion of the standard materials used. Moreover, purity and stability of the standard materials should also be taken into accounts, because impurities and deterioration, such as thermo-oxidative deterioration, have undesirable influence on the accuracy of the measurement.

On the other hand, sapphire has been used as the standard material in specific heat capacity measurements by conventional calorimeters, such as an adiabatic calorimeter (refs. 3 and 4), as well as those by the DSC's (ref. 1). In the theory of DSC, the proportionality coefficient between the heat capacity and the base line increment is exactly the same as the proportionality coefficient between the peak area and the latent heat. Furthermore, sapphire is more favorable than the above other standard materials in many points. For instance, it is highly stable, and high purity material is readily available with accurate data of the specific heat capacity (ref. 4).

Considering these facts, the present author has made an attempt to measure

0040-6031/85/$03.30

the heat of transition or fusion by DSC with sapphire as the standard material and obtained excellent results, as is described in this report. The accuracy of measurement of the heat of transition or fusion is remarkably improved, because of high accuracy of the specific heat capacity of sapphire. Other advantages over the conventional method are also discussed in this paper.

EXPERIMENTAL

Materials

Substances measured are indium, tin, lead, zinc, potassium nitrate and high density polyethylene (PE), as are described in Table 1. The standard material of sapphire is a disc specimen supplied by Perkin-Elmer Co.

Apparatus

A Perkin-Elmer DSC-2 was used, and the measurements were made at the heating rate of 5 K/min under the flow of nitrogen. Two sorts of sample pan were used; one is an aluminum pan usually used and the other is made of polytetrafluoroethylene (PTFE). The DSC data were recorded at every 12 seconds in the steady state and at every 1 second in the transition or fusion region. The data acquisition and processing were made with a data logger (Hewlett Packard HP 3497A) and a personal computer (Hewlett Packard HP 9816S).

The usual procedure for the specific heat capacity measurement was applied (ref. 1). In the case of aluminum sample pan, the same pan was used for the standard materials of sapphire and the blank test, and a different pan was used for the sample. The correction was made for the difference in the weight between the two pans by using the specific heat capacity data of aluminum (ref. 5). In the case of PTFE pan, the same pan was used for sapphire, the blank test and the sample. The specific heat capacity measurement was made at every 1 K in the steady state and at every 1/12 K in the transition or fusion region.

RESULTS AND DISCUSSION

First of all, the DSC curve of the empty pan and that of the sapphire specimen were obtained. The difference in the base lines between the two curves is a product of the heat capacity of the sapphire specimen, the heating rate and the proportionality coefficient. The proportionality coefficient, K, was estimated from the difference in the base lines and the specific heat capacity of the sapphire (ref. 4), and it is plotted as a function of temperature in Fig. 1. The temperature dependence is clearly shown especially in the low temperature range. To elucidate the accuracy of the above specific heat capacity measurement, the specific heat capacities, c_p, of some standard materials (ref. 6) were measured in the same temperature range. A typical result of platinum is shown in Fig. 2 with reported values (ref. 6), and the agreement is very good, though the specific heat capacity of platinum is small.

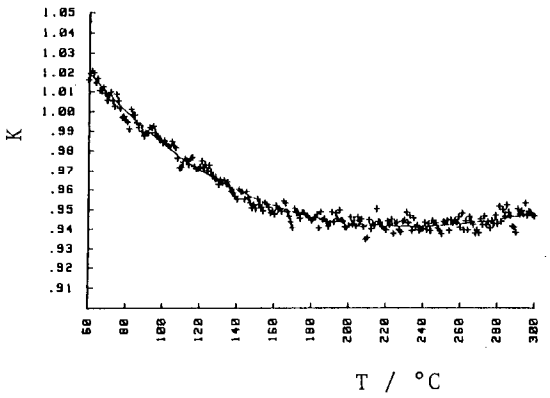

Fig. 1. Temperature dependence of proportionality coefficient

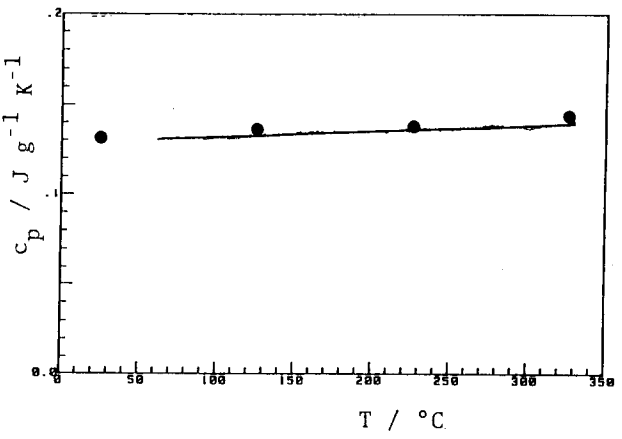

Fig. 2. Specific heat capacity of platinum. Literature data are shown with ●.

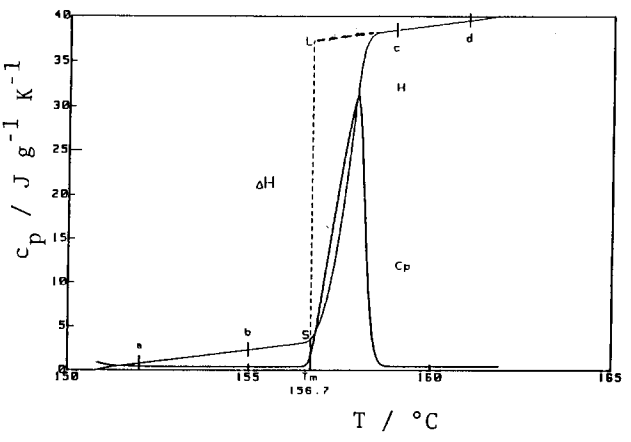

Fig. 3. Apparent specific heat capacity and enthalpy increase of indium

A typical result of indium of high purity is reproduced in Fig. 3. The observed DSC curve was converted to the curve of the specific heat capacity versus the temperature. However, the temperature on the abscissa is not corrected, though the correction is necessary especially in the melting region, as is made in DSC purity determination (ref. 1), so that the specific heat capacities in the melting region are apparent values. By integrating the specific heat capacity thus measured, we obtain enthalpy increase as a function of temperature, as is shown in Fig. 3. Taking into accounts of the fact that the above data are the apparent data, linear enthalpy increases in the solid and liquid states are extrapolated to the melting region, and the heat of fusion, ΔH, is estimated from the difference in the extrapolated lines of the enthalpy at the extrapolated onset temperature, T_m.

To observe the effect of heat transfer from the microheater to the sample, the fusion of the pure indium was observed with the aluminum sample pan and the PTFE sample pan, and the results are shown in Fig. 4. A diffuse peak of the apparent specific heat capacity was obtained in the case of PTFE sample pan, and this is caused by the low heat transfer coefficient (refs. 7 and 8). The fusion of indiums from the different sources was also observed and reproduced in Fig. 4. The powdered sample shows also a diffuse peak, and the cause of this form seems to be due to the low heat transfer within the sample powder. Similar forms of peak were observed for the powder samples of tin and zinc.

The measured heats of fusion are summarized in Table 1. As is clearly seen, agreements are excellent except the powdered sample of zinc. The differences between the data obtained with the aluminum pan and that with the PTFE pan are at worst less than 2% for all samples including the fusion of polyethylene and the transition of potassium nitrate, both of which occur in certain wide temperature ranges. The heat of fusion of high density polyethylene was also measured with the two sorts of sample pan and is estimated by the method proposed in this paper and the conventional method with indium as the standard material. The data estimated by the conventional method are slightly less than those by the present method, and the cause of the difference seems to be the temperature dependence of the proportionality coefficient in the melting range of polyethylene, as is seen in Fig. 1.

As mentioned above, the accuracy of the conventional method depends on those of the heats of fusion of standard materials, and the recommended values differ from each other, as is seen in Table 2. Moreover, the conventional method needs many standard materials to obtain the temperature dependence of the proportionality coefficient in a wide temperature range. In contrast with this, the method proposed by the author needs only one standard material with the highly accurate data of the specific heat, so that the accuracy can be remarkably improved with less effort. Moreover, the same standard material

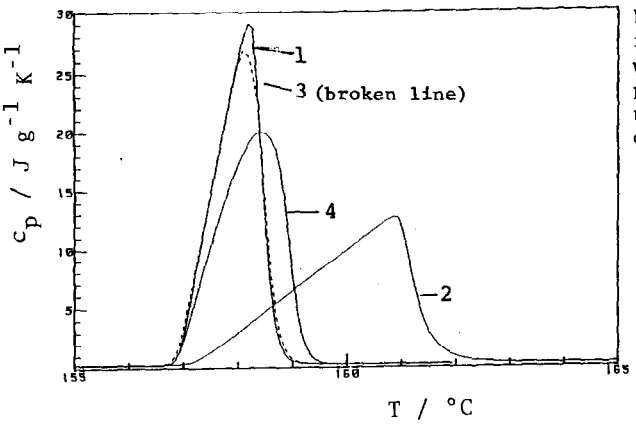

Fig. 4. Apparent specific heat capacity of indium from different sources with different sample pans; indicated curve numbers are the same as order in Table 1 below.

Table 1 Results of Temperature and Heat of Transition and Fusion

Sample	Purity (Source)	Sample Pan	T_m °C	ΔH J/g
In	99.999%	Al	156.9	28.4
In	99.999%	ptfe	157.2	28.9
In	a	Al	156.8	28.5
In	b	Al	156.9	28.5
Sn	99.999%	Al	231.7	60.3
Sn	99.999%	ptfe	233.2	60.0
Sn	a	Al	231.7	60.1
Sn	c	Al	232.0	60.3
Sn	b	Al	231.7	60.2
Pb	99.999%	Al	326.8	22.2
Pb	99.999%	Al	326.6	22.0
Pb	a	Al	326.5	22.2
Pb	c	Al	327.1	21.8
Zn	99.999%	Al	419.7	107
Zn	99.99% d	Al	419.9	106
Zn	e	Al	419.6	108
Zn	c	Al	420.8	103
PE	f	Al	125.2	224
				218*
PE	f	PTFE	124.8	228
				221*

Table 2 Recommended Values of Standard Materials

Materials	T_m °C	ΔH J/g	Reference
KNO_3	127.9	50.48	9
In	156.61	28.4	9
	156.15	28.4	5
	156.3	28.5	10
	156.60	28.4	11
	156.4	28.4	12
Sn	231.91	58.87	9
	232	58.87	5
	231.7	60.27	10
	231.88	60.46	11
	231.9	59.4	12
Pb	327.30	23.161	9
	327.4	23.02	5
	327.3	24.7	10
	327.47	23.01	11
	327.4	23.05	12
Zn	419.50	112.95	9
	419.5	113.0	5
	419.4	102.1	10
	419.47	108.4	11
	419	102.1	12

* Measured by the conventional method with In as the standard material.
a, Supplied by Rigaku Denki Co., Ltd.
b, Supplied by National Bureau of Standards (All are granular samples.)
c, Supplied by Perkin-Elmer Co.
d, Supplied by Bureau of Analysed Samples Ltd. (England) B.C.S. No. 19e
e, Purchased from Showa Chemicals Co., Ltd. (guaranteed grade)
f, Supplied by Mitsubishi Petrochemical Co., Ltd. (Yukalon HD-EX 40)

used in the conventional calorimetry can be used in the calorimetric measurements by DSC, and these accuracies can be discussed on the same base.

The author should make another point in this method. Generally, the specific heat capacity changes after the transition and the fusion, and this change causes also change in the base line of the DSC curve. Usually, the peak area is measured by drawing a straight line between points deviating from the base line in the leading and tailing regions, without any reasonable base to do so. By the present method, the heat of transition or fusion in these cases can be estimated reasonably from thermodynamic viewpoint, as is seen in Fig. 3.

It is also made clear that the PTFE sample pan is applicable to the accurate heat measurement. The PTFE sample pan is very useful for measurement of corrosive substances, such as molten salts, although the applicable temperature range is limited between about 320 K and 570 K, due to the crystalline transition and the fusion of the material.

REFERENCES

1) E. M. Barrall II and J. F. Johnson, "Thermal Characterization Techniques" (Ed. by P. E. Slade, Jr., and L. T. Jenkins), p. 1 (Marcel Dekker, 1970)
2) K. H. Breuer and W. Eysel, Thermochim. Acta, 57 (1982) 317.
3) D. C. Ginnings and G. T. Furukawa, J. Am. Chem. Soc., 75 (1953) 522.
4) D. A. Ditmars and T. B. Douglas, J. Res. Natl. Bur. Stands., 75A (1971) 401; D. A. Ditmars, S. Ishihara, S. S. Chang and G. Bernstein, ibid., 87 (1982) 159.
5) R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys" (John Willey & Sons, 1963)
6) E. F. Herington, Pure and Appl. Chem. (1974) 393.
7) T. Ozawa, Netsu Sokutei (Calor. Therm. Anal.), 4 (1977) 45.
8) Anonym, "Thermal Analysis News Letters", No. 9, p. 10 (Perkin Elmer Co., 1970).
9) D. D. Wagman, J. L. Jobe, E. S. Domalski and R. H. Schumm, "American Institute of Physics Handbook" (3rd Ed.) (ed. by D. E. Gray), p.4-222 (McGrow-Hill, 1972)
10) Handbook of Chemistry and Physics (60th Ed.) (CRC Press, 1963)
11) Instruction Manual supplied by Perkin-Elmer Co.
12) Instruction Manual supplied by Rigaku Denki Co., Ltd.