Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THERMOANALYTICAL INVESTIGATIONS ON MELTING AND FREEZING PROCESSES. CALORIMETRIC CALIBRATION OF DTA APPARATUS WITH METAL STANDARDS

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(Received September 30th, 1969)

ABSTRACT

Methods for thermometric and calorimetric calibration of a DTA-apparatus with relatively small time constants are shown. Several metals have been used for this purpose.

A special DTA sample holder for the registration of the differential temperature, and the sample and reference temperatures up to 1600°C, with a resolution better than 0.5°C, is described. A suitable theory includes a linear temperature change in the furnace, several heat resistances and the heat capacity of a non volatile sample. Simultaneous thermogravimetric control was carried out.

A slow heating rate yields more reproducible phase changes in material than a fast one. At the slow rate a separation between beginning and end of the change becomes obvious even with small samples.

The calibration curves can also be used for relatively small samples of a non-metallic material under the same environmetal conditions.

Melting processes proved to be more suitable for calibration than solidifications for reasons of reproducibility. Supercoolings have been observed without exception in form of characteristic temperature jumps.

INTRODUCTION

Differential thermal analysis (DTA) is used as a matter of routine in many laboratories today[2–6,8].

One method for the quantitative measurement of heats of reaction is the use of a substance of known heat of reaction instead of an inert reference material against which the unknown sample reactions or transition phenomena can be measured. It is often difficult, however, to find calibration substances which can be used over the entire temperature range involved.

We have, therefore, evolved a testing method using metal samples to enable a calorimetric calibration curve to be plotted; the same materials can also be used for calibrating the temperature axis. This calibration curve makes it possible to measure reaction heats of non-metallic samples, provided that measurements are taken with the same sample-holder arrangement and under similar test conditions.

It is essential in this connection that any change of weight that may occur, *e. g.* through oxidation of the sample resulting from the use of inert gas not completely free of oxygen or from volatilization or sublimation of the substance concerned, be determined by simultaneous weight recording.

TEST CONDITIONS

A. Set-up

The equipment used is a Mettler Thermoanalyzer. A description of this apparatus has already been published[8], so it will suffice for the present purpose to refer specifically to certain details only.

Fig. 1B shows the crucible carrier (T–TD3) used in these tests. Furnace temperature T_0, sample temperature T_p and reference temperature T_r are measured. The crucible carrier (Fig. 1B) had to be modified for this by transferring the furnace temperature thermocouple from the carrier to a position directly in contact with the furnace in the vicinity of the sample (Fig. 1A). Fig. 1C shows the circuit arrangement associated with the modified crucible carrier for recording sample and reference temperatures in addition to the differential reading. The crucible cups are made of Pt–Rh(10%), and Pt–/Pt–Rh thermocouples are used. The 0.35-mm (diameter) platinum wire linking sample and reference cell was replaced by one of 0.01 mm diameter giving improved insulation between the cells. The scale marked on Fig. 1B indicates the dimensions of the measuring head. The dimensions of the graphite crucibles used are: height 10 mm, diameter at top 5 mm, diameter at bottom 4 mm, wall thickness 0.5 mm, the capacity of the crucible being approx. 0.1 ml. The DTA and temperature amplifiers used are standard Mettler Thermoanalyzer components.

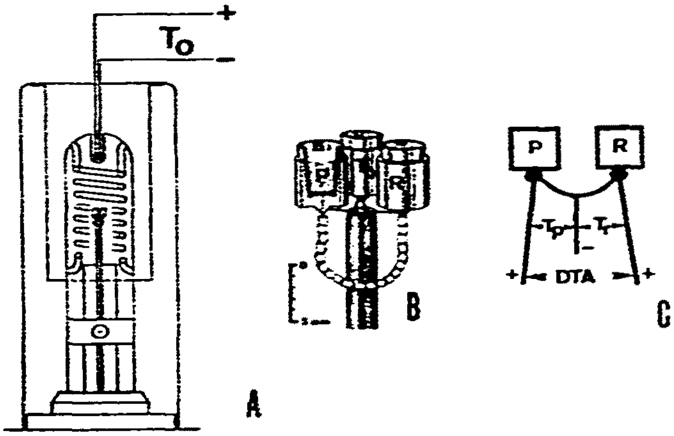

Fig. 1. A, Diagram of furnace with separate control element T_0. B, Crucible holder (type T–TD 3). C, Circuit diagram of modified crucible holder with additional connection for sample and reference temperature measurement. T_0 = furnace temperature; T_p = sample temperature; T_r = reference temperature; P = sample; R = reference substance; DTA = DTA-hot junction.

B. Test Procedure

Reproducibility of results is here of major importance, which means that identical starting procedures and test conditions must be maintained for all samples. Preliminary experiments were carried out to determine the most favorable working conditions. For instance, the chart speed (240 mm/h) is set according to the reactions or changes of state under observation, so as to obtain, at all heating and cooling rates, traces which can readily be evaluated. Further, the sensitivity of all temperature recordings (DTA curve, sample and reference temperature curves) is kept the same (500 μV) throughout, to detect the reasons for and origin of any external interference.

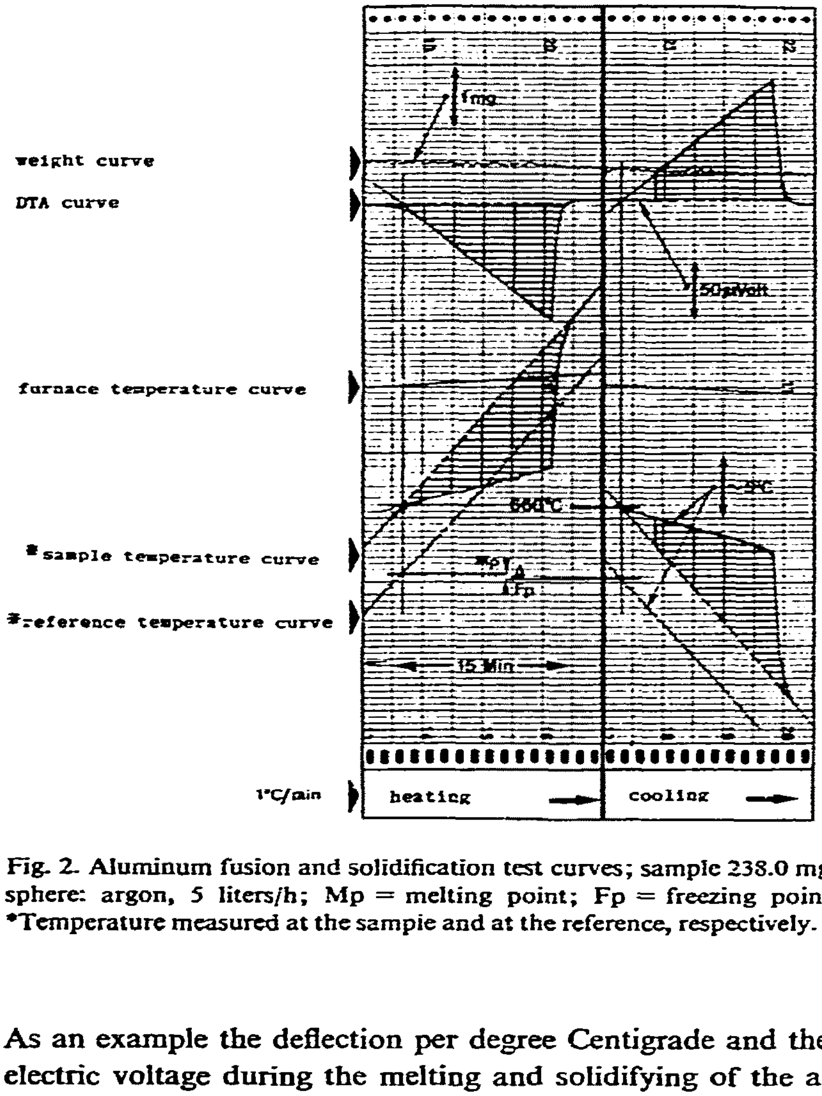

Fig. 2. Aluminum fusion and solidification test curves; sample 238.0 mg = 0.00882 mole; gas atmosphere: argon, 5 liters/h; Mp = melting point; Fp = freezing point; Δ = apparent difference. *Temperature measured at the sample and at the reference, respectively.

As an example the deflection per degree Centigrade and the corresponding thermoelectric voltage during the melting and solidifying of the aluminum are plotted on the axis of ordinates of the DTA and temperature curve (Fig. 2). The experiments were carried out with a standard type quartz furnace as used in the Mettler Thermoanalyzer[8].

THEORY

With the described experimental set-up it seems reasonable to assume the measurement, with practically no time-lag, of a temperature T which lies between sample temperature T^* and furnace temperature T_0 in accordance with the expression

$$T = \frac{R_a T^* + R_k T_0}{R_a + R_k} = T_p \tag{1}$$

in which R_a is the *external thermal resistance* between furnace and measuring point and R_k *a contact resistance* between sample and differential measuring point. The exothermic or endothermic heat effect, Q, resulting from chemical reactions or crystal transitions can be determined with the aid of the equation

$$Q = \frac{1}{R_a} \int_0^\infty \Delta T_b \mathrm{d}t \tag{2}$$

in which ΔT_b is the transient deviation from the base line during a DTA peak due to the thermal effect. Given a constant chart speed and a linear heating rate within the range concerned, the time integral is proportional to the DTA peak area.

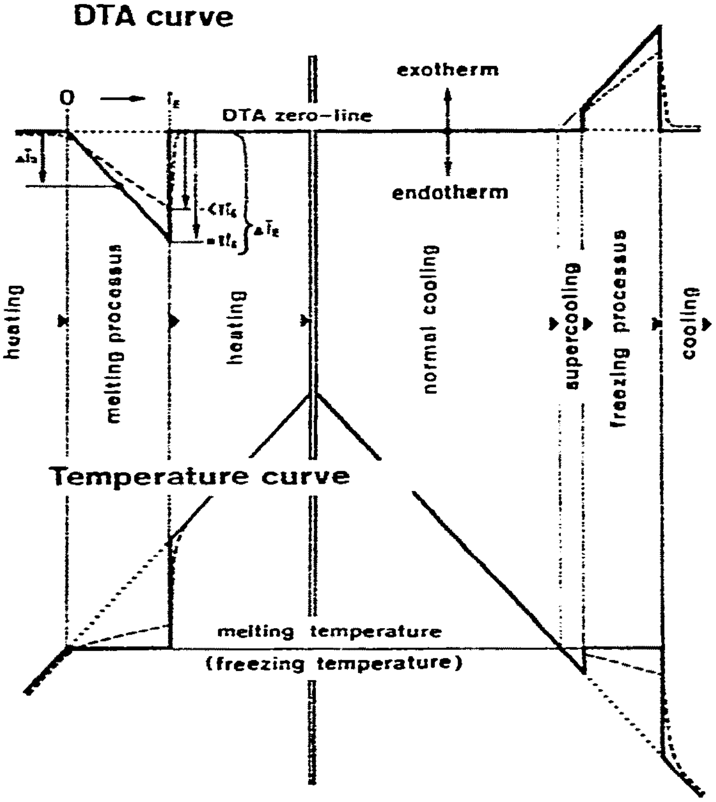

Fig. 3. Theoretical curves for differential temperature and absolute temperature curves during fusion and freezing; ———— ideal curves for pure non-volatile sample, with extremely small time constant ($\ll t_E$) and effective thermal contact ($R_k \to 0$); .... ideal base line during phase change; – – – – – curves with reproducible contact resistance for both cells ($R_k \neq 0$).

In a DTA run it is very desirable that the base line be straight, that is to say, that $\Delta T \approx \Delta T_b$. In many cases, however, the position of the base line cannot be precisely determined, particularly when the heat effect is such that $dQ/dt = 0$ and the heating rate (v) is high. Perfectly horizontal base lines can be assumed for both T and ΔT without loss of accuracy in the analytical results obtained only under constant temperature conditions ($v = 0$).

Given linear temperature control, it can be deduced from Eqn. (1) that

$$T_0 = T^* + v(R_a + R_k)C^* \tag{3}$$

for the normal case in which the heating rate v, is the same for furnace and sample and no appreciable thermal reaction occurs. Both the heat capacity, C^*, of the inserted sample and the relevant resistances, R_a and R_k, should, in initial approximation, be independent of temperature. Similar equations to Eqn. (1) and (3) apply to the symmetrically placed reference cell. The validity of Eqn. (3) can best be checked against the straightness of the DTA base line in agreement with the linearity of the sample-temperature curve. Given a constant furnace heating rate, the dependence of the differential temperature curve on the sample temperature is readily seen, particularly in connection with slow fusion or solidification of pure samples (Figs. 2 and 3). Provided the time constant, $(R_a + R_k)\ C^*$, is very small in comparison with the conversion time, t_E, we get, by initial approximation, for isothermal processes of this kind

$$\frac{dT}{dt} = \frac{R_k}{R_a + R_k} \cdot v \tag{4}$$

and

$$T = T^* + \frac{R_k}{R_a + R_k} \cdot vt + R_k \cdot C^* v \tag{5}$$

in agreement with Eqn. (1). The time base, $t = 0$, relates to the point of intersection between the linearized curve portions in accordance with Eqns. (3) and (4).

Even with pure sample materials, freezing (as opposed to melting) is neither isobaric nor precisely isothermal as a rule, due to the difference in density between enclosed liquid phase and already solidified material at the edge of the sample, particularly if pronounced supercooling has taken place at an earlier stage. For these reasons, it is preferable to base the thermometric and calorimetric calibration of the apparatus on the melting process. Disregarding $R_k C^* \cdot v$, the point of intersection of the DTA base line and the melt isotherm, $t = 0$, can be used for direct determination of the isothermal conversion temperature or to carry out thermometric calibration of T.

In an isothermal melting process,

$$-Q = n\Delta H = \frac{v t_E^2}{2(R_a + R_k)} + C^* v t_E \tag{6}$$

can be used in place of Eqn. (2), n being the molar number, ΔH the molar heat of fusion, and t_E the time for completion of the melting process. This terminal point is clearly indicated by the coincident change in slope of the temperature curve and DTA curve (Figs. 2 and 3). Thus, in the particular case of isothermal transitions, determining the DTA base line and graphically measuring actual peak area becomes unnecessary. The maximum endothermic deviation from the original height of the DTA line

$$\Delta T_E = t_E \left(v - \frac{dT}{dt} \right) \tag{7}$$

is identical with ΔT_b (max.) only when the base line runs horizontally. Substituting Eqn. (4) in Eqn. (7) gives

$$\frac{R_a}{R_a + R_k} = \frac{\Delta T_E}{v t_E} \tag{8}$$

this latter being a number smaller than unity, which represents the ratio between the temperature effects occurring at the sample temperature thermocouple and in the sample, respectively. From Eqns. (6) and (8) it follows that

$$R_a = \frac{t_E \Delta T_E}{2(n \Delta H - C^* v t_E)} \tag{9}$$

and

$$R_k = \left(1 - \frac{\Delta T_E}{v t_E} \right) \cdot \frac{v t_E^2}{2(n \Delta H - C^* v t_E)} \tag{10}$$

A calorimetric calibration of the dynamic apparatus can be carried out over the measured DTA range from ΔT_E and t_E, given known values for v, n, ΔH, and C^* in accordance with Eqns. (9) and (10).

PROCEDURE

The tests were carried out on the described equipment[8]. The samples were selected to enable calibration to be carried out over a temperature range extending from 25 to 1000°C. Table I contains the data relating to origin, purity and melting or freezing point of the substances concerned. The relevant thermodynamic data were taken from the literature[1].

The test samples were lathe-turned from ingot or bar stock to fit the shape of the test crucible. Care must be taken to ensure that no contaminating matter finds its way into the sample during machining and that its surface is thoroughly cleaned afterwards. The crucible material used was spectroscopically pure graphite ("Carbopur" 1 SP 2, mfg. by Schunk & Ebe, of Giessen).

Fig. 4 shows, diagrammatically, the graphite crucible with the metal sample inserted and the crucible holder together with the thermocouple. Fig. 5 shows the deformation of the metal sample due to surface tension after the first melting operation. The resulting alteration in the degree of contact between sample and crucible wall causes noticeable modifications in the shape of the DTA peak which means loss of reproducibility. To overcome this drawback, a covered crucible was used, designed to ensure that the cavity was completely filled by the sample, the weight of the cover being such as to prevent sample deformation and to maintain unvarying contact between sample and crucible wall. The use of a cover has the further advantage of reducing heat exchange between the exposed surface of the sample and the furnace,

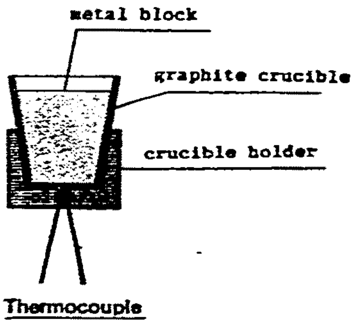

Fig. 4. Diagram of DTA sample holder with crucible, showing location of sample-temperature measurement junction.

TABLE I

DATA OF THE CALIBRATION SUBSTANCES

Calibration substance	*Origin*	*Purity (%)*	*Sample weight (mg)*	*M.p. of calibration substance (°C)*	*M.p.*[a] *(°C)*	*ΔH Fusion*[a] *(kcal/mol)*
Silver	Métaux Précieux SA Zurich	99.99	930.8	960.0	960.9	2.79
Aluminum	NBS Wash. D. C. Sample 44e	pure	238.0	660.0 ±0.2[b]	660.2	2.57
Lead	NBS Wash. D. C. Sample 49e	pure	989.8	327.417 ±0.005[b]	327.43	1.141
Bismuth	Fluka Buchs No. 95372	99.999	663.1		271.01	2.63
Tin	NBS Wash. D. C. Sample 42f	pure	662.9	231.885 ±0.01[b]	231.91	1.68
Gallium	Fluka Buchs No. 48330	99.999	499.8		29.78	1.335

[a] Acc. to A.I.P.[1]. [b] National Bureau of Standards: Standard Sample/Freezing Point on International Practical Temperatures Scale (1948).

rendering it less substance-dependent particularly at high temperatures where heat radiation is a big factor.

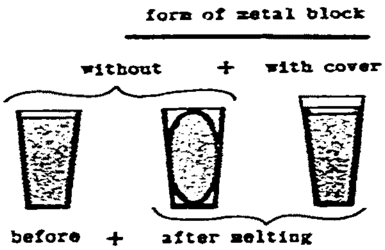

Fig. 5. Sample metal-pellet deformation on fusion in open and in covered crucible.

Each metal used for calibration was heated above the melting point and cooled off prior to beginning actual test measurements. Cycles of melting and freezing, each conducted at a different rate of heating and cooling (0.5, 1.0, 1.5, 2.0, 4. 0, 6.0, 8.0,

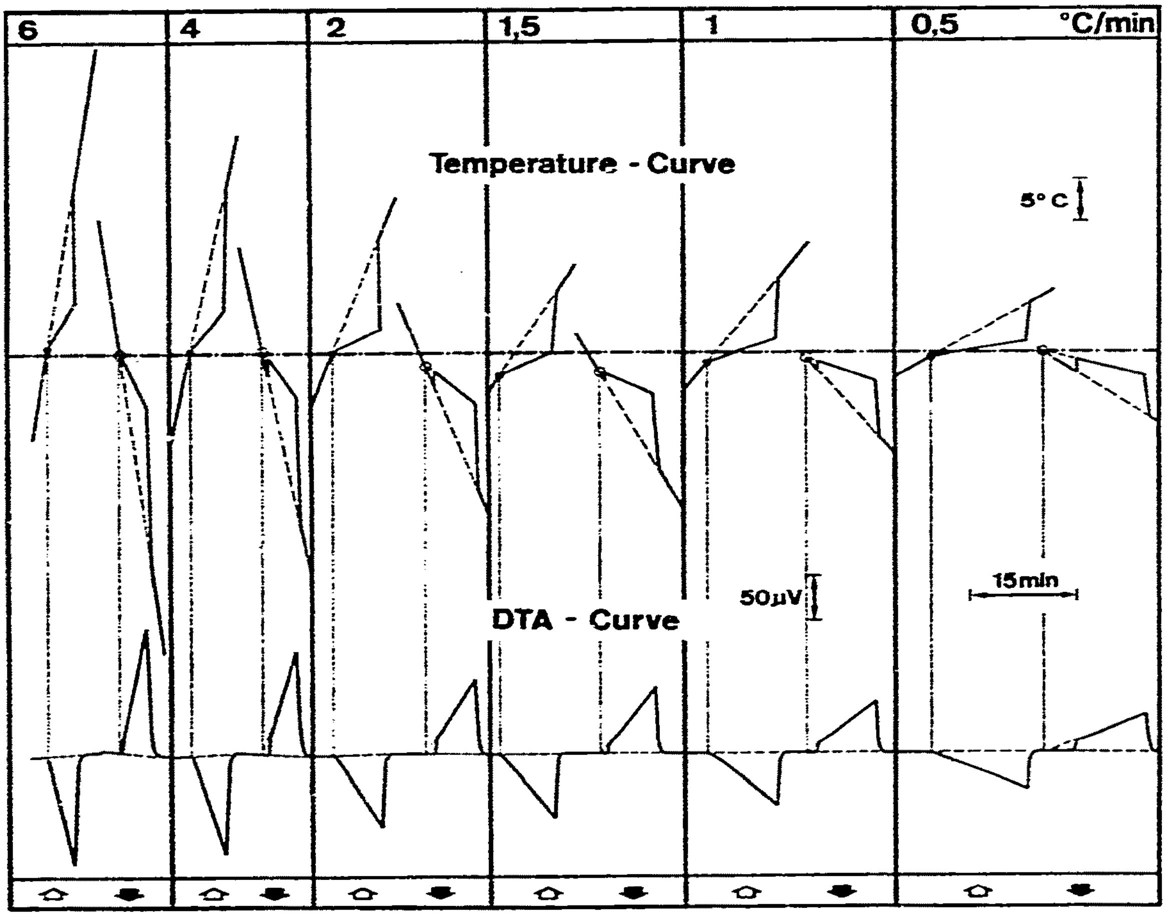

Fig. 6. Differential and absolute temperature curves recording fusion and solidification of silver at various heating and cooling rates. Weighed Sample 930.8 mg = 0.00863 mole; ⇑ linear heating of sample, ○ freezing point, ● melting point, ⬇ linear cooling of sample, . — . — . melting temperature of silver.

and 10.0°/min) were recorded (see example, Fig. 6). All tests were carried out in an atmosphere of repurified, dry argon (flow rate over sample approx. 5 liters/h). It is of the utmost importance that the gas-flow rate be kept constant throughout the whole of a test run in order to prevent any heat transfer fluctuation. The dimensions of the cylindrical metal pallets were as follows: diameter at top 4 mm, height 9 mm, diameter at bottom 3 mm. The respective sample weights of the various metals used for calibration are given in Table I. Temperature and time scales can be read off on the individual curves. Generally speaking, the loss of weight in the course of the tests was negligible, being of the order of approx. 0.1 mg, and is attributable to crucible graphite loss through firing. The reference substance used was 60-mesh aluminium oxide (Dynamit Nobel), of which 140.3 mg was weighed out for each test and vibration-charged in a graphite crucible^9. The diagrams reproduced in Fig. 7 show analogous results obtained with water and adipic acid. The fusion and solidification curves obtained are similar to those obtained for metals. These tests were carried out in open crucibles, so that loss of weight due to evaporation was to be expected. Comparable tests can of course be carried out in a similar manner with hermetically sealed crucibles.

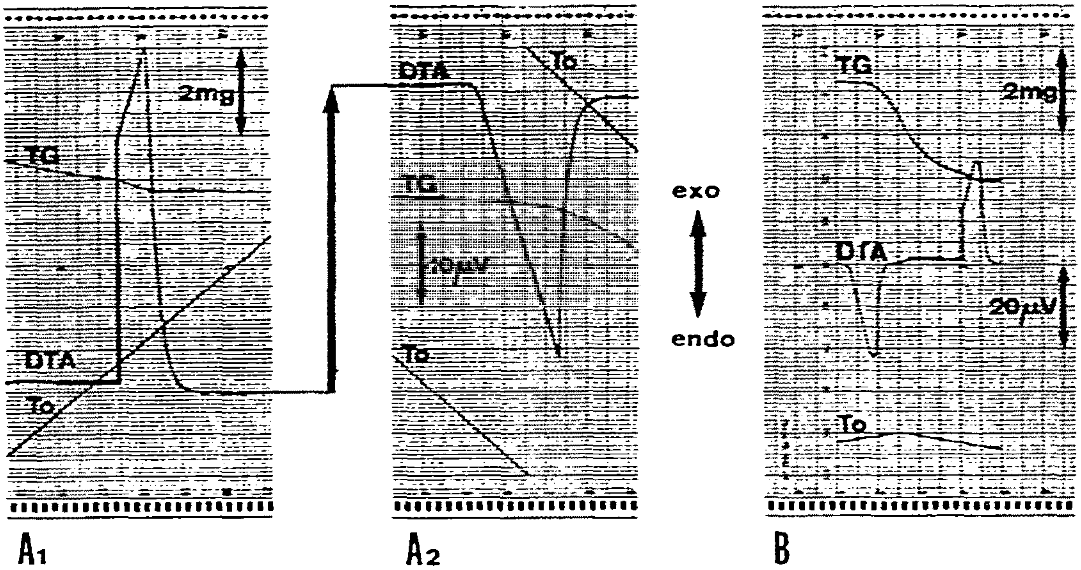

Fig. 7. A_1, A_2, DTA of freezing and melting of water. B, DTA of melting and freezing of adipic acid. (T_0 = Furnace temperature, TG = Weight curve).

RESULTS

Test series using bismuth, lead, aluminum and silver (for silver see Fig. 6) show that the points of intersection between linearized test temperature curves before and after melting or solidifying are practically unaffected by heating rate. The thermoelectric voltages* appropriate to melting temperature according to the A.I.P. Tables[1] (reference junction at 25°C) were compared with the experimentally determined mean thermoelectric voltage (on fusion or solidification) corresponding to the beginning of melting in each. The thermoelectric voltage measured at the sample thermocouple was regularly somewhat lower than expected, the discrepancies amounting to between 58 and 98 μV in the 271–960°C temperature range (Fig. 9A). This corresponds to an error of between 6,4 and 8,3°C in the T reading.

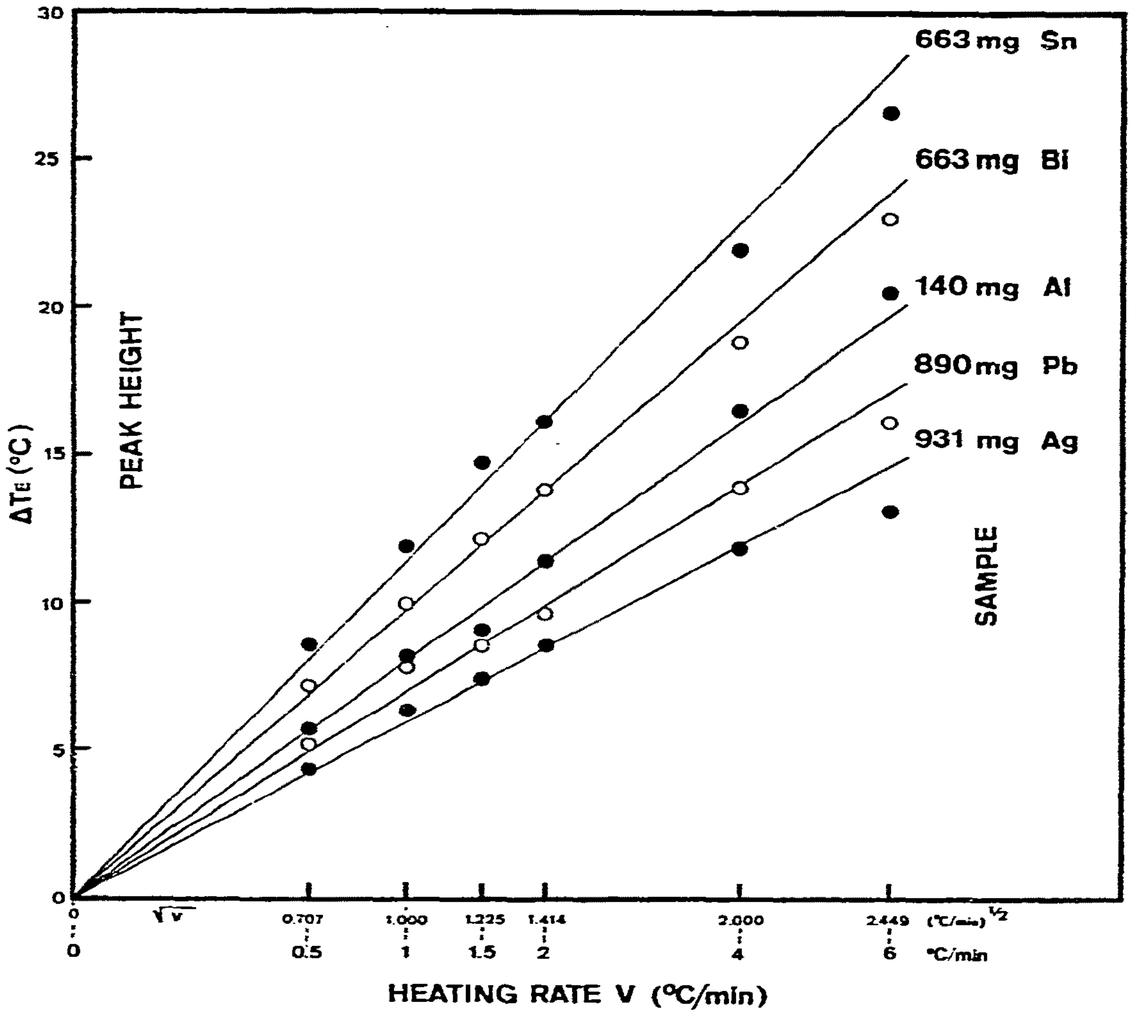

Fig. 8. Actual melting peak heights of different substances at various rates of heating.

Reproducibility of the intersection-point plot at the beginning of freezing was frequently less satisfactory and was, therefore, not used for thermometric calibration. Furthermore, systematic variations as compared with the melting process were

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*Pt–/Pt–Rh (10%)[7].

observed with identical substances, particularly in cases in which marked supercooling occurred.

The thermal resistances of the sample cells used were calculated with the aid of Eqns. (9) and (10) from the DTA curves recorded on fusion, using ΔH values taken from the literature[1]. The reference heating rate (°/min) showed no irregularities. On absolute and differential temperature curves, thermometric deviation from base line remained the same at all times, except for slight non-systematic fluctuations.

Table II gives the mean thermal resistance values at various heating rates between 0.5 and 8.0°/min:

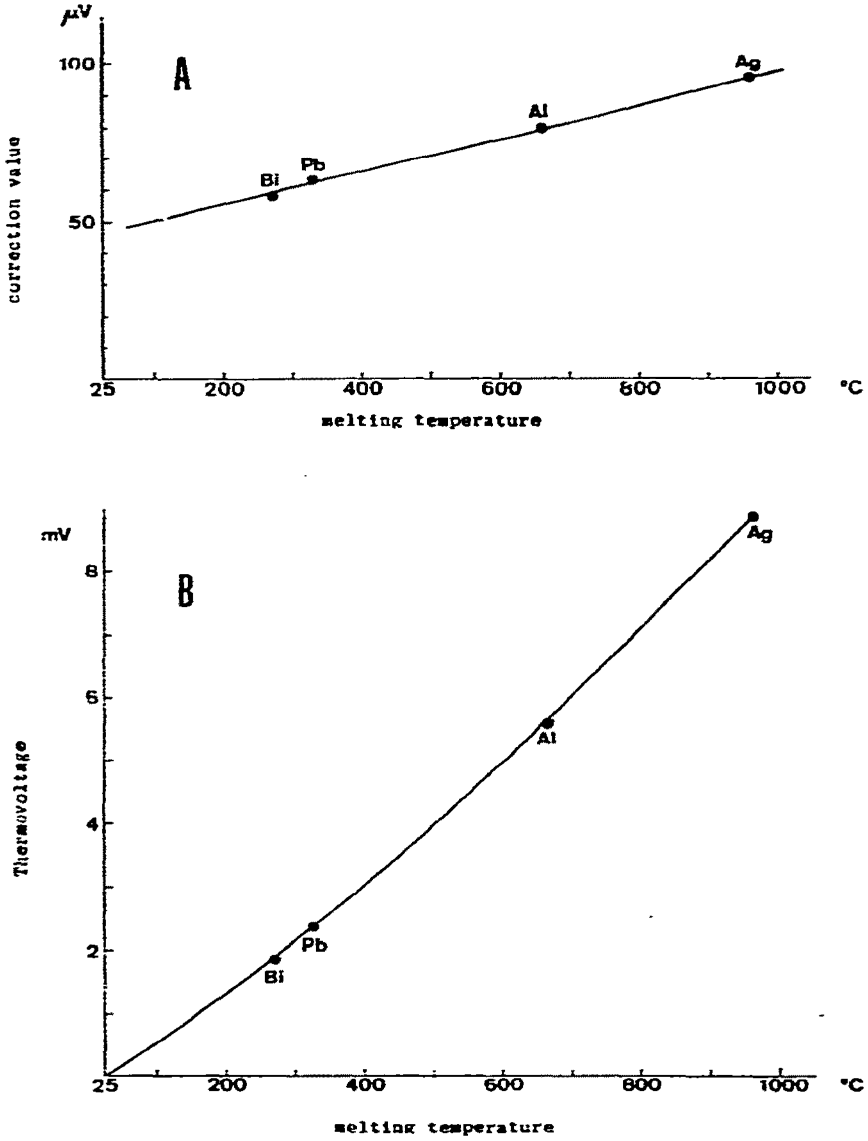

Fig. 9. Calibration of thermocouple (Pt-/Pt-Rh, 10%). A, Correction Factors, increasing linearly with rising temperature (59 μV at 281 °C); B, Comparison of required and recorded melting-point figures at various temperature readings (reference temperature 25 °C).

TABLE II

CONTACT AND EXTERNAL RESISTANCE OF DIFFERENT SUBSTANCES

	Ga	*Sn*	*Bi*	*Pb*	*Al*	*Ag*
R_a*	12.55	9.34	7.27	6.54	2.22	1.23
R_k*	6.6	1.7	1.4	2.0	1.0	0.6

*Min.·°C/cal.

The functional dependence of the external heat transfer rate R_a^{-1} on temperature is shown in Fig. 10.

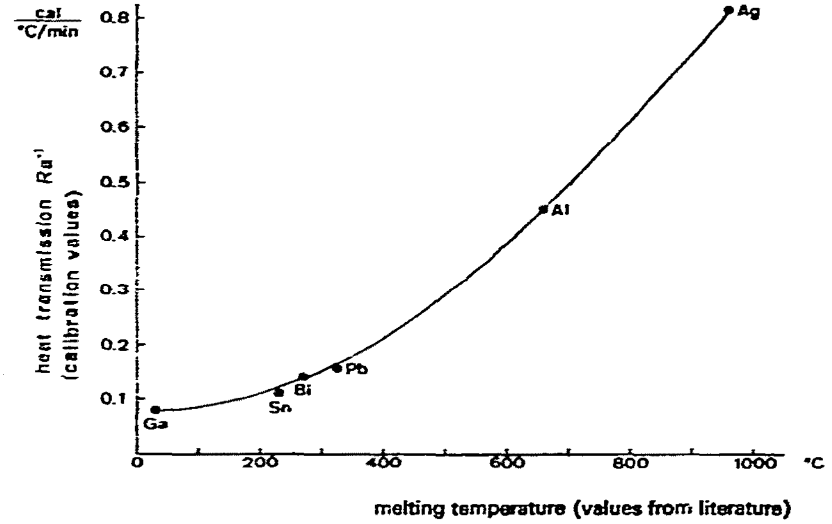

Fig. 10. Calorimetric calibration curve (DTA) under specified test conditions.

DISCUSSION

The shape of the DTA curves (or temperature curves) is qualitatively interpretable in the same way for all fusible pure substances (Fig. 7). According to Eqn. (2) the peak area is proportional to external resistance R_a and, for this reason, approximately adiabatic conditions are desirable for the carrying out of tests of this kind. Samples should be small to reduce contact resistance R_k to a minimum and to enable the time constant R_aC^* to be small. As temperature increases, the heat transfer rate rises (Fig. 10), particularly in regard to radiation. For this reason, peak areas corresponding to the same ΔH values become smaller at higher temperatures than at lower. Excessively small peak areas may also occur as a result of inadequate insulation between the sample and reference.

The curves obtained in all tests carried out at slow cooling rates and sufficiently high chart speeds have given indication of more or less marked supercooling phenomena in the form of characteristic temperature jumps (see Fig. 6). Linearity of deviation from the original level of the DTA line both on fusion and on normal solidification, is assured only at constant contact resistance R_k and pressure and at relatively slow, constant furnace heating rate. Contact resistance R_k was apparently, even in the case of metals of high conductivity, dependent to a great extent on the nature of the sample substance concerned and on the location of its phase limits. In contrast to contact resistance R_k, external resistance R_a proved, as expected, to be very reproducible. This factor is dependent on the nature of the sample, as is borne out by the fact that freezing and melting peak area is approximately the same for any one sample (*e.g.* as shown in Fig. 2). On the other hand, gas-flow rate appears to affect R_a to a marked extent.

In the course of fusion or solidification, slight but noticeable displacements of the DTA and sample temperature curve base lines were found to occur, particularly at abrupt changes of furnace temperature. These displacements could be due to several causes, *e.g.* varying thermal contact between crucible wall and sample or alterations in specific heat value attendant on changes of state or of aggregation. The theoretical prediction that, in respect to the melting of a pure sample, maximum temperature deviation ΔT_E and melting time t_E in the linearized DTA curves, at relatively small time constant (R_a+R_k) C^*, would have an approximately constant product and be approximately proportional or inversely proportional to the root of the heating rate proved experimentally demonstrable (see Figs. 3, 6, and especially 8).

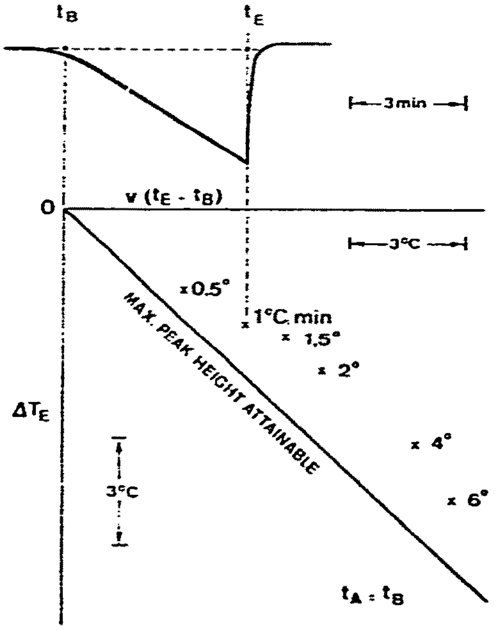

Fig. 11. Actual melting peak heights of aluminum at various rates of heating.

The same applies to solidification on cooling, provided supercooling can be avoided. Fig. 11 shows the actual melting peak heights of aluminum as a function of the heating rates as well as the theoretically attainable maximum values[10,11].

The thermogravimetric curves confirm that the weight of metallic samples remains practically unaltered, although this is not the case with adipic acid and water, both of which give off water vapor in the liquid phase (Fig. 7). After melting, adipic acid is converted into the anhydride. Fig. 7 shows the qualitative behaviour of both substances without quantitative data. In all other respects, the recently published "Recommendations"[5] were compiled with in the compilation and description of the test data.

ACKNOWLEDGMENT

The authors wish to express their thanks to Mr. A. W. Kunz for his careful and meticulous conduct of the tests forming the subject of this paper.

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