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Heat Measurement by Differential Thermal Analysis

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A new method of measuring the heat of transformation is described; the apparatus used in quantitative differential thermal analysis is calibrated by using an electrical heater inserted in the sample cell. The heats of transformation obtained by using the proportionality coefficient thus calibrated are then compared with the reported values. Good agreements are obtained between them.

In a previous paper,[1] one of the present authors reported a new method of measuring heat by differential thermal analysis (DTA). In the apparatus used in this method, a sample cell is placed in a cell holder of a thermally-inert material set in a cavity of a metal block, while a thermocouple is inserted between the cell and the cell holder. In this arrangement, the cell holder serves as a heat-flowmeter in which the temperature gradient occurs; its magnitude corresponds to the heat flowing into the sample cell, and the temperature difference measured is the difference between the temperature gradient in the cell holder of the sample and that of the reference material.

It was also pointed out in the previous paper that

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one of the most serious disadvantages of DTA is the necessity of calibrating the apparatus at the desired temperature and under the desired conditions by using substances with known heats of transformation at that temperature; thus one can not use DTA to measure quantitatively the heat of transformation in a field where direct methods of calorimetry can not be applied. This limitation restricts the potential usefulness of DTA. Since the heats obtained with the DTA apparatus calibrated by the above method contain some error due to inaccuracy in the latent heats of the calibrating substances, the results obtained by DTA are not as accurate as those obtained by other direct methods. Furthermore, this method of calibration is very tedious, because the proportionality coefficient between the peak area and the heat of transformation is a function of the temperature, and usually only one or two values are obtained in each run.

Several methods of calibrating the apparatus with a heater inserted in the sample cell and supplied with a given amount of electric energy have been suggested.[2-4] The measurement of heat with the apparatus thus calibrated has, however, not been investigated thoroughly; few reports have been published on the heats of transformation obtained with an apparatus calibrated by this independent method.

Some attempts to overcome the above-mentioned limitation of DTA have been made in our laboratory; the technique of electrical calibration has been varified to be satisfactory. By this absolute method of calibration, we can apply DTA to a field where its unique features and advantages can be demonstrated.[1] Moreover, since the apparatus is calibrated absolutely, the heats of transformation obtained by this method do not suffer from the error of other methods. In this paper, the method of calibration will be described and examined by an analysis of variances, and the heats of transformation of several substances obtained by this method will be compared with the reported values.

Experimental

Apparatus. The apparatus used is almost the same as reported in the previous paper[1] except for the following few improvements: the cell holder is of a new ceramic; the junction of the thermocouple is fixed with alumina paste (Nishimura Kogyo Co., Ltd.) in a groove cut on the inner surface of the cell holder, as is shown in Fig. 1, and nickel foil is inserted between the cell and the cell holder to improve the thermal contact between them (in some cases the junction is soldered to the foil). The upper part of the metal block is not used. The temperature is controlled by using a PI-type program controller and a SCR regulator purchased from the Ohkura Electric Co., Ltd.

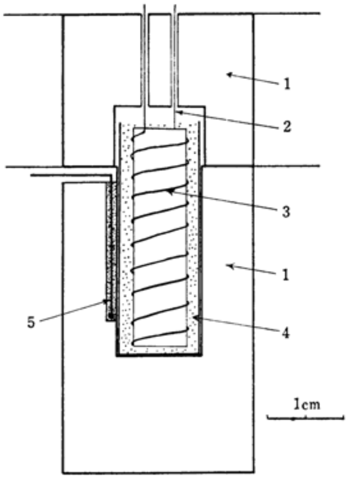

Fig. 1. The arrangement of the cell, the cell holder, the thermocouple and the heater. 1, the cell holder; 2, the lead of the heater; 3, the heater; 4, α-alumina; 5, the thermocouple.

The Method of Calibration. Two types of electric heaters are used, both of the same height as that of the cell; in one of them the iron-chromium heating wire is wound on an alumina insulating tube 6 mm in outer diameter, while the second one consists of two concentric alumina tubes, 6 and 3 mm in outer diameter, wound on the outside with the iron-chromium wire. The lengths of the wires of all the heaters are the same; the diameter is 0.35 mm, and their resistances are 20 ohm. The heater is inserted in the sample cell concentrically, and the gap is filled with 200—300 mesh powder of α-alumina supplied by the Nishio Kogyo Co., Ltd. The leads of nickel (0.3 mm in diameter) are connected to the iron-chromium heating wire by spot welding, the welded points being located in the cell so that the heat produced is dissipated only inside the cell. These leads pass through the thin hole drilled in the top of the cell holder, as is shown in Fig. 1.

The electric power is supplied from a d.c. regulated source purchased from the Showa Electronics Co., Ltd. (155 M). The voltage and the current are measured with a voltmeter and a milliammeter respectively, both of them of $\pm 0.5\%$ precision and purchased from the Yokogawa Electric Works, Ltd. The period of supplying the power to the heater is measured by a stopwatch

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TABLE 1. THE HEATS OF TRANSFORMATION OBTAINED BY THE PRESENT METHOD OF DTA

Sample	This work		Literature		Ref.
	Temp. °C	ΔH cal/g	Temp. °C	ΔH cal/g	
KNO_3[a)]	127	13.0	128	13.8	5
			127.5	11.78	6
			—	12.83	7
			127.9	12.05	8
KNO_3[a)]	331	28.1	338	27.7	5
			334.3	22.75	8
			—	27.20	9
$AgNO_3$[a)]	164	3.03	160	3.9	5
			160	3.44	10
			158.9–160.6	3.49	11
$AgNO_3$[a)]	207	17.0	211	16.2	5
			210	17.57	10
$KClO_4$[a)]	296	26.0	299.8	23.7	12
$PbCl_2$[b)]	501	20.9	498	20.9	5
Stearic acid[c)]	54	49.9	69	47.5	13
			—	59.1	14

a) The G. R. grade reagent manufactured by Kanto Chemical Co., Inc.

b) Recrystallized from E. P. grade reagent (Kanto Chemical Co., Inc.).

c) Purified sample kindly supplied by Professor Kambe of the Institute of Space and Aeronautical Science, the University of Tokyo.

with an accuracy of 1/10 sec. The supplied energy is then evaluated from these observed values. The calibration is made under two conditions, *i.e.*, with the apparatus maintained at a constant temperature and with the apparatus heated (or cooled) at a constant rate.

Materials. The substances used for the measurement of the heat of transformation are listed in Table 1, as are the manufacturers and the method of purification. The reference material is a 200—300 mesh powder of α-alumina supplied by the Nishio Kogyo Co., Ltd.

Results and Discussion

In this type of apparatus, the peak area, A, of the differential thermogram is proportional to the heat evolved or absorbed in the sample as has already been described in the previous paper:[1)]

$$\Delta H \cdot M = K \cdot A \tag{1}$$

where ΔH is the heat of transformation per unit of weight and where M is the weight of the sample. The proportionality coefficient, K, is given by the following expression:

$$K = 2\pi l \lambda_h / \log (R_o/R_i) \tag{2}$$

where R_i and R_o are the inner and the outer radii of the cell holder; l, the length of the cell, and λ_h, the thermal conductivity of the material of the cell holder. Since the proportionality coefficient contains λ_h, it is a function of the temperature. If the above relationship holds and if the heat flowing out through the leads is negligibly small, the proportionality coefficient calibrated electrically at a given temperature should be independent of the type of the heaters, the power supplied to the heater, and the supplying period, and the proportionality coefficients calibrated with the two types of heaters should lie on the same curve when it is plotted against the temperature.

First, the calibrations are made at 350°C with the first type of heater; in this case, the supplied energy is constant and equal to 18 cal, but the periods of dissipating the heat are changed inversely with the power. The thermograms obtained are reproduced in Fig. 2, while the calibrated coefficients are plotted against the period in Fig. 3. Apparently, the coefficient is independent of the period of heating and of the power applied.

Second, the analysis of variances was made on a coefficient calibrated at constant temperatures by using the first type of heater. The elements of the analysis are the voltage and the period of dissipating the heat, the voltages being 2, 3 and 4 V and the periods, 60, 150, and 300 sec. The results of the analysis at the highest temperature are shown in

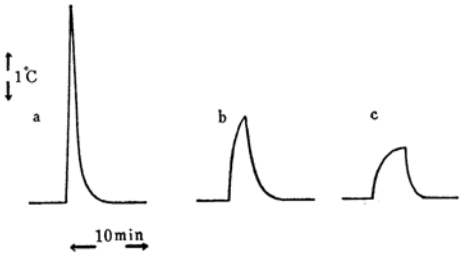

Fig. 2. The differential thermograms produced by a given amount of electrical energy; the power and the period of the dissipation are changed. a, 65 sec; b, 145 sec; c, 250 sec.

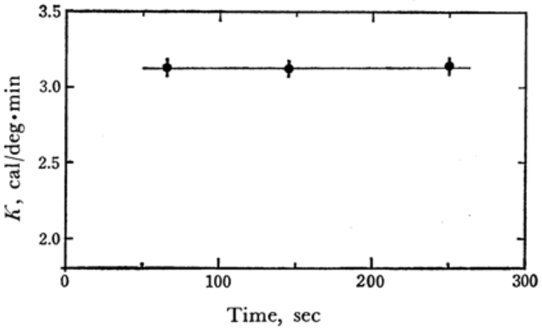

Fig. 3. The proportionality coefficient calibrated by using the thermograms shown in Fig. 2. The range shown is the standard deviation.

TABLE 2. THE RESULTS OF THE ANALYSIS OF VARIANCES OF THE PROPORTIONALITY COEFFICIENT AT 500°C

The element	D. F.	S. S.	M. S.	F.	
Voltage	2	2	1	<1	not significant
Period	2	25	12.5	2.9	not significant
Error	4	17	4.3	—	
Sum	8	44	—	—	

Table 2. The other results, at different temperatures, are the same as those shown in Table 2. As is clear from Table 2, the power and the period have no detectable influence on the calibrated proportionality coefficient. The percentages of the standard deviation are less than ±2%.

Next, we checked the heat flowing out through the leads of the electrical heater; potassium nitrate is placed in the cell with the first type of heater and the proportionality coefficient is estimated by measuring the peak area produced by the transition of potassium nitrate at 128°C. The proportionality coefficient thus obtained is compared with the proportionality coefficient obtained by using potassium nitrate with no heater. These values are the same within the range of experimental error. From these results, we may conclude that the heat flowing out through the leads is negligibly small, so we can calibrate the cell holder, *i.e.*, the heat-flow-meter, by this electrically-calibrating method.

Then, we calibrated the cell holder, heating (or cooling) the system at a constant rate of 60°C/hr. The two types of heaters are both used. The calibrations are made intermittently, and the coefficients are obtained as a function of the temperature. These coefficients are plotted in Fig. 4. In this case, the coefficients are independent of the type of heater. Thus, the calibration of the cell holder can be made easily and quickly.

Finally, the heats of transformation of several substances at a rate of heating of 60°C/hr were measured by using the proportionality coefficients given in Fig. 4. The results are shown in Table 1. The percentage of the standard deviation for each run is estimated to be about ±3%. The agreement between the present results and the reported values is satisfactory.

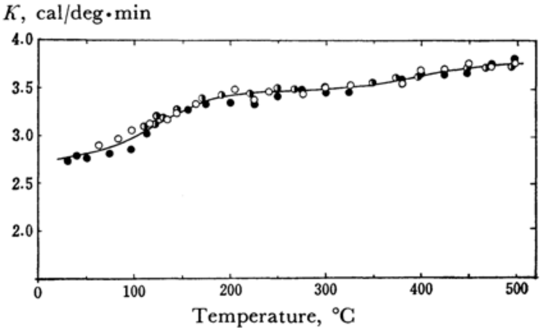

Fig. 4. The temperature dependency of the proportionality coefficient calibrated by using the two types of the heaters: the 1st type of the heater at heating stage (○), the 1st at cooling stage (◑) and the 2nd at heating stage (●).

We may conclude that the above-mentioned electrical and absolute calibration of the cell holder is satisfactory and time-saving, that the information on the heats of transformation of the standard calibrating substances is unnecessary, and that differential thermal analysis can be regarded as an independent method of calorimetry, with unique features. Thus, the differential thermal analysis of this type is reduced to the dynamic operation of Calvet's conduction calorimeter;15) it will be applied to unique fields of research in the future. The precision of differential thermal analysis seems to be governed mainly by the precision of the d.c. amplifier, the recorder, and the measurement of the peak area of the recorded curve.

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