A Microcell for Differential Thermal Analysis*

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(Received August 31, 1964)

In the differential thermal analysis of materials, it is often necessary to use only a small amount of a sample. When the amount of sample is less than 50 mg. in weight, the following methods have been used: (i) The heating rate has been increased in order to obtain a sharper peak. (ii) The sample has been diluted with a large volume of the reference inert material.[1,2] (iii) The sample has been sandwiched between two layers of the reference inert material.[2] (iv) A melting-point capillary tube has been used as a sample cell.[3]

However, each of these methods has some disadvantages. Method i is defective in the drifting of the peak temperature and base line as the heating rate is increased. Methods ii and iii usually involve a troublesome preparation of the sample, such as the homogeneous mixing of sample and reference material. Moreover, relatively large amounts of the sample, more than 10 mg. in weight are needed. In method iv a thermocouple must be inserted directly into the sample, so that the perfect cleaning of the thermocouple before and after measurement is necessary, and care must be taken to position the thermocouple centrally in the tube.

In this work, in order to carry out the differential thermal analysis (DTA) conveniently using a small amount of a sample, simple microcells were used, and the effects on the DTA peak of the amount of sample, the heating rate, the heat capacity of the cell, and the heat transfer coefficient between the cell and the metal block were investigated. The present study has been confined to the melting of benzoic acid.

Experimental

Benzoic Acid. — Benzoic acid, as a standard sample for combustion calorimetry, was obtained from the Resources Research Institute, Japan, and was used without further purification.

Microcells.—The microcell body was a 3 mm.ϕ× 9 mm. platinum rod with two holes, 2 mm.ϕ×3mm. and 2 mm.ϕ×5 mm., on the top and the bottom of the body respectively. The top hole was used as a sample hole, and the bottom hole, as a thermocouple hole. The caps, obtained from the Ishifuku Metal Co., were also made of platinum. The microcell body and the cap are shown in Fig. 1.

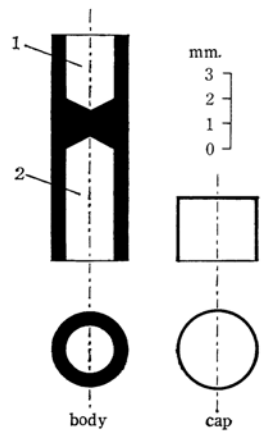

Fig. 1. Microcell.
1, Sample hole; 2, Thermocouple hole

Metal Block.—The metal block body and the lid, shown in Fig. 2, were made of aluminum. The body was a 27 mm.ϕ×27 mm. cylinder with three 6 mm.ϕ×15 mm. holes, and the lid was a 27 mm.ϕ ×5 mm. disk. The microcells and the metal block shown in Fig. 2 were so assembled that the microcells were supported only by the thermocouple and were not in contact with the wall of the metal block.

Apparatus.—A Rigakudenki Co. Automatic Recording Differential Thermal Analyzer and Adiabatic Calorimeter was used. The differential temperatures were measured by a two-junction alumel-chromel thermocouple 0.3 mm.ϕ in diameter.

Differential Thermal Analysis.—Samples, about 1—2 mg. in weight, were placed in the sample hole of a microcell and covered with the cap. The microcells were then laid on the junction of the thermocouple, as is shown in Fig. 2, and heated enough to melt the benzoic acid sample once; after the microcells had then cooled to room temperature, measurements were carried out in air. The weights of the samples were measured before and after every measurement; no appreciable weight loss of sample could be found after such measurements. The reference microcell was used without any reference materials.

* Reported at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

1) E. M. Barrall and L. B. Rogers, *Anal. Chem.*, **34**, 1106 (1962).
2) A. Yamamoto, *Japan Analyst (Bunsekikagaku)*, **12**, 26 (1963).
3) D. A. Vassallo and J. C. Harden, *Anal. Chem.*, **34**, 132 (1962).

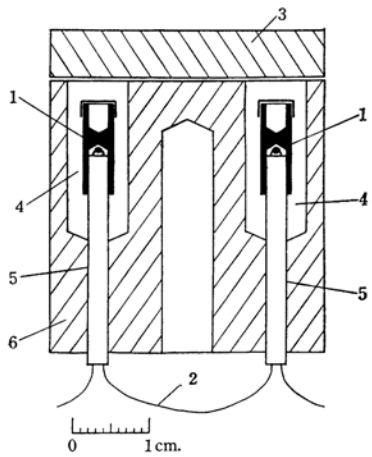

Fig. 2. Metal block and microcell.
1, Microcell
2, Thermocouple lead
3, Lid
4, Hole
5, Insulating tube for thermocouple
6, Metal block

Results and Discussion

The Shape of the DTA Curves.—A typical finding concerning DTA curves for the melting of a benzoic acid sample is shown in Fig. 3. If the amount of sample was less than 1.5 mg. in weight, a normal thermogram (curve a) could be obtained; but when the amount of the sample was more than 1.5 mg. in weight, an abnormal thermogram was obtained (curve b).

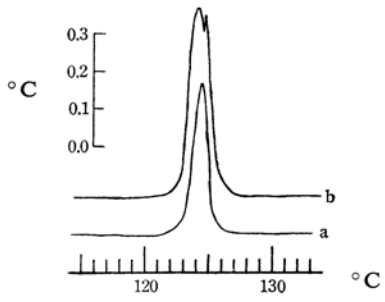

Fig. 3. Differential thermogram of benzoic acid at a heating rate of 1.0°C/min.
a, 1.4 mg. in weight; b, 4.0 mg. in weight

This abnormal curve was probably due to the fact that, as heat is transferred from the bottom to the top of the cylindrical cell, the sample first begins to melt at the bottom; then, a small part of sample stuck on the wall of the cell melts and drops into the molten sample at the bottom.

Effect of the Sample Amount.—DTA's were carried out in order to examine the effect of the sample amount on thermograms at a heating rate of 1.0°C/min. As Fig. 4 shows, the peak area is proportional to the sample amount over all the range. However, the peak height is proportional to the sample amount up to 1.5 mg. in weight and is not reproducible above that amount.

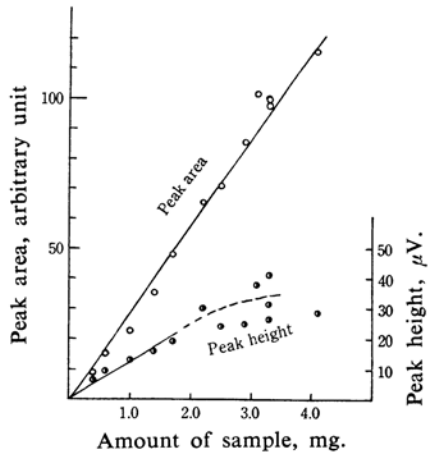

Fig. 4. Effect of sample amount on peak area and peak height at a heating rate of 1.0°C/min.

Effect of the Heating Rate.—The effect of the heating rate is shown in Fig. 5 and Fig. 6 using a 1.4 mg. sample. Figure 5 shows that the peak height increases with the heating rate, while the peak area is almost constant with the heating rate. Figure 6 shows that the peak beginning temperature, which is defined on the thermogram as the intersection point of the extrapolated straight-line portion of the low temperature side of the peak and the base line, and the peak temperature, which

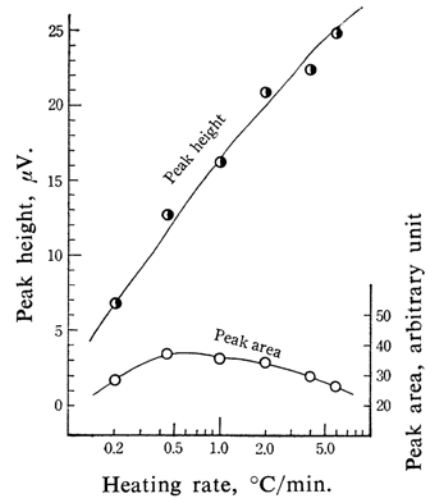

Fig. 5. Effect of heating rate on peak area and peak height using a 1.4 mg. sample.

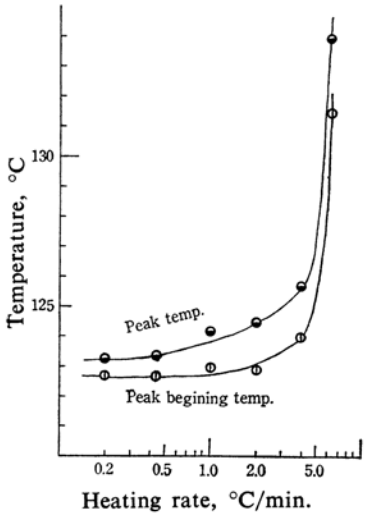

Fig. 6. Effect of heating rate on peak beginning temperature and peak temperature using a 1.4 mg. sample.

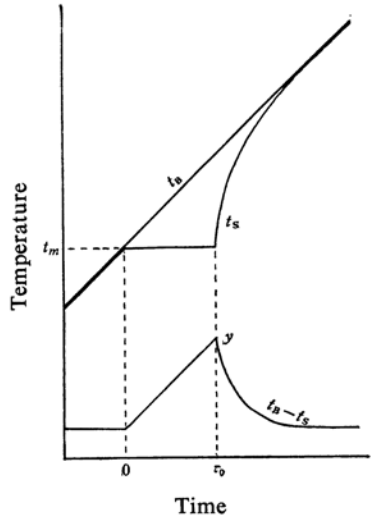

Fig. 7. Illustration of hypothetical thermal process.

is the extrapolated peak temperature, increase with the heating rate; however, if the heating rate is less than 2°C/min., the peak temperature is identical with the melting point within ±1°C.

A Consideration of the Quality of the Microcell.—It is necessary to investigate factors which affect the quality of the microcell in order to make further improvements of the microcell. For this purpose, two hypothetical thermal processes which take place in the microcell were considered.

Process i. — If the cell may be considered to be thermally isolated, a thermal transformation causes a change in the temperature, Y, given by:[4]

$$Y=\frac{Q}{C} \tag{1}$$

where Q=the heat of transformation
C=the mean specific heat capacity of the cell and sample.

In this work, the cell weighed about 1 g., while the samples weighed about 1—5 mg., therefore, C is almost equal to the specific heat capacity of the microcell.

Process ii.—The temperature of the metal block, t_B, is equal to that of the reference cell, t_r, the sample cell, t_c, and the sample, t_s, and increases at a constant heating rate, r, at first. Then, at time $\tau=0$, the sample begins to melt at a constant temperature, t_m, until it finishes melting at time $\tau=\tau_0$. This process is illustrated in Fig. 7; the following equation is obtained:

$$h(t_B-t_s)\,d\tau=C\,dt_s+dQ \tag{2}$$

with the following boundary conditions:

$$\tau=0,\ t_B=t_r=t_c=t_s=t_m$$
$$0\leqq\tau\leqq\tau_0,$$
$$t_c=t_s=t_m=\text{constant melting temperature}$$
$$t_B=t_r=t_m+r\tau$$

where h=the heat transfer coefficient between the cell and the wall of the metal block.

The integration of Eq. 2 gives:

$$\int_0^{\tau_0}h(t_B-t_s)\,d\tau=\int_0^{\tau_0}C\,dt_s+\int_0^{\tau_0}dQ$$
$$hr\tau_0^2/2=Q \tag{3}$$

The maximum temperature difference, Y, between the temperature of the sample and that of the reference cell or block is:

$$Y=(t_B-t_s)_{\tau=\tau_0}=r\tau_0 \tag{4}$$

From Eqs. 3 and 4, one obtains:

$$Y=\sqrt{2rQ/h} \tag{5}$$

Although Eqs. 1 and 5 represent DTA peak heights in hypothetical thermal processes, some factors relating to the quality of the microcell can be interpreted on the basis of these equations. To increase the peak heights or the sensitivity of microcells, the following methods may be recommended on the basis of Eqs. 1 and 5:

(i) The specific heat of the cell, C, should be decreased.

(ii) The heating rate, r, should be increased.

4) W. J. Smother and Y. Chiang, "Differential Thermal Analysis," Chem. Publishing Co., N. Y. (1958), p. 79.

(iii) The heat transfer coefficient, h, between the microcell and the wall of metal block should be deceased.

Of these, method ii, as has been mentioned earlier, is not useful because of the drifting of base line and peak as the heating rate increases. Methods i and iii have already been applied to the microcells in this work; that is, these microcells are made light in weight [method i] and are supported only by the thermocouple, not coming in contact with the wall of the metal block [method iii]. Therefore, further experiments were made to check upon the efficiency of these methods.

Experiments to Check on Methods i and iii. —Three microcells differing in weight were made in order to investigate the effect of the heat capacity of the microcell on peak heights and areas. These microcells differ from each other only in the radius of the sample hole; their surfaces are similar in shape, as is shown in Fig. 8. Therefore, the heat transfer coefficients between each microcell and the wall of the metal block are equal. The results obtained using these cells are shown in Fig. 9 and Fig. 10.

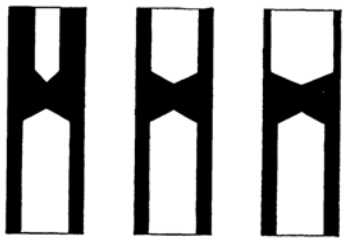

Fig. 8. Three microcells different in weights.

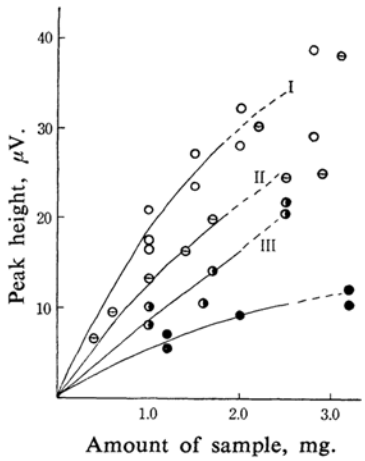

Fig. 9. Comparison of peak heights.
◑, Cell I ○, Cell III
⊖, Cell II ●, in alumina powder

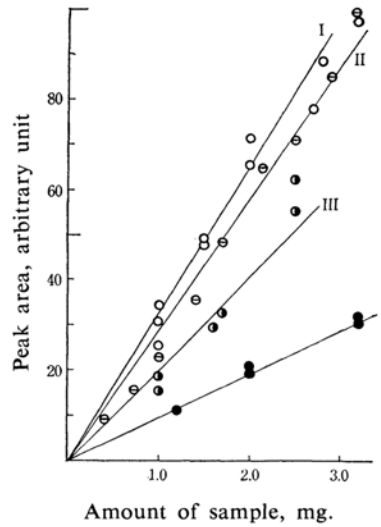

Fig. 10. Comparison of peak area.
◑, Cell I; ○, Cell III;
⊖, Cell II; ●, in alumina pouder.

Further experiments were carried out in order to investigate the effect of the heat transfer between the microcell and the wall of the metal block. The heat transfer coefficient was increased by filling the Hole Space 4 shown in Fig. 2 with alumina powder; that is, air in the space between the microcell and the wall of the metal block was replaced by alumina powder. The results are also shown in Fig. 9 and Fig. 10.

As we anticipated previously from Eqs. 1 and 5, Figs. 9 and 10 show that peak heights or areas increase as the heat capacity of the microcell and the heat transfer coefficient between the microcell and the wall of the metal block decrease. As a conclusion, as a means of improving the quality of the microcell, a smaller cell and finer leads of thermocouple in order to decrease the heat transfer coefficient are recommended.

Summary

Microcells to carry out differential thermal analysis using a small amount of a sample have been described. The features of these cells are that they are small and light in weight, and are supported only by a thermocouple, not coming in contact with the wall of the metal block. The effects have been described of the variation in heating rate and in sample amount. The peak areas of the benzoic acid melting curve are proportional to the sample amount. The melting temperature can be measured with a precision of ±1°C if the heating rate is less than 2°C/min. The

improvement of the quality of the microcell has also been considered.

The author wishes to express his thanks to Dr. Kazuo Amaya, Dr. Taichi Sato, Mrs. Kazuko Sasaki, Mr. Akira Suzuki, and Mr. Kenjiro Kodama of this Institute for their valuable discussions. He also wishes to thank Dr. Yo-ichiro Mashiko for his kind encouragement.

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