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Rocker-type DTA Apparatus for Fluid Samples

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A Rocker-type DTA apparatus, with agitation by rocking, has been developed for use in the thermal analysis of various fluid mixture systems. The heater block, with its assembled cells, is continuously rocked at 20 r.p.m. with a rocking of 180° angle. The glass cell has a volume of about 8 ml and is sealed by means of a burner with a sample of about 5 ml. Distilled water is used as the inert reference in the reference holder. Two thermocouples are inserted in each cell, one to determine the temperature difference and the other for sample temperature measurements. The double thermocouple gives a constant transition temperature of the sample over a wide range of heating rates. The apparatus is applied to solid-liquid and starch-water systems. Variables affecting the DTA thermogram of the $K_2Cr_2O_7$–H_2O system are investigated, and a method is established to correlate the DTA curve with the solubility curve for the system.

It is sometimes necessary to perform the thermal analysis of heterogeneous fluid mixture systems such as solid-liquid and starch-water[1] systems. The most important conditions for the thermal analysis of such systems are to avoid the escape of the vapor of the samples and to avoid composition inhomogeneity in the sample cells. These conditions are usually obtained by the use of a sealed sample holder and by stirring the samples adequately.

Various stirring techniques are available; the final choice is dependent on the nature of the system to be investigated. Propellor-type stirrers driven by a shaft are sometimes used.[2,3] However they cease to operate when a fraction of the sample is solidified, and they allow the vapor of the sample to escape through the gland around the shaft of the stirrers and allow a considerable amount of heat to be conducted from or to the holder through the shaft. An alternative method is to use a sealed-in stirrer operated by means of a solenoid,[4] but in this case the stirrer stops when only a fraction of the sample is solidified and it is necessary to ensure that no electrical interference is produced in the temperature-measuring circuit in the solenoid. To ensure the adequate stirring of the sample inside a sealed holder, the rocking method[5–8] may be used. Here, the agitation of the sample continues until practically all the material has solidified, and at the same time the material is completely sealed in the holder. Gilpatrick *et al.*[8] have also described the use of a commercial rocker unit for phase studies of a molten salt system, NaF–KF–BF_3. In the apparatus to be described here, adequate stirring has also been obtained by applying the rocking method, and the DTA of solid-liquid and potato starch-water systems has been successfully performed.

Experimental

Apparatus. A whole diagram of the apparatus is shown schematically in Fig. 1. The center of gravity of the block assembly and the rack is adjusted to coincide with the shaft, the axle of rotation, so as to assure smooth rotation. The holder contents are then stirred by continuous rocking through an arc of 180° at a speed of 20 rpm achieved by means of a synchronous motor. The heater block is made of aluminum; a cross-section of heater block assembly is shown in Fig. 2. The holder used is made of glass; it is also shown in Fig. 2. The holder has a volume of about 8 ml and is sealed by means of a burner with a content of about 5 ml. The block is heated by a noninductively-wound nichrome wire insulated by a mica sheet against the surface of the block. The heater is controlled by a variable-voltage transformer to give the desired constant heating rates.

Chromel-Alumel thermocouples are used to measure the block, sample, and temperature differences. In the well of each holder, two junctions of the thermocouples are inserted to measure the temperature and temperature differences. This arrangement gives a constant transition temperature of sample over a wide range of heating rates. The electrical leads for the heater and thermocouples are hung in wide U-

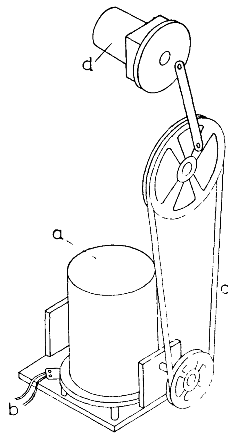

Fig. 1. Schematic diagram of rocker type DTA apparatus assembly. a: heater block with aluminum cover, b: electric lead wires, c: belt, d: synchronous motor.

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[1] S. Tomita, private request.

[2] H. J. Borchardt and F. Daniels, *J. Amer. Chem. Soc.*, **79**, 41 (1957).

[3] K. Tamura, K. Nakatsuka, and R. Fujishiro, This Bulletin, **39**, 20 (1966).

[4] G. Takeya, T. Ishii, K. Makino, and S. Ueda, *Kogyo Kagaku Zasshi*, **69**, 1654 (1966).

[5] G. Waddington, S. Sunner, and W. N. Hubbard, "Experimental Thermochemistry," Vol. 1, ed. by F. D. Rossini, Interscience Publishers, New York, N. Y. (1960), pp. 170, 191.

[6] H. A. Skinner, J. M. Sturtevant, and S. Sunner, "Experimental Thermochemistry," Vol. 2, ed. by H. A. Skinner, Interscience Publishers, New York, N. Y. (1962), pp. 149, 186.

[7] E. W. Comings, "High Pressure Technology," McGraw-Hill, New York, N. Y. (1956), p. 228.

[8] L. O. Gilpatrick, S. Cantor, and C. J. Barton, "Thermal Analysis," Vol. 1, ed. by R. F. Schwenker, Jr., and P. D. Garn, Academic Press, New York, N. Y. (1969), p. 85.

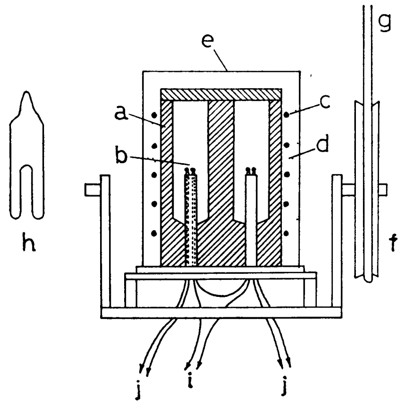

Fig. 2. Cross section of heater block and glass holder.
a: aluminum block, b: thermocouples, c: heater, d: thermal insulator, e: aluminum cover, f: wheel, g: belt, h: glass holder, i: temperature difference, j: temperature.

turns to prevent the breaking of the leads by the repeated bending introduced by the rocking of the assembly. The differential thermocouple emf is preamplified by Okura Model AM-1001 D. C. amplifier and fed to the input of a Rikadenki Model B-341 three-pen recorder. The block and sample temperatures emf are similarly fed to the inputs of the recorder without preamplification.

Materials. Benzoic acid, a standard sample for combustion calorimetry obtained from the Resource Research Institute, Japan, and Tokyo Kasei zone-refined naphthalene were used to calibrate the temperature thermocouple through their melting points. Kokusan Chemical Works extrapure potassium dichromate, potassium nitrate, cobalt sulfate, and Wakō Junyaku potato starch were used without further purification. Distilled water was used as the reference material and as one component of the sample binary mixtures.

Results and Discussion

Some Examples. Figure 3 shows the effect of the heating rate on the peak temperatures.

Blank-run DTA curves of distilled water in both holders are shown in Fig. 4 and 5. The regular variation in the base line synchronous with the rocking cycle is increased with the increase in the sample temperature and the heating rate. The blank run in Fig. 4 is performed under a high heating rate in order to observe the irregularity of base line, while general runs with actual samples are performed under a mod-

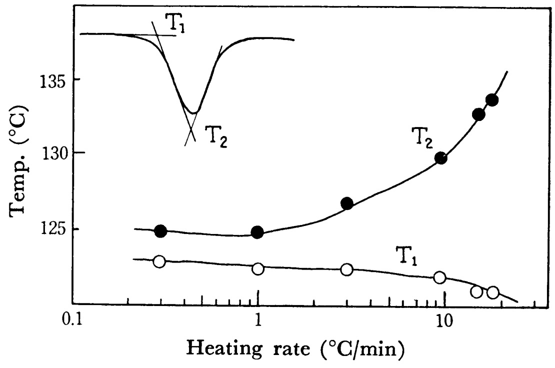

Fig. 3. Effect of heating rate on peak temperatures of benzoic acid melting.

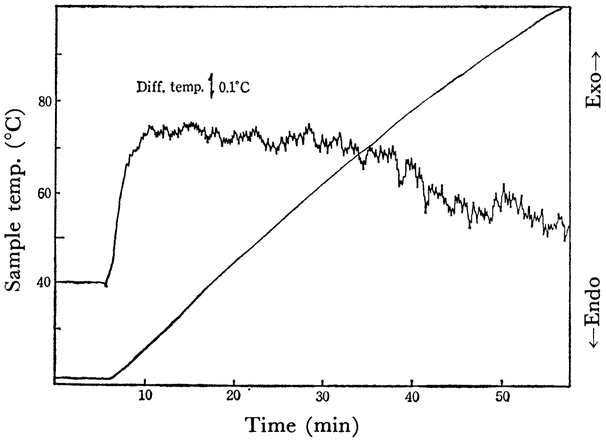

Fig. 4. Rocking DTA curve for H_2O in both holders.

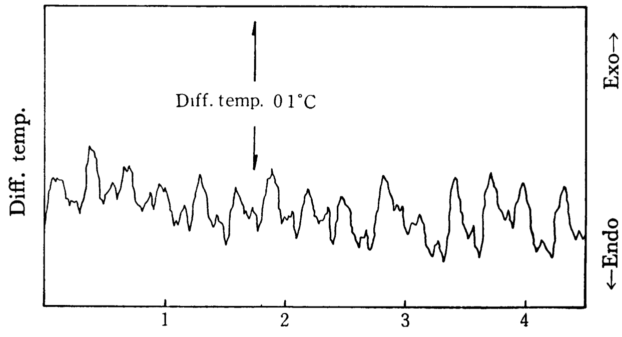

Fig. 5. Rocking DTA curve for H_2O in both holders at about 80°C.

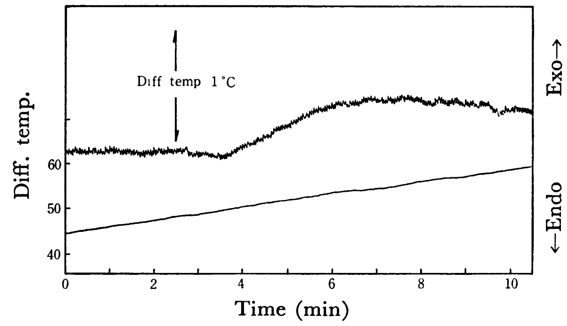

Fig. 6. Rocking DTA curve for $K_2Cr_2O_7$-H_2O ($K_2Cr_2O_7/H_2O=0.354$ wt. fraction).

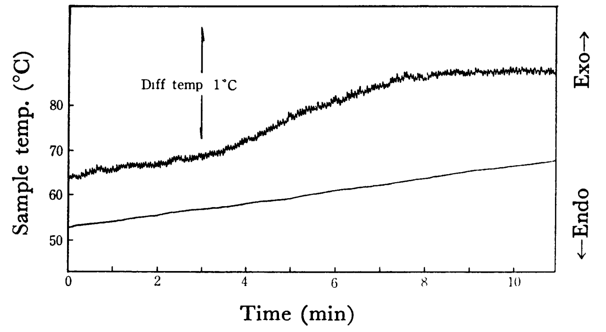

Fig. 7. Rocking DTA curve for KNO_3-H_2O ($KNO_3/H_2O=1.13$ wt. fraction).

erate heating rate, nearly equal to or less than about 1°C/min., and have more smooth base lines than the run in Fig. 4.

DTA curves of various solid-liquid mixture systems of known compositions are shown in Figs. 6 to 8. A shift in the position of the base line to a new level is observed in Figs. 6 and 7. The temperature at which the shift occurs is nearly in agreement with the dissolution temperature in the literature.[9] The dissolution temperature, at which the solid phases in a mixture of the prepared compositions dissolve completely, are 50°C for $K_2Cr_2O_7/H_2O=0.354$ and 62°C for $CoSO_4/H_2O=1.13$,[9] while the shifts are found at about 50—63°C respectively. The two peaks at 53°C and 59°C are considered to be due to the dehydration reactions of $CoSO_4 \cdot 7H_2O$, but the peak temperatures cannot be identified with any one of the dehydration temperatures in the literature.[9]

The base-line shift is also found for the potato starch-water system, as is shown in Fig. 9. The shift temperature of about 60—62°C is in agreement with the gelatinization temperature of the starch in water.[10] The direction of the shift is from a lower heat capacity at a lower temperature to a higher capacity at a higher temperature. This display is graphically analogous to that shown in the DTA thermogram of a glass transition in a high polymer.

DTA curves of a Solid-liquid System. The thermal analysis of a solid-liquid mixture system with this apparatus has been studied in some detail by investigating the thermal behavior of the $K_2Cr_2O_7$-H_2O system and the variables affecting the appearance of the DTA curve of the system. The requirements to achieve a reproducible DTA curve and a sharp shift (see Fig. 6) in the neighborhood of the dissolution temperature are as follows:

(1) the solid phase should be fine powder;

(2) the sample holder should be in good thermal contact with the wall of the DTA block and

(3) the proper heating rate should be chosen so as to give a precise solubility temperature from the shift of the DTA curve.

(1) and (3) are necessary to maintain the system under thermochemical equilibrium as much as possible during the course of the thermal analysis, while (2) is required to obtain a sharp shift of the curve.

The shift temperatures were selected from various portions of the DTA shift curve, as is illustrated in Fig. 10. Point A is the intersection of the extrapolated straight-line portion of the side of the shift with the base line at a lower temperature, while C is the extrapolated intersection with the base line at a higher temperature. Point B is the middle point of the AC line. The effect of the heating rate on the shift tem-

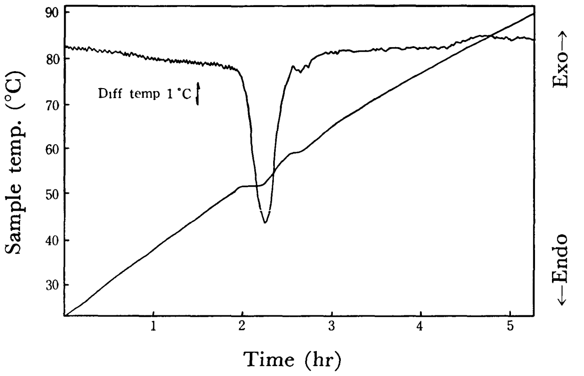

Fig. 8. Rocking DTA curve for $CoSO_4$-H_2O ($CoSO_4$+H_2O)=0.444 wt. fraction)

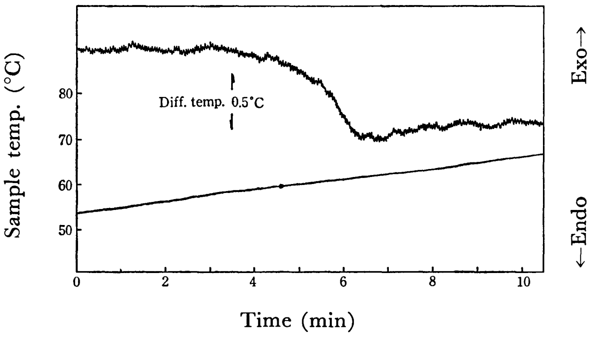

Fig. 9. Rocking DTA curve for gelatinization of potato starch in water. Potato starch 5.04 wt. % in solution.

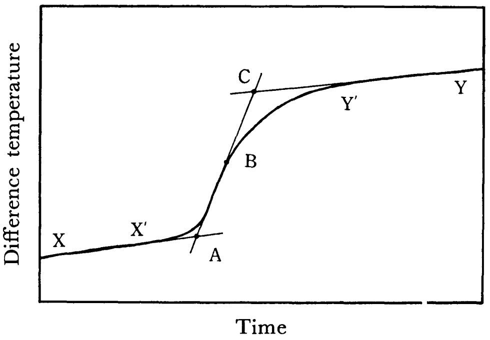

Fig. 10. A typical DTA curve for solid-liquid system.

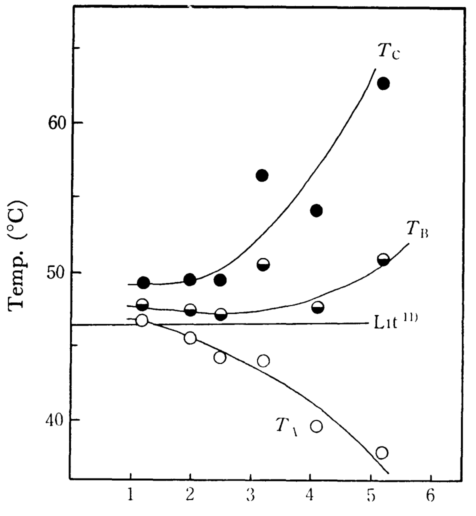

Fig. 11. Effect of heating rate on shift temperatures of DTA curve for $K_2Cr_2O_7$-H_2O.

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9) The Chemical Society of Japan (ed.), "Kagaku-Benran," Maruzen, Tokyo (1958), p. 581.

10) J. Nikuni (ed.), "Denpun-Handbook," Asakura-Shoten, Tokyo (1961), p. 79,

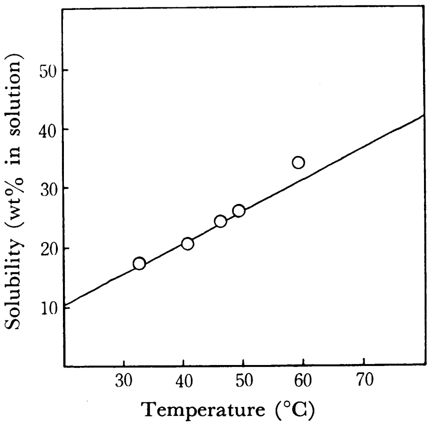

Fig. 12. Solubility curve of $K_2Cr_2O_7$ in water.
○: Experimental, ——: Literature.[11]

peratures at which the various points occurred during the dissolution process of the system is shown in Fig. 11. Temperature T_A, estimated at Point A, approaches the dissolution temperature[11] of the system in the prepared composition as the heating rate decreases and is approximately equal to the dissolution temperature at 1°C per minute. Since the best measure from T_A at 1°C per minute was thus obtained, this temperature was selected for other compositions of the systems. The temperatures, T_A, for the various compositions thus obtained are shown in Fig. 12; a comparison with the solubility curve from the literature[11] shows a satisfactory agreement between them.

Discussion of the DTA Shift Curve. In the DTA apparatus described here, adequate and continuous stirring is achieved by rocking; one can, therefore, assume a uniform temperature inside the holders and can set down equations describing the heat flow into the sample and reference holders as follows;

$$C_s \frac{dT_s}{dt} = h_s(T_b - T_s) + \frac{dQ}{dt} \tag{1}$$

$$C_r \frac{dT_r}{dt} = h_r(T_b - T_r)\,. \tag{2}$$

Notations:

C=heat capacity of the holder

h= coefficient of heat transfer between the holder and the wall of the metal block

T=temperature

t=time

Q=heat evolved or absorbed in the sample holder

s, r, b=subscripts denote the quantity of the sample holder, the reference holder, and the metal block respectively

By subtracting (2) from (1), by rearranging, and by using the $y = T_s - T_r$ relation, one obtains;

$$C_s \frac{dy}{dt} + (C_s - C_r)\frac{dT_r}{dt} = -h_s y + (h_s - h_r)(T_b - T_r) + \frac{dQ}{dt}. \tag{3}$$

When the system under consideration is in a steady state, $dQ/dt=0$, the above equation becomes;

$$(C_s - C_r)\frac{dT_r}{dt} = -h_s y_0 + (h_s - h_r)(T_b - T_r), \tag{4}$$

where the subscript 0 denotes the quantity in the steady state. From (2) and (4), one obtains;

$$y_0 = \left(\frac{C_r}{h_r} - \frac{C_s}{h_s}\right)\frac{dT_r}{dt}. \tag{5}$$

The $y_0 = (T_s - T_r)_0$ quantity is the height of the base line of the DTA curve in a steady state, and dT_r/dt is the heating or cooling rate of the system.

Let us consider the DTA curve shown in Fig. 10, which is a typical curve in the DTA of a solid-liquid system. Equation (5) becomes;

$$\left(\frac{C_r}{h_r} - \frac{C_{s,\,\mathrm{I}}}{h_s}\right)\frac{dT_r}{dt} = y_{0,\,\mathrm{I}} \tag{6}$$

for the lower temperature part of the XX' base line, and;

$$\left(\frac{C_r}{h_r} - \frac{C_{s,\,\mathrm{II}}}{h_s}\right)\frac{dT_r}{dt} = y_{0,\,\mathrm{II}} \tag{7}$$

for the higher temperature part of the Y'Y base line. Considering the relation:

$$y_{0,\,\mathrm{II}} > y_{0,\,\mathrm{I}} \tag{8}$$

$$dT_r/dt > 0 \tag{8'}$$

for the curve, we obtain the following inequality relation from (6) and (7);

$$C_{s,\,\mathrm{I}} > C_{s,\,\mathrm{II}}\,. \tag{9}$$

Now let us consider a solid-liquid system in a closed vessel. We suppose that there are a pure solid state, a completely mixed liquid solution, and a negligible space of the vapor phase, and that the system is under a thermochemical equilibrium.

M=weight of the liquid phase

m=weight of the solid phase

C_{SL}=heat capacity per weight of the solid-liquid system in a closed vessel

C_L=heat capacity per weight of the liquid phase

C_S=heat capacity per weight of the solid phase

H_S=heat of solution per weight of the solid

$x = m/(M+m)$

T=temperature

During the heating of the system, the small quantity of heat input, dQ, has three components: two specific-heat components, $MC_L dT$ and $mC_S dT$, which raise the temperature of the system by dT, and heat-of-solution component, $H_S(-dm)$, where dm is the weight of the solid which dissolves when the temperature is raised by dT. Therefore, we obtain:

$$dQ = MC_L dT + mC_S dT + H_S(-dm),$$

and;

$$C_{SL} = \frac{1}{M+m}\frac{dQ}{dT} = C_L + x(C_S - C_L) - H_S\frac{dx}{dT} \tag{10}$$

for the heat capacity of the solid-liquid system.

Now we will confine our discussion to the $K_2Cr_2O_7$-H_2O system at the temperature range of about 10°C involving the dissolution temperature. As the temperature of the system rises, the C_{SL} quantity is approximately constant or varies linearly with T as may be

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[11] The Chemical Society of Japan (ed.), "Kagaku-Benran," Maruzen, Tokyo (1958), p. 634.

seen from a consideration of the variation of the three terms on the right-hand side of (10) in this system. At the dissolution temperature at which the solid phase completely dissolves into the liquid phase ($x=0$), the specific heat capacity becomes equal to C_L, and we have a discontinuous variation of the specific heat:

$$(C_{SL}-C_L)_{x=0} = -H_S \frac{dx}{dT}. \tag{11}$$

Since there are these experimental facts:

$H_S>0$ (the heat of solution is endothermic)

$dx/dT<0$ (the solid phase dissolves as the temperature rises)

for the $K_2Cr_2O_7$-H_2O system, we obtain this inequality relation;

$$C_{SL,\ x=0} > C_{L,\ x=0}. \tag{12}$$

(12) may be compared with (9). Since, in (9), the heat capacity, $C_{S,I}$, at lower temperature is that of the solid-liquid-mixture phase, and since $C_{S,II}$ at higher temperature is that of the liquid-solution phase, the relation (12) deduced from thermochemical consideration is in agreement with that (9) deduced from the analysis of the DTA shift curve.

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