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A New Method of Quantitative Differential Thermal Analysis

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This paper presents a rigorous new theory of differential thermal analysis, taking account of the temperature gradient in the sample. From this consideration, a new quantitative method is proposed, where a solid-cell holder of low thermal conductivity is set between a sample cell and a metal block, and a thermocouple is inserted tightly between the outside wall of the cell and the cell holder. By means of this arrangement, the peak area becomes proportional to the heat of transformation, irrespective of the kinds and the states of samples and operational variables. The experimental verification using various samples and the effect of several operational variables, such as the heating rate, the concentration of a diluent, the packing density, and the depth of the packing sample, are also shown; satisfactory results are obtained. Two new concepts, the sensitivity and the response time of the system, are proposed and evaluated. Conventional methods are criticized, and the inherent limitations of differential thermal analysis are discussed.

Differential thermal analysis has been widely used in scientific and engineering fields to study clays, soaps, polymers and various other organic and inorganic materials[1-3] since Le Chaterier's first employment of its prototype in 1887.[4] By this method we can record the temperature difference between a sample and a thermally-inert reference material heated at a constant rate by an external furnace, and thermal transformations occurring in the sample can thus be recognized as deviations from the base line in the record of the temperature difference against the time, which forms a differential thermogram.

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3) W. W. Wendlandt, "Thermal Methods of Analysis," Interscience Publishers, New York (1964).

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Although numerous reports have hitherto been published, there remain problems about the quantitative differential thermal analysis, namely, the method of estimating the heat of transformation by differential thermal analysis. In order to evaluate the heats of transformation from differential thermograms, Vold[5] suggested a theory which requires a knowledge of the heat capacity of the sample. If her theory is further developed, a relation can be derived which corresponds to the theories of Kerr and Kulp;[6] Speil, Swerdlow, Pask and Davices;[7] Evans, Hutton and Mathews,[8] and so on, who all indicate that the area enclosed by the peak and the base line in a differential thermogram is proportional to the heat of transformation. However, in these theories the experimental condition for the constant of the proportionality between the heat and the area is not shown to be independent of the sorts of the samples and other experimental factors, because the effects of the volume and the shape of the sample are neglected in the theories.

On the other hand, considering these effects Soulé[9] and Nagasawa[10] suggested that the proportionality constant contains the apparent density and apparent thermal conductivity of the sample; furthermore, Boersma[11] pointed out, for the same reasons, that quantitative differential thermal analysis by the conventional methods is inherently impossible, because the proportionality constant becomes a function of the apparent thermal conductivity of the sample. Soulé thus suggested a method which makes the proportionality constant independent of the thermal conductivity of the sample and other operational factors, but his method has not yet been developed. Strum[12] extended Boersma's theory and introduced a method of quantitative differential thermal analysis, but it is a rather complicated one. Otsubo and Yamaguchi[13] also published their rigorous treatment of heat conduction within the apparatus of differential thermal analysis and devised an approximate method of estimating the heat; their theory is, however, essentially equivalent to Vold's theory, and also the value of the specific heat of the sample is needed if we are to analyze the data. Naturally, therefore, the theory is limited in application. Strella[14] recently proposed a new method, but it is a complicated one and seems to contain some rough assumptions. Therefore, quantitative differential thermal analysis has not yet been established.

Recently Speros and Woodhouse[15] reported on "quantitative differential thermal analysis," but theirs is essentially a differential enthalpic analysis,[16] one which has different theoretical bases, different advantages, and a limited application, because the temperature difference between the sample and the reference material must be nullified and the error of such operation has a serious effect at a higher temperature; this is also the case in an adiabatic calorimeter.

Although the direct measurement of the specific heat by an adiabatic calorimeter (or differential enthalpic analysis) is an absolute, excellent method, the differential thermal analysis has the following advantages over it: (1) the simplicity and ease of the operation and the analysis of the data; (2) its applicability to cooling processes and to measurements under a high pressure[17] and/or at a higher temperature, and (3) its applicability to chemical reactions and exothermic phenomena such as crystallization.[18] Therefore, it is still important to establish quantitative differential thermal analysis.

In the present paper, the author will report a theory of broad vision from which he has derived a new, simple and convenient method of estimating the heat of transformation by differential thermal analysis; the experimental verification of the method will also be shown. From these considerations we can elucidate the sensitivity of the apparatus, the resolution of the peaks, the influence of some operational factors on the differential thermograms, and the inherent limitations of differential thermal analysis.

Theoretical Considerations

As has been mentioned above, there have been no rigorous treatments of the temperature gradient in the sample in the previous theories of differential thermal analysis. Now, an exact elucidation of the temperature gradient should be attempted. In a conventional apparatus, the sample and the reference material are packed in a pair of cavities of a metal block, and a temperature-detection device is inserted into the center of each cavity. In some cases,[19] the sample and reference cells with the

5) M. J. Vold, *Anal. Chem.*, **21**, 683 (1949).
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temperature-detection devices are inserted in the cavities of the metal block without touching the walls at all. In the method described in this paper, the sample and reference cells are put into cell-holders set in the cavities of the metal block, while the temperature-detection devices are located between the cells and the cell holders. These arrangements are illustrated in Fig. 1. The cell holder is made of thermally-inert solid material of a low thermal conductivity in which a temperature gradient develops corresponding to the heat flow into the sample, as will be seen later.

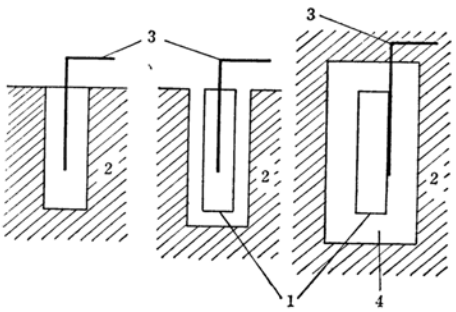

Fig. 1. The three types of the arrangements of the cell (1), the metal block (2), the temperature detection device (3) and the cell holder (4).

Now, let us consider the temperature gradient in the sample, the reference material and the cell holders. We can derive the equations of the heat flow for these materials by assuming that the heat transfers by conduction only, that the heat is not lost at the interface between the cell holder and the cell, and that the temperature of the inner surface of the cell holder is equal to that of the surface of the cell. The metal block is heated at a constant rate, a, of heating (or cooling). It is also assumed that the metal block has so large a heat capacity and thermal conductivity, and/or that it is controlled so strictly in its heating rate, that the heating rate of the metal block is not disturbed by the heat of transformation occurring in the sample. For the sake of simplicity the shape of the cell is cylindrical and it is long enough for us to be able to neglect the heat flow through the ends. The heat loss through the temperature-detection device is also neglected.

Within the sample:

$$\lambda_s \nabla T_s = c_s \rho_s \frac{\partial T_s}{\partial t} + \rho_s \Delta H \frac{\partial m}{\partial t} \tag{1}$$

and within the cell holder:

$$\lambda_h \nabla T_h = c_h \rho_h \frac{\partial T_h}{\partial t} \tag{2}$$

where:

∇ = a Laplacian

λ = the thermal conductivity

T = the temperature

c = the specific heat

ρ = the apparent density

t = the time

ΔH = the heat of the transformation of the sample per unit mass

$\frac{\partial m}{\partial t}$ = the rate of the transformation in mass,

and where the subscripts s and h denote the sample and the cell holder.

The boundary and initial conditions of the above equations are as follows:

$$T = at \qquad \text{at } r = R_o \tag{3}$$

$$\lambda_s \frac{\partial T_s}{\partial r} = \lambda_h \frac{\partial T_h}{\partial r} \qquad \text{at } r = R_i \tag{4}$$

$$T_s = T_h \qquad \text{at } r = R_i \tag{5}$$

and

$$T_s = T_h = 0 \qquad \text{at } t = 0 \tag{6}$$

where

r = the distance from the central axis

R_o = the outer radius of the cell holder

R_i = the inner radius of the cell holder

= the radius of the cell

These equations can be applied to other arrangements of the sample. Namely, if R_o is made equal to R_i, the solution becomes one for a conventional appearatus. In an apparatus such as (b) in Fig. 1, the temperature is measured at the center of the sample, and the solution of the equations can be applied if one neglects the heat transfer by convection and radiation in the air gap between the cell and the metal block.

Assuming a cylindrical symmetry, we have the next solutions of Eqs. 1 and 2, when the transformation does not occur in the sample; i. e., $\partial m/\partial t = 0$ (see in Appendix).

$$T_s = at - \frac{a}{4\lambda_h}\left[c_h\rho_h(R_o^2 - R_i^2) + 2R_i^2(c_s\rho_s - c_h\rho_h)\log\frac{R_o}{R_i}\right] - \frac{ac_s\rho_s}{4\lambda_s}(R_i^2 - r^2) + \sum_{n=0}^{\infty} \boldsymbol{A}_n(r)\exp\left(-\frac{t}{\tau_n}\right) \tag{7}$$

$$T_h = at - \frac{a}{4\lambda_h}\left[c_h\rho_h(R_o^2 - r^2) + 2R_i^2(c_s\rho_s - c_h\rho_h)\log\frac{R_o}{r}\right] + \sum_{n=0}^{\infty} \boldsymbol{B}_n(r)\exp\left(-\frac{t}{\tau_n}\right) \tag{8}$$

where $\boldsymbol{A}_n(r)$'s and $\boldsymbol{B}_n(r)$'s are functions of r only, and where τ_n's are the roots of the equation:

$$\sqrt{\lambda_h c_h \rho_h}\boldsymbol{J}_0\left(R_i\sqrt{\frac{c_s\rho_s}{\lambda_s\tau_n}}\right)\Big[\boldsymbol{J}_1(R_i x)\boldsymbol{Y}_0(R_o x) - \boldsymbol{J}_0(R_o x)\boldsymbol{Y}_1(R_i x) = \sqrt{\lambda_s c_s \rho_s}\boldsymbol{J}_1\left(R_i\sqrt{\frac{c_s\rho_s}{\lambda_s\tau_n}}\right) \times [\boldsymbol{J}_0(R_i x)\boldsymbol{Y}_0(R_o x) - \boldsymbol{J}_0(R_o x)\boldsymbol{Y}_0(R_i x)] \quad (9)$$

where x is equal to $\sqrt{c_h\rho_h/\lambda_h\tau_n}$, where $\boldsymbol{J}_0$ and $\boldsymbol{J}_1$ are Bessel functions of the zero and 1st orders respectively, and where $\boldsymbol{Y}_0$ and $\boldsymbol{Y}_1$ are Neuman functions of the zero and 1st orders respectively.

The following equations are derived analogously for the reference material and its cell holder:

$$T_r = at - \frac{a}{4\lambda_h}\left[c_h\rho_h(R_o^2 - R_i^2) + 2R_i^2(c_r\rho_r - c_h\rho_h)\log\frac{R_o}{R_i}\right] - \frac{ac_r\rho_r}{4\lambda_r}(R_i^2 - r^2) + \sum_{n=0}^{\infty}\boldsymbol{C}_n(r)\exp\left(-\frac{t}{\tau_n'}\right) \quad (10)$$

$$T_{h'} = at - \frac{a}{4\lambda_h}\left[c_h\rho_h(R_o^2 - r^2) + 2R_i^2(c_r\rho_r - c_h\rho_h)\log\frac{R_o}{r}\right] + \sum_{n=0}^{\infty}\boldsymbol{D}_n(r)\exp\left(-\frac{t}{\tau_n'}\right) \quad (11)$$

where the subscripts r and h' denote the reference material and its cell holder respectively, where $\boldsymbol{C}_n(r)$'s and $\boldsymbol{D}_n(r)$'s are functions of r only, and where τ_n''s are the roots of the equation:

$$\sqrt{\lambda_h c_h \rho_h}\boldsymbol{J}_0\left(R_i\sqrt{\frac{c_r\rho_r}{\lambda_r\tau_n'}}\right)[\boldsymbol{J}_1(R_i x')\boldsymbol{Y}_0(R_o x') - \boldsymbol{J}_0(R_o x')\boldsymbol{Y}_1(R_i x')] = \sqrt{\lambda_r c_r \rho_r} \times \boldsymbol{J}_1\left(R_i\sqrt{\frac{c_r\rho_r}{\lambda_r\tau_n'}}\right)[\boldsymbol{J}_0(R_i x')\boldsymbol{Y}_0(R_o x') - \boldsymbol{J}_0(R_o x')\boldsymbol{Y}_0(R_i x')] \quad (12)$$

where x' is equal to $\sqrt{c_h\rho_h/\lambda_h\tau_n'}$.

The last terms of Eqs. 7, 8, 10 and 11 form the Bessell-Fourier series expressing the transient temperature; they are related to the temperature distribution in the steady state.

As the temperatures are measured at the interfaces between the cells and the cell holders in the present method, the temperature difference between the sample and the reference material, ΔT, is given by:

$$\Delta T = T_s - T_r = \Delta T_b + \sum_{n=0}^{\infty}\boldsymbol{A}_n(R_i)\exp\left(-\frac{t}{\tau_n}\right) - \sum_{n=0}^{\infty}\boldsymbol{C}_n(R_i)\exp\left(\frac{t}{\tau_n'}\right) \quad (13)$$

where:

$\Delta T_b = a(C_r - C_s)/K$

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

$C_s = \pi R_i^2 c_s\rho_s l$ = the heat capacity of the sample plus the cell

$C_r = \pi R_i^2 c_r\rho_r l$ = that of the reference material plus the cell

l = the length of the cell.

The height of the base line is ΔT_b, and the other terms give the transient temperature.

From Eq. 13 it is apparent that it is necessary for the heat capacity of the reference material to be equal to that of the sample, as has already been pointed out by Vold[5]; the necessity of this remains in our method derived by the rigorous treatment. The differential method eliminates the error due to the fluctuation of the base line caused by the fluctuating rate of heating, if the above necessity is fulfilled, and it is preferable that τ_n''s be nearly equal to τ_n's; i. e., it is preferable that the reference material have a similar effective thermal conductivity. The role of the reference material is neither more nor less than this elimination.

The values of $\boldsymbol{A}_n(r)$'s, $\boldsymbol{B}_n(r)$'s, $\boldsymbol{C}_n(r)$'s and $\boldsymbol{D}_n(r)$'s do not play an important role in the measurement, and so we need not know their exact values, because these series converge to zero in the intervals of the order of $5\tau_n$ and $5\tau_n'$, which are important ones. It is necessary to know. The largest values of τ_n's and τ_n''s, τ_0 and τ_0' are the response times of the system, and they give the order of the time necessary for the system to attain to a steady state. If the values of τ_0 and τ_0' are large, the measurement of the transformation occurring at a lower temperature becomes obscure, because the system has not attained to the steady state before it reaches the transformation temperature. It should be noted that τ_n and τ_n' do not depend on the point of the temperature measurement and the heating rate, but on the thermal properties and the geometry of the system. It should also be pointed out that τ_n is important to the measurement in yet another way, as will be discussed below.

We should now like to discuss the other transient state after the transformation. Suppose that the transformation in the sample is completed at $t = t_c$ and that the temperature distribution is different from that of the steady state. As the same equations, 1 and 2, and the same boundary conditions, 3, 4 and 5, hold for this case, the transient temperature distribution is given corresponding to different initial conditions, because the temperature distribution at the steady state and the τ_n's are determined irrespective of the initial temperature distribution (see Appendix).

$$T_s = at - \frac{a}{4\lambda_h}\left[c_h\rho_h(R_o^2 - R_i^2) + 2R_i^2(c_s\rho_s - c_h\rho_h)\log\frac{R_o}{R_i}\right] - \frac{ac_s\rho_s}{4\lambda_s}(R_i^2 - r^2) + \sum_{n=0}^{\infty} \boldsymbol{E}_n(r)\exp\left(-\frac{t-t_c}{\tau_n}\right) \quad (14)$$

$$T_h = at - \frac{a}{4\lambda_h}\left[c_h\rho_h(R_o^2 - r^2) + 2R_i^2(c_s\rho_s - c_h\rho_h)\log\frac{R_o}{r}\right] + \sum_{n=0}^{\infty} \boldsymbol{F}_n(r)\exp\left(-\frac{t-t_c}{\tau_n}\right) \quad (15)$$

where the last terms are the Bessell-Fourier series related to the temperature distribution at t_c, and where the τ_n's are, as before, the roots of Eq. 9.

Thus, the transient temperature disappears in the time interval of the order of $5\tau_0$, which determines the resolution of the adjacent peaks and which should be called "the response time" determining the resolving power of the system. It is of interest to note that the response time of the system is not given in the dimension of temperature but in that of time, and that, if the second transformation occurs within the temperature range of the order of $5a\tau_0$, the peaks may overlap. These facts suggest the advantage of a low heating rate. However, there is a possibility of resolving these overlapped peaks in a different way. If τ_0 is large enough compared to the other τ_n's, which may be true in most cases, the transient temperature of the Bessell-Fourier series can be approximated by a single exponential function. Thus, if one plots the logarithm of $(\Delta T - \Delta T_b)$ against the time beginning at the top of the peak, the points lie on a straight line after the completion of the transformation. Such a procedure not only resolves the overlapped peaks, but also gives, though only approximately, the time of the completion of the transformation, the determination of which is important in the measurements of binary mixtures, high polymeric samples, and chemical reactions, because these changes occur over a wide range of temperature. This linearity can also be used to separate the peaks. For example, in order to ascertain the melting behavior of high polymers, one must plot the change in the crystallinity against the temperature. By using differential thermal analysis, this can be done by separating the peaks with these exponentially-decaying curves. Ke[20] divided the peak into components, but his method of division should be revised on the basis of the present facts. The above-mentioned linear relationship was pointed out and shown experimentally by Vold[5] and by Otsubo et al.,[13] but it should be noted that τ_0 determines the resolving power and that it can be estimated by Eq. 9 in designing the apparatus.

20) B. Ke, *J. Polymer Sci.*, **42**, 15 (1960).

Finally we consider the area under the peak, for which the relation (see Appendix) holds:

$$\Delta H \cdot M = K \cdot A \quad (16)$$

where M is the mass of the sample and A is the area of the peak. The proportionality coefficient, K, is given above; it is related to the geometry and thermal conductivity of the cell holder, not to the thermal properties of the sample. Therefore, the coefficient is the constant characteristic of the apparatus. This fact is the basis of this quantitative differential thermal analysis; the cell holder serves as the heat-flow-meter, developing within itself the proportional magnitude of the temperature gradient to be measured. The proportionality coefficient can be evaluated by the measurement of a sample of a known heat of transformation. As it is related to the thermal conductivity, it would be a function of the temperature and one needs to measure the transition of the known latent heat over the workable temperature range in order to evaluate the proportionality coefficient.

As has already been pointed out by Boersma,[11] in the conventional method, the sample plays two quite different parts, parts which conflict with each other: (a) a producer of heat to be measured, and (b) a heat measureing resistance in which the heat flow develops a temperature gradient necessary for the measurement. Thus, in the conventional model, the temperature gradient within the sample is essential. However, in the present method the temperature gradient within the sample can be reduced without sacrificing the sensitivity of the apparatus. If one introduces a certain device to diminish the temperature gradient within the cell, the peaks will be sharpened, and the accuracy of the temperature measurement and the resolution of the peaks may even be increased.

Essentially, this method of quantitative differential thermal analysis is a technique for measuring the heat by the temperature gradient existing in the given inert material, through which the heat flows into the sample cell.

Let us now discuss the optimum design of the

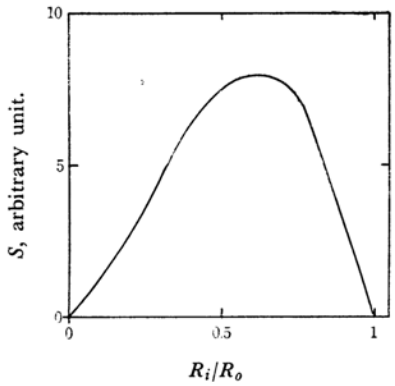

Fig. 2. The sensitivity versus the ratio, R_i/R_o.

cell holder. The "sensitivity" of the apparatus, S, could be defined as the peak area per the unit heat of transformation occurring in the unit volume of the sample:

$$S = A/\rho_s \Delta H = V_s/K \tag{17}$$

Namely,

$$S = R_i^2 \log (R_o/R_i)/2\lambda_h \tag{18}$$

The sensitivity increases with the second power of the radius of the cell. It may easily be seen that, for a given R_o, the optimum ratio of R_i to R_o is $e^{-1/2}$; the sensitivity is plotted against the ratio in Fig. 2. If R_i is fixed, the sensitivity increases logarithmically with an increase in R_o.

For a glass transition[21-24] or a second-order transition, where the specific heat of the sample changes without latent heat, a step-by-step change in the base line is recorded as being due to the change in the heat capacity of the sample. The height of the step-by-step change is derived:

$$\Delta T_{b2} - \Delta T_{b1} = aS\Delta c_s \rho_s \tag{19}$$

where ΔT_{b1} and ΔT_{b2} are the temperature differences in the steady state before and after the transition respectively, and where Δc_s is the change in the specific heat of the sample. In this case, the change in the base line depends on the sensitivity and the heating rate, and thus higher heating rates are preferred. The response time to the new base line would also be of the order of $5\tau_0$.

Thus, we have a theoretical basis for estimating the heat of transformation by differential thermal analysis, and the expressions of the response time and the sensitivity have been given. The inherent limitations of the differential thermal analysis should now be considered. In the derivation given above, the heat capacity of the sample is implicitly assumed to be constant. If the heat capacity changes at the thermal transformation, the base line must change after the peak; the estimation of the peak area should suffer from these changes. The theoretical treatment can be derived considering these changes in the thermal properties of the sample; the corrected area is shown in Fig. 3, where the time interval, τ_c, has the following value (see Appendix):

$$\tau_c = c_h \rho_h \left(R_o^2 - R_i^2 - R_i^2 \log \frac{R_o}{R_i} \right) \Big/ 4\lambda_h \log \frac{R_o}{R_i} + c_s' \rho_s' R_i^2 \log \frac{R_o}{R_i} \Big/ 4\lambda_h \tag{20}$$

where c_s' and ρ_s' are the specific heat and the density of the sample after the transition, and where τ_c contains those unknown values. Therefore, no accurate correction can be made unless those values are known. Strella[14] suggested a method of correction, but his theory contains rough assumptions and it seems that, using it, the error due to the assumptions would become larger than the correction.

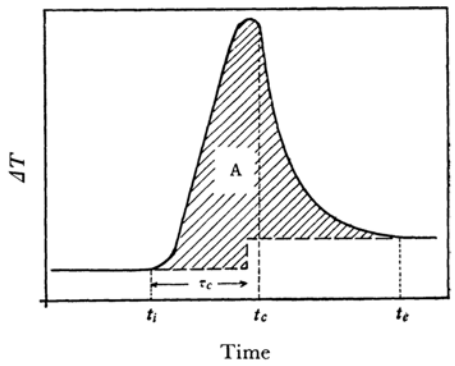

Fig. 3. The corrected peak area.

The end effect neglected in the theory should also be considered; this effect would add some terms to the proportionality coefficient and could be decreased if the length of the cell is large enough in comparison with its diameter. The heat flow through the leads of the temperature-detection device is also neglected; it would also add some correction terms to the proportionality coefficient if the leads pass through the metal block and if the heat flows into the cell through the leads not from the outside but from the metal block.

Finally, let us give the proportionality coefficient, the sensitivity and the response time for other types of arrangements and discuss them briefly. For the most conventional type (as is shown in (a) of Fig. 1), because $R_o = R_i = R$ and $r = 0$ (see Appendix):

$$K = 4\pi l \lambda_s \tag{21}$$

$$S = R^2/4\lambda_s \tag{22}$$

and:

$$J_0(R\sqrt{c_s \rho_s/\lambda_s \tau_n}) = 0 \tag{23}$$

For the type shown in (b) of Fig. 1 (see Appendix):

$$K = 4\pi l/[1/\lambda_s + (2/\lambda_a) \log (R_o/R_i)] \tag{24}$$

$$S = R_i^2[1/4\lambda_s + (1/2\lambda_a) \log (R_o/R_i)] \tag{25}$$

Here the τ_n's are the roots of an equation similar to Eq. 9, where λ_h, c_h and ρ_h are replaced with those of air, λ_a, c_a and ρ_a respectively. If λ_s is much larger than λ_a,

$$K \fallingdotseq 2\pi l \lambda_a / \log (R_o/R_i) \tag{26}$$

The proportionality coefficient becomes the coefficient independent of the kind and the state of the sample, but the heat exchange by radiation and convection disturbs the proportionality, especially above 300°C.

21) M. L. Dannis, *J. Appl. Polymer Sci.*, **7**, 231 (1963).
22) S. Strella, ibid., **7**, 569 (1963).
23) B. Wunderlich, D. M. Bodily and M. H. Kaplan, *J. Appl. Phys.*, **35**, 95 (1964).
24) A. R. Haly and M. Dole, *J. Polymer Sci.*, B, **2**, 285 (1964).

Experimental

Apparatus.—In designing the apparatus, the assumptions made in the mathematical derivations must be taken into account, besides the arrangement of the cell, the cell holder and the temperature-detection device; the metal block must have a large enough heat capacity and heat transfer coefficient; it is preferable that the thermal conductivity of the cell holder be low and have a small temperature dependency; the solid cell holder must cover the entire surface of the cell; it should make a good, reproducible thermal contact with the surface of the cell if possible, and the temperature gradient in the system has a cylindrical symmetry (in other words, the length of the cylinder must be long enough compared with its radius). The temperature gradient in the metal block must be negligibly small. The response time and sensitivity must also be taken into account.

The purpose of constructing our apparatus is to study the thermal behavior of high polymeric meterials. Hence, the apparatus is expected to be operated up to 600°C and it must be suitable to a sample with a low thermal conductivity. The following apparatus is constructed for the above purpose, but the principles of the design considered in this research are essentially applicable to other fields of research.

According to the above considerations, the apparatus shown in Figs. 4 and 5 is constructed. The metal block consists of three separable parts, which cover the cell holders, as is shown in Fig. 4; these are made of nickel because of its thermal stability. Although copper and aluminum are preferred because of their higher thermal conductivities, these metals are not stable at high temperatures. In the block are drilled six cylindrical cavities, in which are inserted the cell holders, the cells, and the thermocouples. In two of the six cavities are set reference cells with the same heat capacity as that of the sample; in three of them, a sample cell, and in the sixth and last one a reference cell with a half-amount of the reference material. The temperature difference between the last reference cell and the ordinary reference cell serves as a monitor to indicate the false deflection of the base line due to the fluctuation of the heating rate or other accidential causes. The other three temperature differences between the three sample cells and the two reference

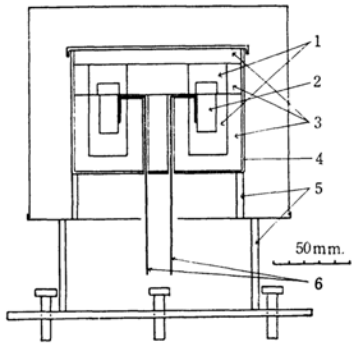

Fig. 4. The apparatus.

1 Cell holder 2 Cell
3 Metal block 4 Heater
5 Quartz support 6 Thermocouple

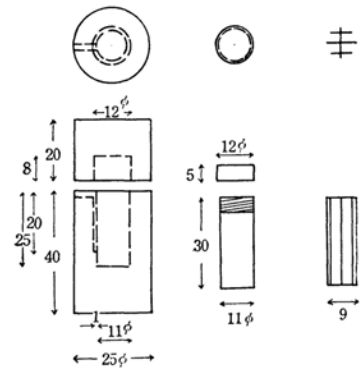

Fig. 5. The cell holder, the cell and the heat distributor.

cells are recorded. This arrangement makes possible the simultaneous measurement of three samples.

The block is inserted into a furnace made of a nickel cylinder. Nichrome wire about 0.3 mm. in diameter is wound on the mica film with which the side and bottom of the furnace are convered. As the heat capacity of the block is several hundreds times as large as that of the sample and the reference materials plus the cells, the linear heating of the block would not be disturbed by the heat of transformation occurring in the sample. Therefore, the control of the temperature of the furnace, not of the block itself, is suitable in this case in order to reduce the fluctuation of the heating rate, because of the faster response to control; furthermore, the narrow air gap between the block and the furnace absorbs the fluctuation of the short period and plays a role analogous to an electrical smoothing circuit.

Fused quartz is chosen as the material of the cell holder for the reasons mentioned above and because of its strength. The transition at 573°C of quartz has had little effect on the thermograms previously obtained, probably because of its small heat effect and its differential use. The shape of the holder is shown in Fig. 5. The thermocouple is inserted through the side groove. In determining the dimensions and the material of the holder, the proportionality coefficient, K, is calculated to be about 6 cal./°C min. at 100°C; the response times, τ_0's are also calculated and tabluated in Table I. These values are satisfactory, because $5a\tau_0$ is about 2°C at the heating rate of 30°C/hr. except for water.

The cell is made of stainless steel, SUS 27, or nickel;

Table I. The response times of systems*

$\sqrt{\frac{\lambda_s}{c_s\rho_s}}$	$\sqrt{\lambda_s c_s \rho_s}$	τ_0	τ_1	Corresponding substances
4	2	0.6	0.2	Metals
0.65	0.356	0.7	0.2	Inorganic salts
0.1	0.1	0.8	0.3	Organic substances
0.3	0.1	5.7	1.1	Water

* The cell holder is made of fused quartz; $\sqrt{\lambda_h/c_h\rho_h}=0.65$ and $\sqrt{\lambda_h c_h \rho_h}=0.356$. The dimensions of the quantities are expressed by cm., g., min., cal. and °C.

Table II. The results of the measurements of the transformations

Sample*	The temp. of transformation, °C obt.	lit.	K**	σ***	ΔH_{lit} cal./g.	Ref.
KNO_3 (a, GR)	135	128	2.09	0.07	12.8	25),26)
	337	338	2.70	0.06	25.2	27),28)
Ag_2S (a, EP)	177	179	2.60	0.12	4.076	26)
$KClO_4$ (a, GR)	304	299.8	2.84	0.07	23.7	29)
$NaNO_3$ (b, GR)	310	306.2	2.50	0.09	41.3	26),30),31)
C_2Cl_6 (c, EP)	49	44.9	1.85	0.20	2.59	32)
	75	71.2	2.53	0.28	8.295	32)
Pentaerythritol (c, GR)	191	187.8	2.53	0.20	77.1	32)
CBr_4 (a, GR)	49	47	1.71	0.07	4.81	33)
	97	90.1	2.13	0.04	2.9	27)
$K_2Cr_2O_7$ (e, GR)	401	398	2.53	0.07	28.9	27)
Stearic acid (d)	69	69	1.87	0.12	47.5	32)
Palmitic acid (d)	60	62.5	2.03	0.11	51.2	34)
Benzophenone (c, GR)	46	48.2	1.85	0.09	23.5	32)
$PbCl_2$ (a, EP)	500	498	3.87	0.16	20.9	27)
$AgNO_3$	168	160	2.56	0.13	3.47	35),36)
	213	211	2.75	0.12	17.6	36)
Benzoic acid (GR)	125	123.2	2.14	0.09	3.48	32),37),38)
Phenanthrene (c, EP)	100	99.3	2.64	0.16	25.0	32)
NH_4NO_3 (f, GR)	89	84.2	2.15	0.20	4.0	27)
	130	125.2	2.36	0.12	12.6	27),32)
Azoxybenzene (c, EP)	35	34.6	1.76	0.10	21.6	32)
Bibenzoyl (c, GR)	98	94.9	1.74	0.12	22.2	32)
Biphenyl (c, EP)	70	69.8	2.00	0.22	28.7	32)
p-Nitroaniline (c, GR)	152	147.5	2.34	0.30	36.5	32)
Hexamethylbenzene (c, EP)	110	110.9	2.40	0.20	2.59	32)
	164	163.9	2.67	0.27	30.3	32)
trans-Cinnamic acid (c, GR)	137	133	2.13	0.07	36.5	39)
Azobenzene (c, GR)	69	69.1	1.98	0.07	28.9	32)
Li_2SO_4 (a, EP)	580	575	4.87	0.21	62	27)
Na_2WO_4 (a, EP)	583	587.8	4.85	0.16	28.4	29)
	586	589				
Sn (g, EP)	235	232	2.38		15.1	27),40)
Pb (a, GR)	332	327.6	2.70		5.50	27)
α-Naphthol (a, GR)	80	95	2.37	0.19	38.8	32)
LiBr (a, GR)	553	550	3.43	0.27	36	41)

* The manufacturer and the grade of the samples are described in the parenthesis: a refers to Kanto Chemical Co., Ltd., b, Showa Chemical Co., Ltd., c, Tokyo Chemical Co., Ltd., d, purified sample kindly supplied by professor Kambe of the Institute of Space and Aeronautical Science, The University of Tokyo, e, Kokusan Chemical Co., Ltd., f, Tomiyama Pure Chemical Industrial Co., Ltd., g, Sumida Chemical Co., Ltd.

** The dimension of K is cal./°C min.

*** The standard deviation of K.

25) A. Mustajoki, *Ann. Acad. Sci. Fennicae Ser. A*, **VI**, 99, 11pp (1962); *Chem. Abstr.*, **57**, 5365e (1962).

26) A. Arell, *Ann. Acad. Sci. Fennicae Ser. A*, **VI**, 101, 3pp (1962); *Chem. Abstr.*, **57**, 2941g (1962).

27) K. K. Kelley, *Bull. U. S. Bur. Mines*, **584** (1960).

28) V. A. Sokolov and N. E. Shmidt, *Izvest. Sektora Fiz.-Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S. S. S. R.*, **27**, 217 (1956); *Chem. Abstr.*, **50**, 15200b (1956).

29) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, *Circular Natl. Bur. Standards*, **C500** (1952).

30) A. Mustajoki, *Ann. Acad. Sci. Fennicae Ser. A*, **VI**, No. 5, 17pp (1957); *Chem. Abstr.*, **52**, 5111g (1958).

31) V. A. Sokolov and N. E. Shmidt, *Izvest. Sektora Fiz.- Khim. Anal., Inst. Obshchei i Neorg. Khim., Akad. Nauk S. S. S. R.*, **26**, 123 (1955); *Chem. Abstr.*, **50**, 3059i (1956).

32) Chem. Soc. Japan, Ed., "Kagaku Benran," 2nd ed., Maruzen, Tokyo (1958).

33) J. G. Marshall, L. A. K. Staveley and K. R. Hart, *Trans. Faraday Soc.*, **52**, 19 (1956); *Chem. Abstr.*, **50**, 13588c (1956).

34) T. L. Ward and W. S. Singleton, *J. Phys. Chem.*, **56**, 696 (1952); *Chem. Abstr.*, **46**, 9930c (1952).

35) A. Arell, *Ann. Acad. Sci. Fennicae Ser. A*, **VI**, No. 100, 3 (1962); *Chem. Abstr.*, **57**, 2941d (1962).

36) G. J. Janz and F. J. Kelly, *J. Phys. Chem.*, **67**, 2848 (1963).

37) G. T. Furukawa, R. E. McCoskey and G. J. King, *J. Res. Natl. Bur. Standards*, **47**, 256 (1951); *Chem. Abstr.*, **46**, 4348g (1952).

38) A. A. Sklyankin and P. G. Strelkov, *Zhur. Priklad. Mekh. i Teck. Fiz.*, No. 2, 100 (1960); *Chem. Abstr.*, **56**, 5464f (1962).

39) Chem. Soc. Japan, Ed., "Kagaku Benran," 1st ed., Maruzen, Tokyo (1952).

40) K. G. Khomyakov, V. A. Kholler and S. A. Zhvanko, *Vestnik Moskov. Univ.*, **7**, No. 3, *Ser. Fiz.-Mat. i Estestven. Nauk*, No. 2, 41 (1952); *Chem. Abstr.*, **46**, 9404g (1952).

41) M. Blanc, *Compt. rend.*, **246**, 570 (1958); *Chem. Abstr.*, **52**, 9741g (1958).

its shape is shown in Fig. 5, which also shows the heat distributor, which is put into the cell to reduce the temperature gradient in the cell, to sharpen the peak, and to increase its accuracy and resolving power.

The whole system mentioned above is covered with a shield case preventing heat loss to the outside, and the apparatus is placed in a vacuum chamber.

As is shown in Fig. 4, the thermocouple leads pass through the metal block and the cell holder and are inserted between the interface and into the groove cut on the inner surface of the cell holder. These passages prevent the heat from flowing directly to the outside through the leads. The heat flows from the metal block into the sample cell through the thermocouple leads, but the proportionality of the peak area to the heat of transformation could be said to hold, taking account of this heat flow, which would add a certain correction term to the proportionality coefficient, because no heat flows into the cell from other parts of the apparatus. If a similar thermocouple and a similar insulating tube are always used, this heat flow occurs reproducibly.

An alumel-chromel thermocouple 0.3 mm. in diameter, manufactured by Hoskins Mfg. Co., is used with an alumina insulating tube 1 mm. in outer diameter. As the electromotive force of the thermocouple increases almost linearly with an increase in the temperature, the thermocouple is preferable for differential thermal analysis.

A cam-driven program controller of the three-position action type, purchased from the Chino Works, Ltd. (model E 142), is used to control the furnace temperature from 0 to 600°C; the power supplied to the furnace is controlled by the three-position action of the controller. Furthermore, the voltage of the supplied power is increased at the heating cycle with a synchronous motor when the temperature is not higher than the set point, and decreased at the cooling cycle when the temperature is not lower. A multipoint recorder with a 250 mm.-wide strip-chart, a d. c. amplifier (model AM101) and a relay-box (Ohkura Electric Co., Ltd.) recorded the four temperature differences and the temperature of the reference material as functions of the time. The full-scale span of the recorder corresponds to 60 μV. of the output of the differential thermocuples when fed through the d. c. amplifier at its highest sensitivity; it also corresponds to a 600°C rise in the temperature of the reference material. The dotting period for each point is 36 sec. Almost all runs are made at a heating rate of 30°C/hr. under an ambient pressure.

Materials.—The materials to be tested are used without purification. The manufacturer and the grade are listed in Table II. The 200—300 mesh powder of α-alumina from Nishio Kogyo Co., Ltd. is used as the reference material. Quartz sand of a 99.8% purity, occurring in Fukushima Prefecture and supplied by Nihon Optical Co., Ltd., is used as the diluent.

Results

To prove the validity of the theory, we should be able to show experimentally that the proportionality coefficient, K, does not depend on the sample and the operational variables, but on the temperature. Two types of experiments are made. (1) The measurements to obtain the proportionality coefficient are done on various kinds of samples of known heats of transition, including organic materials, inorganic salts and metals. The smoothed curve of the coefficients must be drawn against the temperature. (2) The coefficient is obtained for the transition of potassium perchlorate at 299.8°C, changing such operational variables as the heating rate, the packing density, the concentration of the diluent, and the depth of packing the sample. The same value of the coefficient must be obtained irrespective of the values of the variables.

First, the difference in the base line between the beginning and the end of the peak must be considered. As has been pointed out in connection with theoretical considerations, no true correction of the difference can be made unless the specific heat and the density of the sample are known. Therefore, the base line under the peak is taken as a straight line between the base line at the beginning and that at the end. Any error due to the above approximation would be small, because the differences in the base line, even if they exist, are small compared with the peak areas in most of the cases described below.

Next, we must check the reproducibility of the data which are obtained in investigations of the transitions of ammonium nitrate at 84°C and 125°C by the method of an analysis of the variance, where the elements are the cell holder, the cell, and the cylindrical cavity. The results of the analysis shows that the variance in the proportionality coefficient contains the variance of the cell holder because of the poor interchangeability, which is presumably due to the low precision of the machining. The standard deviation due to the experimental error amounts of about 7%; if one uses a given cell holder and measures the heat with this apparauts, the error of a single measurement may be 7%. In the following experiment three cell holders are used; they show middle values of the proportionality coefficient among the twelve and do not differ appreciably from one another.

Three methods of determing the temperature of the transformation have been used: the temperature is obtained at the point where the peak starts to develop, or at the top of the peak, or at the intersection of the line extrapolating the steeply-rising portion of the peak to the initial base line. The choice of method depends on the particular apparatus. The best estimate of the temperature of the transformation with our apparatus is obtained at the intersection. The temperatures obtained by this estimation are included in Table II. The average deviation of the measured temperature from the reported temperature is +2°C. A typical peak is reproduced in Fig. 6.

The results of Experiment (1) are tabulated in

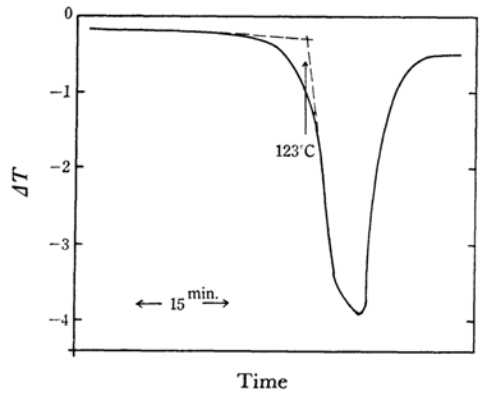

Fig. 6. A typical peak of benzoic acid.

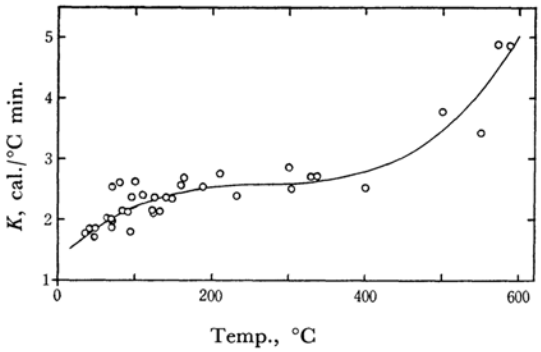

Fig. 7. The proportionality coefficient versus the temperature.

Table II, which also lists the measured temperatures of transformation, their literature values, and the literature heats of transformation, ΔH_{tit}. The proportionality coefficients are plotted in Fig. 7; the best fit was obtained by the method of the least squares, with a confidence limit of 95%. The formula of the smoothed curve is:

$$K = 1.507259 + 8.782709\times 10^{-3}\,T - 1.808468 \times 10^{-5}\,T^2 + 6.324056\times 10^{-14}\,T^4 \qquad (27)$$

where T is the temperature in °C. Considering the great variety of samples, their thermal conductivities, and particle sizes, Fig. 7 is sufficient to indicate that the proportionality coefficient is a function of the temperature only and that it is independent of the kinds and states of the samples. The standard deviations of the mean values of the proportionality coefficient of three or more measurements are 2% to 13%, as is shown in Table II; these errors are caused partly by the difference in the cell holders. Large deviations are found in the measurements of organic samples, presumably because of their broad peaks. The scattering of the points about the smoothed curve in Fig. 7 is due to the random error of the measurements, the difference in the cell holders, and the error in the reported values of the heat of transformation. The variance in the points is the sum of the three variances.

Now, we observe the dependency of the proportionality coefficient on the operational variables. The effects of the heating rate, the packing density, the concentration of the diluent and the depth of packing the sample are shown in Figs. 8, 9, 10 and 11 respectively. The packing density is varied as follows: for the most densely packed one, the powder sample is tamped into the cell as tightly as possible; for the second, the sample is poured into the cell, tapping the cell repeatedly; for the third, the sample is poured and tapped slightly, and for the most loosely packed one, the sample is poured lightly. To vary the concentration of the diluent, the weighed amounts of the powder sample and the diluent are mixed in a mortar and packed into the cell with a similar density. Except for the last effect, the operational variables have no effect on the proportionality coefficient.

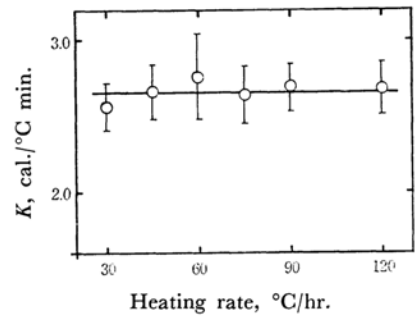

Fig. 8. The effect of heating rate. The range shown is the standard deviation.

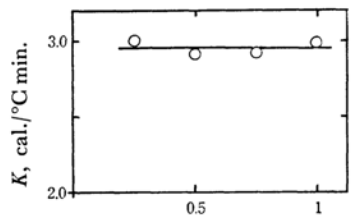

Fig. 9. The effect of packing density.

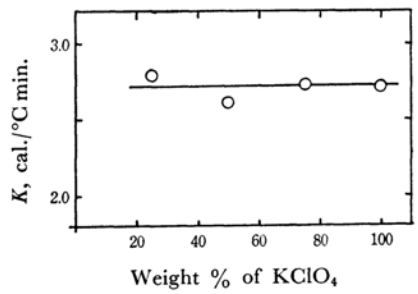

Fig. 10. The effect of diluent.

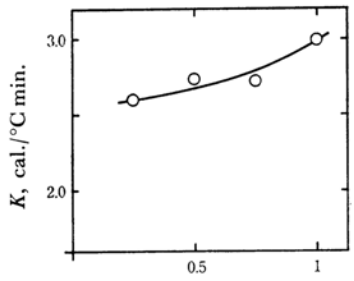

Fig. 11. The effect of the depth of packing the sample. The ratio of the depth of packing the sample to the depth of the cell is abscissa.

as has been expected in the theoretical considerations. The last effect would disturb the heat flow of the cylindrical symmetry and the consequent temperature gradient along the cylindrical axis would change the value of the proportionality coefficient. This finding suggests that the sample must be filled up to the top of the cell, even though loosely.

Besides these experiments, the effect of the diluent is tested by using the reference material of alumina as the diluent; the proportionality coefficient varies in this case. Alumina does not seem suitable as a diluent, probably because of the intereaction between the sample and the diluent.

These results shown above give an assurance of validity of the theory. We may conclude that the proportionality coefficient does not depend on the kind and state of the sample, but that it depends on the temperature only, as has been expected in the theoretical considerations, and that the estimation of the heat of transformation occurring in the sample is possible by this type of quantitative differential thermal analysis.

It would be explained by loose thermal contact due to a little air gap between the cell and the cell holder that the value of the proportionality coefficient obtained is smaller than the expected one of 6 cal./°C min. The linear relation of $\log(\Delta T - \Delta T_b)$ against the time after the completion of the transformation is verified experimentally; it is shown in Fig. 12. The response times, τ_0's, are also examined on some organic and inorganic samples and found to be about 1.5 min. for most samples. A reasoning similar to the above explanation of the proportionality coefficient applies to the discrepancy between the obtained response time and the calculated ones in Table I. It should also be noted that the effect of the heat distributor in the cell is neglected in the calculation of the response times.

To show an effect of the metal heat distributor in the cell, the peaks with or without the distributor are compared. The peak area does not change, but the peak becomes broader without the distributor. The transition of potassium perchlorate is completed 12 min. after the peak is reached without the distributor, but it is completed after 3 min. at the same heating rate when the distributor is used. The time of the completion is almost the same for different samples.

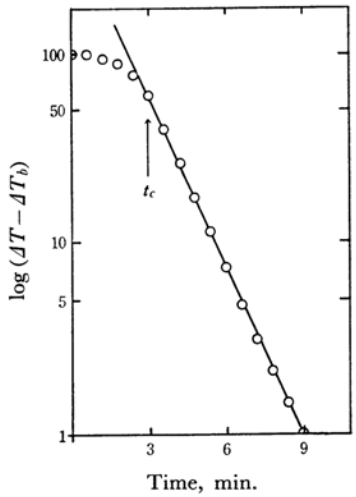

Fig. 12. The change of the temperature difference after the completion of the transformation of potassium perchlorate.

Discussion

Even after Boersma's suggestion of the inherent impossibility of quantitative differential thermal analysis, there have still been published a number of papers on the theme. For example, on the effect of the heating rate on the peak area, Barrall et al.[42] found, on several kinds of samples, that the peak area is decreased by a decrease in heating rate, showing zero area at a zero heating rate, with the type of apparatus where the microsample cell is suspended in an air oven. On the other hand, with a different type of apparatus such as (b) of Fig. 1, Barrall et al.[43] found a similar but more complicated dependency of the peak area of the mixture of silver nitrate; in this case the area is proportional to the heat of transition of the silver nitrate present when the areas at different heating rates are extrapolated to a zero heating rate. Ke[44] found the area of the melting of annealed Marlex 6000 to be independent of the heating rate. Suga et al.[45] reported similar findings except in the case of very low heating rates. In the cases mentioned

42) E. M. Barrall II, R. S. Porter and J. F. Johnson, *Anal. Chem.*, **36**, 2172 (1964).
43) E. M. Barrall II and L. B. Rogers, ibid., **34**, 1101 (1962).
44) B. Ke, *J. Polymer Sci.*, A, **1**, 1453 (1963).
45) H. Suga, H. Chihara, S. Seki, K. Nakatsuka and T. Shinoda, *J. Chem. Soc. Japan, Pure Chem. Sect. (Nippon Kagaku Zasshi)*, **82**, 24 (1961).

above, the area is compared among transitions of a single sample; therefore, the same sampling procedure should give the same proportionality coefficient.

The effect of the diluent is such that, if the sample content is low and if the packing state is changed slightly from run to run by fixing the particle size and the manner of packing the mixture, then the thermal conductivity and consequently the proportionality coefficient will become nearly constant. This effect was noted in the paper of Barrall et al.[43] on salicylic acid diluted with carborundum, and in Yamamoto's paper[46] on benzoic acid diluted with fused silica powder. However, as the diluent has other effects (e. g., the interaction with sample, resulting in a false peak),[47,48] the quantitative differential thermal analysis by using a diluent has limitations, besides the facts that the manner of packing has an influence on the area[46] and the sensitivity decreases because of a diluted active component.

With the type of apparatus in which the sample cell with the thermocouple on its outside is suspended in an air oven, Barrall et al.[42] found that the proportionality coefficient, calibrated with a few materials, shows a linear dependency on the temperature as has been observed in the present paper. David[49] compared with reported values the heats of the transition of eight samples calculated from the area and the proportionality coefficient calibrated on tin; he obtained satisfactory agreements with a similar apparatus. It should be noted here that, in the two papers[42,49] mentioned above, the thermocouple is located on the outside of the cell, that the air gap is between the cell and furnace wall, and that the observed transitions occur below 300°C. In these cases, the air gap would play the same role as the cell holder in the present paper if convection and radiation could be neglected. The results would be less satisfactory if the measurement were made above 300°C, where radiation transfers heat and David's theory would not hold.

Recently, Yagfarov[50] proposed a method of thermography with which one can obtain the values of specific heat, thermal conductivity and thermal diffusivity simultanously. The peak is obtained at the transformation of the sample by the principles of conventional differential thermal analysis; he postulated that the heat of transformation can be estimated from the peak and the thermal conductivity thus obtained. However, the thermal conductivity can not be obtained in the peak region because the thermal conductivity and the state of the packing of the sample have a tendency to change during the transformation. These difficulties were not discussed, and the heat of transformation estimated experimentally was not described, in his paper.

The results obtained in this research can not be of a very high precision, but they do seem encouraging. If the low interchangeability of the cell holder and its poor thermal contact with the block and the cell could be improved, the accuracy would be improved appreciably. In fact, a preliminary experiment with a ceramic cell holder shows an improved reproducibility, for the standard deviation is 3.3% for an average measurement.

However, the most serious defect of the differential thermal analysis as a technique for measuring the heat of transformation is the necessity of calibrating it with a sample of a known heat of transformation. Hence, the accuracy of the method depends on that of the other absolute method of heat measurement. In order to bring out the unique merits of differential thermal analysis, it should be applied to the field of higher temperatures and high pressures; research for developting the absolute differential thermal analysis is now keenly needed.

As an analytical technique, the method proposed in this paper seems to have fair advantages over the other types of differential thermal analysis, because it does not suffer from operational variables and because it improves the reproducibility of the peak of the thermogram. The new concepts presented in this paper, i. e., the response time and the sensitivity, would be helpful for designing new apparatuses.

Attempts are now in progress in our laboratory to improve the apparatus and to make the method an absolute one; this work will be reported on shortly. These improvements will reduce the differential thermal analysis to a dynamic operation of a calorimeter of Calvet's type;[51] it will be a calorimeter with unique features and unique applicability. Both this apparatus and Calvet's are based on the same theoretical back-grounds, so the theory can also be applied to a calorimeter of Calvet's type.

The capable assistance of Hiroshi Isozake in the assembly and operation of the apparatus is gratefully acknowledged. Thanks are also due to Professor Hirotaro Kambe of the Institute of Space and Aeronautical Science, The University of Tokyo, for his encouraging discussions.

Appendix

To derive the temperature change in the sample cell and the cell holder, the temperature is divided into three parts:

46) A. Yamamoto, *Japan Analyst*, **12**, 26 (1963).
47) H. Morita and H. M. Rice, *Anal. Chem.*, **27**, 336 (1955).
48) E. M. Barrall II and L. B. Rogers, ibid., **34**, 1106 (1962).
49) D. J. David, ibid., **36**, 2162 (1964).
50) M. S. Yagfarov, *Russ. J. Inorg. Chem.* (English translation), **6**, 1236 (1961).
51) E. Calvet, *Compt. rend.*, **226**, 1702 (1948); ibid., **236**, 486 (1953).

$$T = T_1 + T_2 + T_3 \tag{A-1}$$

where T_1 represents the temperature at the steady state, where T_1+T_2 is the initial transient temperature, and where T_3 is the additional temperature due to the heat of transformation. First, the temperature gradient at the steady state is considered; then the transient state and the peak are calculated by using the linearity of differentiation, which makes possible the above separation of the temperature. All these temperatures must be derived as functions of the coordinate for the arrangement of (c) in Fig. 1.

If we designate by q the heat flowing into the inner part per unit time through a cylindrical plane of a unit length, and the radius by r, q is the heat necessary to heat up the inner part at the rate of a at the steady state, and the temperature gradient at r occurs by the necessity of letting the heat q flow. Then, for $0 \leq r \leq R_i$:

$$q = \int_0^r 2\pi r a c_s \rho_s \mathrm{d}r \tag{A-2}$$

and for $R_i \leq r \leq R_o$:

$$q = \int_{R_i}^r 2\pi a c_h \rho_h \,\mathrm{d}r + \pi R_i^2 a c_s \rho_s \tag{A-3}$$

The temperature gradient is:

$$q = 2\pi r \lambda_s \partial T_{s1}/\partial r \qquad \text{for } 0 \leq r \leq R_i \tag{A-4}$$

and:

$$q = 2\pi r \lambda_h \partial T_{h1}/\partial r \qquad \text{for } R_i \leq r \leq R_o \tag{A-5}$$

By combining Eqs. A-2 and A-4, and Eqs. A-3 and A-5, the integration of them gives T_{s1} and T_{h1}: for $0 \leq r \leq R_i$:

$$T_{s1}(r) - T_{s1}(R_i) = a c_s \rho_s (r^2 - R_i^2)/4\lambda_s \tag{A-6}$$

and for $R_i \leq r \leq R_o$:

$$T_{h1}(r) - T_{h1}(R_o) = a c_h \rho_h (r^2 - R_o^2)/4\lambda_h + a R_i^2 \log (r/R_o)(c_s \rho_s - c_h \rho_h)/2\lambda_h \tag{A-7}$$

As the temperature of the metal block, $T_{h1}(R_o)$, is equal to at,

$$T_{s1}(r) = at - \frac{a}{4\lambda_h}\left[c_h \rho_h (R_o^2 - R_i^2) + 2R_i^2 (c_s \rho_s - c_h \rho_h) \log \frac{R_o}{R_i}\right] - \frac{a c_s \rho_s}{4\lambda_s}(R_i^2 - r^2) \tag{A-8}$$

$$T_{h1}(r) = at - \frac{a}{4\lambda_h}\left[c_h \rho_h (R_o^2 - r^2) + 2R_i^2 (c_s \rho_s - c_h \rho_h) \log \frac{R_o}{r}\right] \tag{A-9}$$

Secondly, the initial transient period must be taken into account. For this period, the next differential equations hold, because conditions and solutions must be added to those of the steady state to fulfil the overall conditions.

$$\lambda_s \nabla T_{s2} = c_s \rho_s \partial T_{s2}/\partial t \tag{A-10}$$

$$\lambda_h \nabla T_{h2} = c_h \rho_h \partial T_{h2}/\partial t \tag{A-11}$$

with the boundary conditions:

$$T_{h2} = 0 \qquad \text{at } r = R_o \tag{A-12}$$

$$\lambda_s \partial T_{s2}/\partial r = \lambda_h \partial T_{h2}/\partial r \qquad \text{at } r = R_i \tag{A-13}$$

$$T_{s2} = T_{h2} \qquad \text{at } r = R_i \tag{A-14}$$

and with the initial conditions:

$$T_{s2} = \frac{a}{4\lambda_h}\left[c_h \rho_h (R_o^2 - R_i^2) + 2R_i^2 (c_s \rho_s - c_h \rho_h) \log \frac{R_o}{R_i}\right] + \frac{a c_s \rho_s}{4\lambda_s}(R_i^2 - r^2) \tag{A-15}$$

$$T_{h2} = \frac{a}{4\lambda_h}\left[c_h \rho_h (R_o^2 - r^2) + 2R_i^2 (c_s \rho_s - c_h \rho_h) \log \frac{R_o}{r}\right] \tag{A-16}$$

Assuming the cylindrical symmetry, the solutions of the above partial differential equations are typical;[52] they are given below:

$$T_{s2} = \sum_{n=0}^{\infty} \alpha_n \boldsymbol{J}_0\left(r\sqrt{\frac{c_s \rho_s}{\lambda_s \tau_n}}\right)[\boldsymbol{J}_0(R_i x)\boldsymbol{Y}_0(R_o x) - \boldsymbol{J}_0(R_o x)\boldsymbol{Y}_0(R_i x)] \exp\left(-\frac{t}{\tau_n}\right) \tag{A-17}$$

$$T_{h2} = \sum_{n=0}^{\infty} \beta_n \boldsymbol{J}_0\left(R_i\sqrt{\frac{c_s \rho_s}{\lambda_s \tau_n}}\right)[\boldsymbol{J}_0(rx)\boldsymbol{Y}_0(R_o x) - \boldsymbol{J}_0(R_o x)\boldsymbol{Y}_0(rx)] \exp\left(-\frac{t}{\tau_n}\right) \tag{A-18}$$

where x is equal to the x used in Eq. 9, and where α_n's and β_n's are constants. In order to fulfil the boundary and initial conditions, A-12, A-13, A-14, A-15 and A-16, τ_n's are defined by the roots of Eq. 9, and α_n's and β_n's are determined to express the initial temperature distribution. By adding Eq. A-8 to Eq. A-17, and Eq. A-9 to Eq. A-18, we obtain Eqs. 7 and 8.

Thirdly, the other transient temperature is derived. The temperature distribution at the time of the completion of the transformation, t_c, can be expressed as a certain function of r, which is the initial condition for this case. As the same expressions of Eqs. A-10 to A-14 are applicable, the solutions, i. e., Eqs. 14 and 15, are derived similarly to Eqs. 7 and 8. It is apparent from the above considerations that T_3 is diminished to a negligibly small value, after a long enough time has elapsed, and then the additional temperature due to the heat of transformation reaches a form of peak.

Finally, the peak area from the beginning of the peak, t_i, to its end, t_e, is calculated.

$$\lambda \nabla T_3 = c\rho \partial T_3/\partial t + \Delta H \rho \partial m/\partial t \tag{A-19}$$

The initial and final conditions are as follows:

$$T_3 = 0 \qquad \text{at } t = t_i \tag{A-20}$$

$$T_3 = 0 \qquad \text{at } t = t_e \tag{A-21}$$

and the boundary conditions are:

$$T_3 = 0 \qquad \text{at } r = R_o \tag{A-22}$$

$$T_{s3} = T_{h3} \qquad \text{at } r = R_i \tag{A-23}$$

and:

$$\lambda_s \partial T_{s3}/\partial r = \lambda_h \partial T_{h3}/\partial r \qquad \text{at } r = R_i \tag{A-24}$$

The integration of Eq. A-19 from t_i to t_e gives:

$$\lambda \int_{t_i}^{t_e} \nabla T_3 \,\mathrm{d}t = c\rho \int_{t_i}^{t_e} \mathrm{d}T_3 + \rho \Delta H \tag{A-25}$$

52) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, Oxford (1959).

According to the initial and final conditions,

$$c\rho\int_{t_i}^{t_e} dT_3 = 0 \qquad \text{(A-26)}$$

and the integration of T_3 from t_i to t_e is the desired peak area, A. Then, the integration of Eq. A-25 over the volume, V, as with Boersma,[11] gives:

$$\lambda\int_V dV\Delta A = \int_V \rho\Delta H\, dV \qquad \text{(A-27)}$$

Namely,

$$\lambda\int_F dF\, \boldsymbol{grad}\, A = \rho V\Delta H \qquad \text{(A-28)}$$

where F is the surface of the cylinder; considering the cylinderical symmetry, we have:

$$F\lambda\frac{\partial A}{\partial r} = \rho V\Delta H \qquad \text{(A-29)}$$

Taking into account that the heat is produced or consumed in the sample only, Eq. A-29 is separated into two equations: for $R_i \leq r \leq R_o$:

$$\frac{\partial A(r)}{\partial r} = \rho_s\Delta H V_s/\lambda_h F(r) \qquad \text{(A-30)}$$

where V_s is the volume of the sample, and for $0 \leq r \leq R_i$:

$$\frac{\partial A(r)}{\partial r} = \rho_s\Delta H V(r)/\lambda_s(r) \qquad \text{(A-31)}$$

As $T_3=0$ at $r=R_o$, for $R_i \leq r \leq R_o$:

$$A(r) = \frac{M\Delta H\log(R_o/r)}{2\pi l\lambda_h} \qquad \text{(A-32)}$$

and for $0 \leq r \leq R_i$:

$$A(r) = \frac{M\Delta H}{2\pi l}\left[\frac{\log(R_o/R_i)}{\lambda_h} + \frac{(R_i^2-r^2)}{2\lambda_s R_i^2}\right] \qquad \text{(A-33)}$$

All the derived equations are functions of r, the position of the temperature-detection device, and if we let r equal R_i, i. e., if the temperature-detection devices are inserted at R_i, the equation becomes equal to Eq. 16. If r is made equal to 0 and if the radiation and convection can be neglected, the equation becomes applicable to the type (b) of Fig. 1. Equation applicable to the conventional method is also derived, when R_o is made equal to R_i and r, equal to 0.

Let us consider the case where the specific heat, the density, and the heat conductivity change abruptly to new values, c_s', ρ_s' and λ_s', at the temperature of transformation, T_t. The base line after the peak becomes different from the one prior to the peak, reflecting this change in thermal properties; Eq. 16 can not be applied to this case; for it, however, an expression can be derived for the apparatus of the type (c) in Fig. 1.

The heat flowing through the cylindrical plane in the cell holder with the radius of r, into the cell and the inner part of the cell holder from t_i to t_e is equal to the heat necessary to heat the inner part from the temperature distribution at t_i to the new temperature distribution at t_e, plus the heat of transformation. The temperature distributions at t_i and t_e must first be derived. As the sample at the outermost part of the cell begins to be transformed at t_i, the temperature at this point is equal to the temperature of the transformation. Therefore, for $0 \leq r \leq R_i$:

$$T_s = T_t - \frac{ac_s\rho_s}{4\lambda_s}(R_i^2 - r^2) \qquad \text{at } t = t_i \qquad \text{(A-34)}$$

and for $R_i \leq r \leq R_o$:

$$T_h = T_t + \frac{a}{2\lambda_h}R_i^2(c_s\rho_s - c_h\rho_h)\log\frac{r}{R_i} + \frac{ac_h\rho_h}{4\lambda_h}(r^2 - R_i^2) \qquad \text{at } t = t_i \qquad \text{(A-35)}$$

when $t=t_e$, at $r=R_o$:

$$T_h = T_t + a(t_e - t_i) + \frac{a}{2\lambda_h}R_i^2(c_s\rho_s - c_h\rho_h)\log\frac{R_o}{R_i} + \frac{ac_h\rho_h}{4\lambda_h}(R_o^2 - R_i^2) \qquad \text{(A-36)}$$

for $R_i \leq r \leq R_o$:

$$T_h = T_t + a(t_e - t_i) + \frac{a}{2\lambda_h}R_i^2(c_s\rho_s - c_h\rho_h)\log\frac{R_o}{R_i} + \frac{ac_h\rho_h}{4\lambda_h}(R_o^2 - R_i^2) - \frac{ac_h\rho_h}{4\lambda_h}(R_o^2 - r^2) - \frac{a}{2\lambda_h}R_i^2(c_s'\rho_s' - c_h\rho_h)\log\frac{R_o}{r} \qquad \text{(A-37)}$$

and for $0 \leq r \leq R_i$:

$$T_s = T_t + a(t_e - t_i) + \frac{a}{2\lambda_h}R_i^2(c_s\rho_s - c_h\rho_h)\log\frac{R_o}{R_i} + \frac{ac_h\rho_h}{4\lambda_h}(R_o^2 - R_i^2) - \frac{a}{4\lambda_h}R_i^2(c_s'\rho_s' - c_h\rho_h)\log\frac{R_o}{R_i} - \frac{ac_h\rho_h}{4\lambda_h}(R_o^2 - R_i^2) - \frac{ac_s'\rho_s'}{4\lambda_s}(R_i^2 - r^2) \qquad \text{(A-38)}$$

The heat necessary to bring the system from the state described by Eqs. A-34 and A-35 to the state described by Eqs. A-37 and A-38 includes the following: (1) the heat to heat up the sample from the initial temperature (Eq. A-34) to T_t with the specific heat of c_s and the density of ρ_s; (2) the heat of the transformation of the sample, $M\Delta H$; (3) the heat to raise the temperature of the sample from T_t to the temperature distribution of Eq. A-38 with the specific heat of c_s' and the density of ρ_s', and (4) the heat necessary to heat the cell holder from the state of Eq. A-35 to Eq. A-37. Now suppose that the transformation did not take place. Then, the base line would not change and the heat flowing through the cylindrical plane, with the radius r, during the interval is $a(t_e - t_i)[\pi R_i^2 c_s\rho_s + \pi(r^2 - R_i^2)c_h\rho_h]$. Therefore, it we represent the additional temperature due to the transformation by ΔT_t, which is the temperature difference between the peak and the extrapolated initial base line,

$$2\pi r\lambda_h\frac{\partial}{\partial r}\int_{t_i}^{t_e}\Delta T_t(r,t)\,dt = a(t_e - t_i)\pi R_i^2(c_s'\rho_s' - c_s\rho_s) + \frac{a\pi c_s'\rho_s'}{4\lambda_h}R_i^4\log\frac{R_o}{R_i}(c_s\rho_s - c_s'\rho_s') + \frac{a\pi}{8\lambda_s}R_i^4[(c_s\rho_s)^2 - (c_s'\rho_s')^2] + \Delta H\pi R_i^2\rho_s + \frac{ac_h\rho_h\pi}{4\lambda_h}(c_s\rho_s - c_s'\rho_s')(2r^2\log R_o + r^2 - 2r^2\log r - R_i^2) \qquad \text{(A-39)}$$

By integrating Eq. A-39 and making r equal to R_i, we obtain:

$$\int_{t_i}^{t_e} \Delta T_t \, dt = \frac{R_i^2 \rho_s \Delta H}{2\lambda_h} \log \frac{R_o}{R_i} + \frac{a(t_e - t_i)}{2\lambda_h} R_i^2 \log \frac{R_o}{R_i} (c_s' \rho_s' - c_s \rho_s) + \frac{a c_h \rho_h}{8\lambda_h^2} R_i^2 (c_s \rho_s - c_s' \rho_s') \left(R_o^2 - R_i^2 - R_i^2 \log \frac{R_o}{R_i} \right) + \frac{a R_i^4}{16 \lambda_s \lambda_h} \log \frac{R_o}{R_i} (c_s^2 \rho_s^2 - c_s'^2 \rho_s'^2) + \frac{a c_s' \rho_s'}{8\lambda_h^2} R_i^4 (c_s \rho_s - c_s' \rho_s') \left(\log \frac{R_o}{R_i} \right)^2 \quad \text{(A-40)}$$

The left side of Eq. A-40 is the area enclosed by the peak, the extrapolated initial base line and the straight line drawn perpendicularly at $t = t_e$. This equation can be converted to the next one by considering Eqs. 16 and 19:

$$M \Delta H = K \left[\int_{t_i}^{t_e} \Delta T_t \, dt - (\Delta T_{b2} - \Delta T_{b1}) \{ (t_e - t_i) - \tau_c \} \right] + a\pi R_i^4 \left(\frac{c_s^2 \rho_s^2}{\lambda_s} - \frac{c_s'^2 \rho_s'^2}{\lambda_s'} \right) \quad \text{(A-41)}$$

If some devices are used to decrease the temperature gradient in the cell, the last term of Eq. A-41 due to the change in the temperature distribution in the cell may be neglected; the corrected peak area is as is shown in Fig. 3 and Eq. 20.