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A STUDY OF THE THERMAL EFFECTS OBSERVED IN DTA.
Part 2. The influence of sample and reference system parameters on a typical DTA curve

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ABSTRACT

A mathematical model is used to study the influence of changes in the physical properties of a sample, as it undergoes a reaction, on the characteristics of the DTA curve produced. Some of the earlier methods used to obtain activation energies from DTA peaks are shown to be in error if the sample physical properties change during the reaction. Peak shape is particularly influenced by changes in specific heat and peak area is affected by changes in conductivity. Large changes in specific heat can cause considerable distortion of the DTA curve.

INTRODUCTION

In the previous paper in this series [1], a mathematical model was developed to study the effect of sample and holder parameters on the transfer of heat in a DTA apparatus. In that paper, the model was used to investigate the effect of differing sample radii and physical properties on the area, shape and peak temperature of a typical DTA peak. The parameters remained constant during a run but were varied between runs to assess the effect of such changes. In this paper, any one or all the parameters have been varied during that reaction process that produces the DTA peak, in order to investigate the effect of such changes on the progress of the DTA curve before, during and after the peak. The effect of these changes on the area, shape and peak temperature is also discussed. The effect of the variation of the parameters with temperature on the DTA curve is also studied.

In modern equipment, the sample size is purposefully made small, in order to minimize the influence of heat transfer on the resulting DTA curve,

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so that the results can be used in kinetic studies. There are, however, instances where small sample size presents its own problems. When studying reactions in multicomponent mixtures, it is often difficult to ensure that a small sample is representative of the original industrially used mixture. In such a situation, it is often necessary to increase the sample size in order to obtain meaningful results. In such cases, this paper will give an insight into the usefulness or otherwise of measurements made on DTA curves produced from larger samples. The effects described here will still appertain to small samples but to a much less extent.

VARIATION OF PARAMETERS

In the model [1], heat transfer into the sample and reference materials via the holder is assumed to take place by conduction alone, no account being taken of heat transfer by radiation or convection. The inclusion of radiation factors in the finite difference equations would lead to greater complexity. It can be shown, however, that if the temperature gradient within the sample is small, then the radiative factor can be expressed as an extra conductivity factor. Thus, in this study, the only effects considered were changing conductivity, density and specific heat. No allowance has been made for mass loss during the evolution of gas from the sample during decomposition, although the ability to alter density during the reaction might in some measure account for this effect.

Variation with temperature

In this study, the variations of the physical properties of the reference material were assumed to follow a law given by the equation:

$$N_R = N_0(1 + cT) \tag{1}$$

where N_R is the value of a given property at a temperature T, N_0 is the value of a given property at absolute zero, and c is a constant. A polynomial equation has not been used here, in order to simplify the computer processing. Two similar equations may be used to describe any one of the physical properties of the sample both before and after a reaction:

$$N_B = N_1(a + bT) \tag{2}$$

and

$$N_A = N_2(1 + aT) \tag{3}$$

where N_B is the value of a given property at any temperature before the sample has reacted, N_A is the value of the given property at any temperature after the sample has reacted, and N_1 and N_2 are the values that the unreacted and reacted sample would have at absolute zero; a and b are constants.

Variation with reaction

Obviously during a reaction which produces a DTA peak, the sample properties will change, but there is little experimental evidence to indicate the way in which such changes occur. In view of this fact, it has been assumed here that the value of any property during a reaction will depend on the relative amounts of unreacted and reacted component present, and this can be expressed mathematically by the expression

$$N_c = (1-x)N_B + xN_A \tag{4}$$

where N_c is the value of a given property during the reaction and x is the fraction of the sample which has reacted up to the given temperature.

Fusion reactions, with the rapid volume change accompanying them, cannot be dealt with in the present model.

As the influence of the holder is not under consideration in this paper (its effects are studied in Part 3 [2]), it will be assumed that the sample and reference materials are held in a cylinder of material of infinite conductivity, so that the peripheries of the cylindrical sample and reference materials will rise in temperature at a controlled linear rate. It will be assumed that the rate of heat generation or absorption at any point within the sample is proportional to the rate of reaction at that point.

Reaction mechanisms

As stated in the first paper [1] the mathematical equation used to model the reaction has the form

$$dx/dt = A(1-x)^n \times \exp(-E/RT) \tag{5}$$

where x is the fraction reacted at time t and dx/dt is the rate of that reaction; A is the pre-exponential rate constant, which for this study was given the value exp(20.85) in units of 1/time; the activation energy E was given the value of 17.56 kJ mol^{-1}; R is the gas constant and T the absolute temperature.

The temperatures of the periphery of both the sample and reference materials were varied according to the equation

$$T = T_0 + \phi t \tag{6}$$

where T_0 is the starting temperature (usually 573 K) and ϕ is the programmable rate of heating (deg s^{-1}). At this starting temperature the reaction rate is negligible.

Alternative reaction equations could have been used, but other authors have used this same equation to deduce the characteristics of DTA curves.

TABLE 1

Symbols used

	Thermal conductivity [a]	Density [b]	Specific heat [c]
Sample			
Before reaction	k_u	p_u	c_u
After reaction	k_r	p_r	c_r
Reference	k_R	p_R	c_R

[a] Units, W m^{-1} K^{-1}.
[b] Units, kg m^{-3}.
[c] Units, J kg^{-1} K^{-1}.

The present authors are thus able to make direct comparison of their results with those of other authors. In later papers, it is intended to use other equations, representing alternative reaction mechanisms. A discussion of such equations is given in ref. 3.

The techniques of the finite difference equations used to obtain the results are described in an earlier paper [1].

Symbols

The symbols used in this paper referring to the thermal conductivity, density and specific heat of the sample, before reaction, sample after reaction and reference material are given in Table 1.

Definitions and other symbols are as follows:

A_S	Area calculated as DT_{SR} multiplied by time (K s)
DT	change in Offset before and after a DTA peak
DT_{SR}	temperature difference between T_S and T_R
Offset	deviation of the base line from zero difference temperature when a reaction is not occurring
T_{AR}	temperature of maximum reaction in the rate equation alone (eqn. 5)
T_R	temperature along the central axis of the reference at the maximum of the DTA peak (°C)
T_S	temperature along the central axis of the sample at the maximum of the DTA peak (°C)
dx/dt_{ar}	maximum rate of reaction given by the rate equation alone
ϕ	controlled heating rate at periphery of sample and reference materials

RESULTS

Initially the properties of the reference material will be assumed to remain constant throughout the reaction and equal in value to the equivalent properties of the sample material before the reaction. Initially the properties of the sample will vary with the extent of the reaction but will be independent of temperature.

As it is assumed that the temperature profile along the length of the sample is constant, the effect of increased sample size can only be shown by increase of sample radius.

Changes of physical properties during a reaction

Computations show that if the sample (and reference) properties do not change during a reaction, then the baseline of the DTA curve remains the same before and after a peak. Thus, the measurement of DTA peak area is relatively easy, and using computer techniques can be calculated during the run. However, these results show that if there is a change in any one of the sample physical properties during a reaction, then the baseline level changes. As the relationship between the physical properties and temperature during the reaction is usually not known, then it is not possible to define a precise baseline.

However, with the mathematical model used it is possible to describe a baseline across the DTA peak by making a second computation of the curve across the "peak" region. During this computation, no heat is generated or absorbed. Here the generated baseline is that which reflects any change in the physical properties. All areas measured in this and subsequent papers are those defined by the DTA curve and this calculated baseline. Many different techniques have been used to define the baseline. However, the results of this work have led to a practical method of baseline construction which the authors believe gives the best measurement of area under a DTA curve [4]. In the reaction, the effect of change of conductivity during a reaction is considered first, followed by a section dealing with the effect of changing specific heat and a final note on the effect of change in density.

Change of conductivity during a reaction

General effect on the DTA curve. The effect of such changes on peak area, peak temperatures (both sample and reference), differential temperature and offset are shown by quoting some examples. The effects produced by conductivity changes during the reaction are given in Table 2 with the resulting DTA curves in Fig. 1.

These results may now be summarized:

(1) A reduction in the thermal conductivity of the sample during a reaction causes the sample peak temperature to be higher than if no change had occurred. The offset is negative, that is the baseline moves in an endothermic direction after the peak.

(2) An increase in the thermal conductivity of the sample produces a lower peak temperature, and the final offset is positive, i.e. the baseline moves in an exothermic direction after the peak.

TABLE 2

Effect of a change of conductivity on a DTA peak [a]

Curve in Fig. 1	k_u	k_r	T_S	DT_{SR}	A_S	DT	T_R
(a)	0.12	0.12	516.0	−6.027	3062.5	0	522.0
(b)	0.12	0.096	522.0	−8.468	3460.6	−2.55	530.45
(c)	0.12	0.132	513.2	−5.297	2902.3	+0.93	518.46
(d)	0.12	0.144	510.3	−4.527	2762.8	+1.70	514.88

[a] Sample and reference radius, 0.35 cm; $p_u = p_r = p_R = 2.5 \times 10^3$ kg m^{-3}; $C_u = C_r = C_R = 840$ J kg^{-1}; heating rate = 10 K min^{-1}. If the "standard" Arrhenius type equation (eqn. 5) is plotted under the same heating rate conditions the maximum dx/dt occurs at 513.8°C.

(3) An increase in conductivity during the reaction causes the peak area to be reduced. As noted in the previous paper [1], under conditions where the sample and reference materials are in a good conducting material and the thermocouples are along the central axes of the sample and reference materials, then the area of a typical DTA peak is affected by the conductivity of the sample material.

(4) The effects noted in (1) and (2) are less marked in the sample peak temperature than in the reference peak temperature and this is the major reason why sample peak temperatures should be quoted in preference to

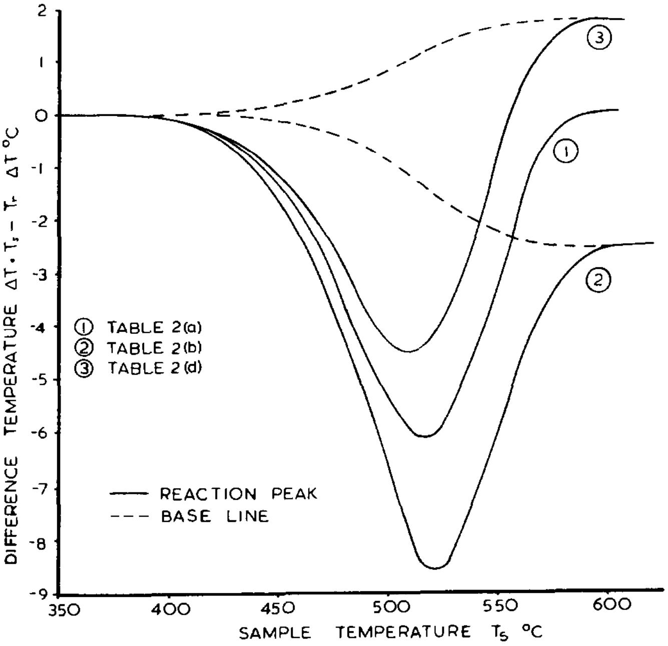

Fig. 1. Influence of conductivity change during a reaction.

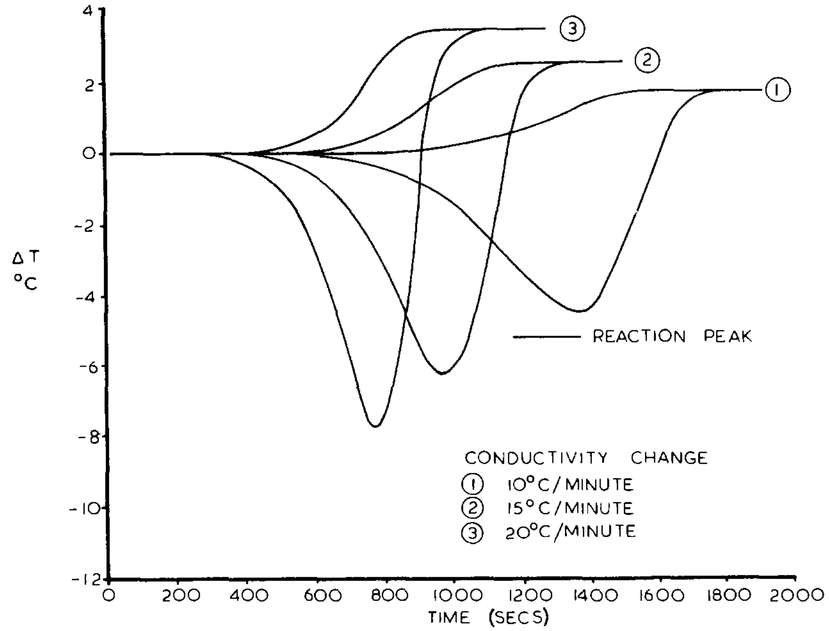

Fig. 2. Effect of different rates of heating with conductivity change.

peak reference temperature. Further, DTA curves should always be plotted as difference temperature versus sample temperature. Area measurement is in units of K s, so that when measuring peak areas from a graph the DTA curve should be plotted as difference temperature against time. Modern computerized equipment can be programmed to do this automatically.

Effect of heating rate. The results quoted above were for a fixed heating rate of 10 K min^{-1}. According to Kissinger [5] a plot of ln(heating rate)/T_S^2 versus $1/T_S$ for a series of DTA curves for a single material will produce a straight line of slope $-E/R$ (see eqn. 5). The results given above show that T_S varies with conductivity but the extent of this variation with heating rate is not known.

Two sets of computations were carried out at different heating rates. In the first set, the reaction was allowed to proceed without change of conductivity and in the second, the conductivity varied with reaction. The results are given in Fig. 2 and Table 3 and the values of T_{AR} are also included for the different heating rates. If the results for T_{AR} are used in the Kissinger equation, a straight line results (not surprisingly) and an activation energy of 175.316 kJ mol^{-1} compared with the entered value of 175.6 kJ mol^{-1}. A similar plot of data for T_S (k unchanged) produced an activation energy of 168.6 kJ mol^{-1} (about 4% low). A straight line could not be obtained using the results for T_S ($\mathrm{D}k = 0.12$ to 0.144). Thus, the Kissinger equation [5] is only valid where there are no changes in conductivity during the reaction.

TABLE 3

Effect of change in conductivity on a DTA peak at different heating rates [a]

Curve in Fig. 2	ϕ K min^{-1}	T_{AR}	T_S (k unchanged)	T_S (Dk = 0.12 to 0.144)
(3)	20	533.7	536.7	530.8
(2)	15	525.4	528.1	522.2
(1)	10	513.8	516.0	510.3
	5	494.9	496.2	488.0

[a] This table shows the peak temperatures (°C) for the "standard" Arrhenius type equation (eqn. 5), a DTA curve in which there has been a conductivity change, and one where no change has taken place at different heating rates.

According to Piloyan et al. [6] a plot of difference temperature (DT) versus $1/T$ during the early part of a DTA peak (up to the maximum) should produce a straight line of slope $-E/R$. The results of computations suggest that this is only valid for values of DT, of about 1/5th of maximum, and then only if there is no conductivity change during the reaction.

Relationship between heat absorbed and peak area. In all calculations, it is assumed that the rate of heat absorption is proportional to the rate of reaction, or in equation form

$$\mathrm{d}H/\mathrm{d}t = -Bp\ \mathrm{d}x/\mathrm{d}t \tag{7}$$

where B is the heat absorbed per unit mass reacted (J kg^{-1}) and p is the density. Thus, to alter the total heat of reaction in the computations only, the value of B is varied (a negative B representing heat absorbed (endothermic), a positive value of B representing heat emitted (exothermic)).

Computations were carried out to assess the influence of changes in conductivity on DTA peak areas produced by different heats of reaction. The results are shown in Table 4 and Fig. 3. Note that the change in offset DT is independent of the heat absorbed per unit mass and depends only on the change of conductivity. The area under the DTA peak is directly proportional to the heat of reaction.

T_S is sensibly independent of the heat of reaction whereas T_R increases with increasing heat of reaction. There is no linear relationship between the

TABLE 4

Effect of a change in conductivity on a DTA peak for different heats of reaction

Curve in Fig. 3	B	T_S	DT_{SR}	A_S	DT	T_R
(1)	−42000	510.35	−4.53	2762.8	1.701	514.88
(2)	−63000	510.82	−7.14	4142.4	1.701	517.96
(3)	−84000	510.84	−9.67	5519.6	1.701	520.21

Measured from the equilibrium position prior to reaction.

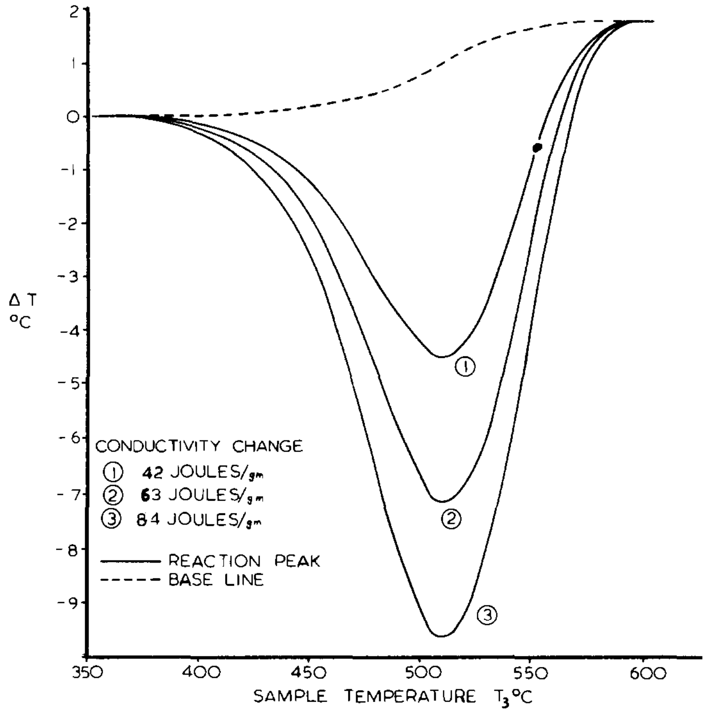

Fig. 3. Influence of change of conductivity during a reaction with different reaction heats.

peak height and the heat of reaction so that DTA peak heights cannot be used as a rapid method of the estimation of the heat of a reaction.

Effect of sample radius. The effects produced in samples of differing radii by the change in conductivity during a reaction are tabulated in Table 5 and the DTA curves are presented in Fig. 4.

Both the change in offset and the peak area are proportional to the square of the radius. Thus, increasing the radius rapidly increases any offset generated. The assumption has been made that the temperature gradient along the periphery parallel to the axis for both sample and reference materials is zero; then the area is proportional to the sample volume, a not

TABLE 5

Effect of change in conductivity [a] on a DTA peak in samples of different radii

Curve in Fig. 4	Radius (cm)	T_S	DT_{SR}	A_S	DT	T_R
(1)	0.25	509.70	−2.419	1416.8	+0.868	512.13
(2)	0.35	510.35	−4.527	2762.8	+1.701	514.88
(3)	0.50	511.01	−8.320	5585.6	+3.472	519.33

[a] Conductivity changed during the reaction from 0.12 to 0.144 W m^{-1} K^{-1}; $T_{AR} = 513.80$.

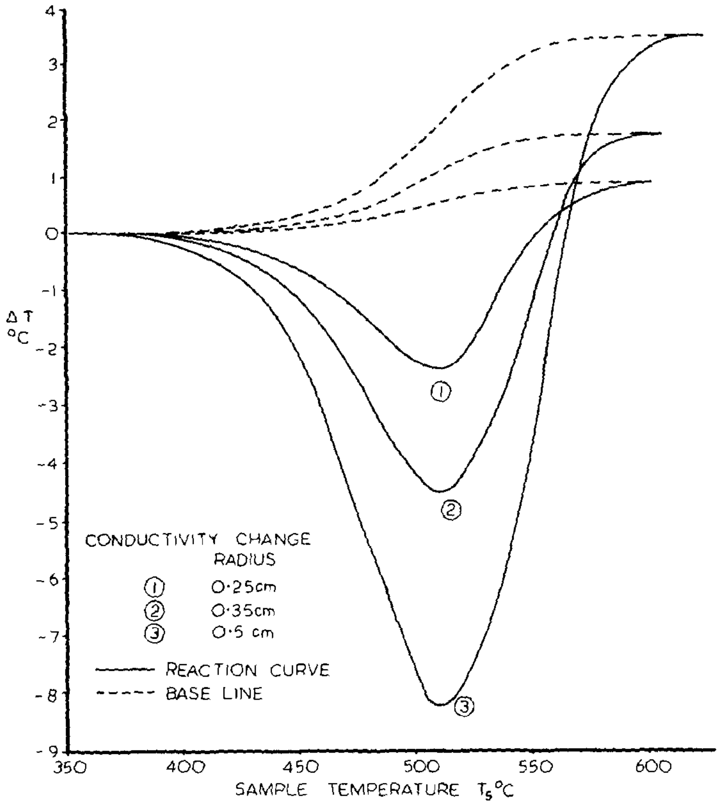

Fig. 4. Effect of conductivity change in samples of different radii.

too surprising result. However, the curves (Fig. 4) for these results also show that the peak shape for larger samples is more distorted. If use is to be made of peak shape, then small samples are imperative.

Change of specific heat during a reaction

General effect on the DTA curve. In this assessment, all variables other than specific heat were kept constant. The radii of the sample and reference materials were each 0.35 cm, the conductivity and density of both materials were 0.12 W m^{-1} K^{-1} and 2.5×10^3 kg m^{-3} respectively. The results are summarized in Table 6.

The change in offset is directly proportional to the change in specific heat during the reaction, but the peak area is sensibly independent of this change. Both the sample and the reference material temperatures at DT_{SR} are affected by the extent of the change in specific heat, but this is primarily a result of the distortion produced in the curve by the baseline change. Indeed where this change produces an offset greater than DT_{SR}, then there is no recognizable peak. If, however, the baseline is computed, it will be seen that there is area between this baseline and the DTA curve. This is the computed

TABLE 6

Effect of a change in specific heat on a DTA peak

Curve in Fig. 5	C_u $(\times 10^2)$	C_r	T_S	DT_{SR}	A_S	DT	T_R
	8.4	8.4	516.0	−6.21	3062.5	0	522.21
	8.4	4.2	505.51	−3.62	3036.3	+5.10	509.13
	8.4	12.6	525.05	−9.33	3087.5	−5.10	534.38
**d	8.4	29.4	No peak		3175.5	−25.52	

area given in Table 6 (marked **d). It will be noted that the baseline (Fig. 5) is of a similar shape to the DTA curve, but displaced from it. The change of specific heat used for this example is rather large, but a similar effect is observed when a small heat of reaction occurs with a small specific heat change. In practical terms a DTA curve of sodium carbonate shows a peak at 470 °C due to an inversion in the material which has a very similar shape to the one just described [8]. A DTA curve having this shape is usually said to be due to a second order transition, but the curve given here has been produced using a first order reaction equation associated with a change in specific heat during the reaction. Indeed it has been shown here that the

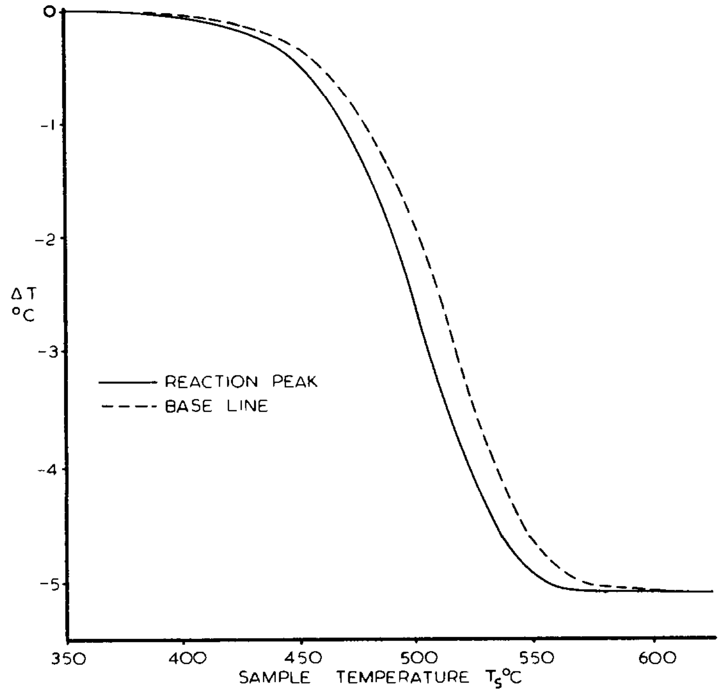

Fig. 5. Influence of changing specific heat and small heat of reaction.

form of the curve is controlled largely by the specific heat change during the reaction. There is also a heat of reaction associated with the reaction. Thus, this shape of DTA curve does not necessarily imply a second order transition.

Relationship between the heat absorbed and peak area. If the above calculations are repeated using different heats of reaction, the following remarks may be made:

(i) The change in offset is independent of the heat of absorption and depends only on the change in the specific heat during the reaction.

(ii) If measurable, the area between the baseline and the DTA curve is proportional to the heat of reaction and is not influenced by the change in specific heat.

(iii) The peak height (DT_{SR} to offset) is not a linear function of the heat of reaction.

Effect of sample radius. When the effects of changing specific heat in samples of different radii are considered, the calculations show that the change in offset is proportional to the square of the radius and that the peak area is proportional to the square of the radius, i.e. the volume of the sample.

These findings are identical to those observed for a conductivity change, and when such change occurs, there is more distortion of the DTA curve when using larger samples.

Change of density during a reaction

In these computations, very similar effects were observed to those found when the specific heat changed during the reaction.

Overall consideration of DTA plot

We can now consider the effect of changes in all the above three properties on the DTA plot. It follows from the above considerations that the change in the offset is,

(1) proportional to 1/(fractional change in conductivity), (2) proportional to the fractional change in density, and (3) proportional to the fractional change in specific heat. The offset is also proportional to (4) the square of the sample radius, (5) the rate of heating, and (6) is independent of the heat of reaction. We may write this mathematically as

$$\text{Offset} = M\phi \frac{D_p D_c r^2}{D_k}$$

where M is a constant, ϕ is the heating rate (K s^{-1}), D_p is the change in density, D_c is the change in specific heat, D_k is the change in conductivity, and r is the radius. The value of M found using the computed results is 1–4.

If DT_u is the offset before a reaction we can write

$$DT_u = \phi \frac{(p_R C_R r^2)}{(4k_R)} - \frac{(P_u C_u r^2)}{(4k_u)}$$

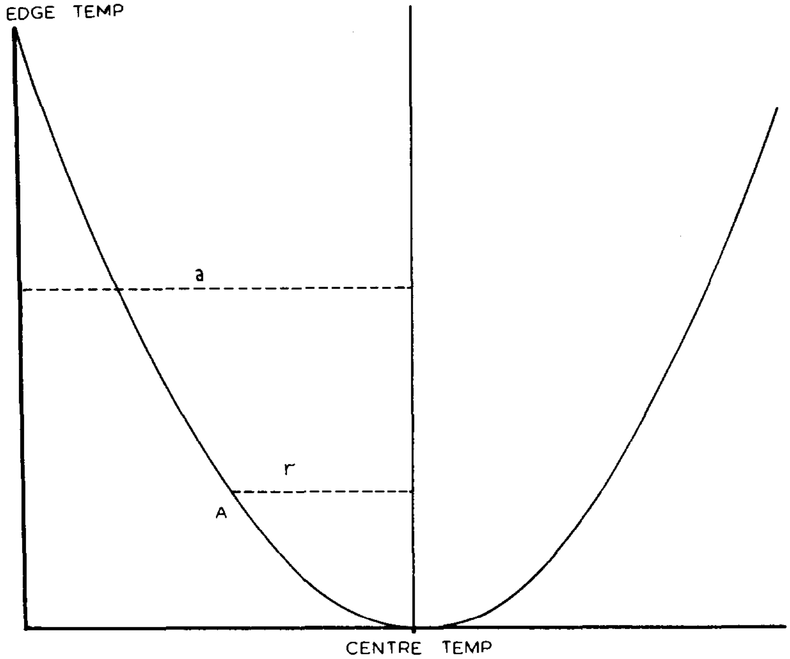

Fig. 6. Temperature profile across a cylindrical sample during heating.

A similar expression is obtained for the offset after a reaction

$$\mathrm{DT_r} = \phi\frac{\left(p_\mathrm{R}C_\mathrm{R}r^2\right)}{(4k_\mathrm{R})} - \frac{P_\mathrm{r}C_\mathrm{u}r^2}{(4k_\mathrm{r})}$$

The change in offset $\mathrm{DT_r} - \mathrm{DT_u}$ is given by

$$\phi\frac{\left(p_\mathrm{u}C_\mathrm{u}r^2\right)}{(4k_\mathrm{u})} - \frac{p_\mathrm{r}C_\mathrm{r}r^2}{(4k_\mathrm{r})}$$

Thus, for an increase in the conductivity during a reaction, i.e. $k_\mathrm{r} > k_\mathrm{u}$ there is a positive offset.

We can now specifically consider the area under a DTA peak, and the effect of differences in physical properties of sample and reference materials.

Area under a DTA peak

Ideally, the temperature profile across the sample and reference materials should be parabolic when heated peripherally, and no reaction is proceeding (eqn. 6). If we assume that this condition holds even when a reaction is proceeding, then at any point A within the sample of radius a at a distance r from the center (Fig. 6), the temperature difference from the periphery to the point in question will be

$$\mathrm{DT_A} = \mathrm{DT}(1 - r^2/a^2)$$

where DT is the difference in temperature between the periphery and the central axis. If we differentiate this equation with respect to r, we have

$$\frac{\mathrm{dDT_a}}{\mathrm{d}r} = \frac{-2r\mathrm{DT}}{a^2}$$

at the surface $r = a$ then

$$\frac{\mathrm{dDT_A}}{\mathrm{d}r} = \frac{-2\mathrm{DT}}{a}$$

If the reaction were exothermic, heat would have to be removed from the surface, or when exothermic, heat must be supplied at the surface. Now the surface area of the cylinder is $2\pi al$ where l is the length of the sample. Using the conductivity law the rate of heat transfer across the surface per unit length will be

$$\frac{\mathrm{dDT_A}}{\mathrm{d}_r} \times 2\pi ak$$

(conductivity law) i.e.

$$\frac{-2\mathrm{DT}}{a} \times 2\pi ak = 4\pi \mathrm{DT}k$$

Now the total heat change will be the heat of reaction represented by the area under the DTA curve. Therefore the total heat change is

$$\int_{t_1}^{t_2} 4\pi \mathrm{DT}k \, \mathrm{d}t$$

where t_1 and t_2 are the times when the DTA curve departs from and returns to the offset respectively, which is equated to the heat absorbed or emitted by the sample. This is $Hp\pi a^2$ where H is the heat per unit mass, p the density, and a the radius. But $\int_{t_1}^{t_2} \mathrm{DT}\,\mathrm{d}t$ is the area under the DTA peak so that

$$\text{area} = \frac{Hpa^2}{4k}$$

Thus the areas obtained from computations both here and earlier [1], support this theoretical approach, indicating that in this cell design the peak area is dependent on the conductivity of the sample material. This makes calibration almost impossible. If there are changes in the specific heat and density during the reaction, there are slight deviations in peak area from this formula due possibly to the non-parabolic temperature profile during the reaction. When the conductivity changes from k_u to k_r during the reaction, then the area calculated from the theoretical formula, using the average value $(k_u + k_r)/2$, is very close to the computed value.

Effect of differences in physical properties of sample and reference materials

In this section, only differences in conductivity between the two materials are considered. The findings are as follows.

If the conductivity of the reference material is greater than that of the sample at the commencement of heating, a negative offset develops and remains constant throughout the experiment, (if there is no change in the conductivity) but the peak temperature and area are unaffected. The same is true if the reference conductivity is lower than that of the sample. The offset is positive. If the conductivity of the sample changes during the reaction, this offset will also change, being above the zero baseline if the reference conductivity is lower than, and below if the conductivity is higher than that of the sample. In this situation, one can have a positive offset DT before the peak and a negative value after the peak. Similar effects are observed when other physical properties differ between sample and reference material.

If the sample and reference materials possess different conductivities (which remain constant throughout the experiment), and the sample density changes during the reaction, the computed results show that the offset changes after the reaction. The peak sample temperature and area are both unaffected by these changes.

CONCLUSIONS

It is clear that for the offset to be zero and remain so across a recorded DTA curve, all the physical properties of the sample and reference materials must be identical and remain so throughout the whole experiment. In practice, this is almost impossible to achieve. DTA curves with changes of offset both before, during and after a reaction are to be expected. One way in which these changes may be reduced, is by dilution of the sample material with the inert reference material. In gaining a minimal change of offset, there is inherently a loss of sensitivity in the recording of smaller peaks. In many instances, this dilution procedure may be undesirable because of the possibility of reactions occurring between the sample and diluent.

In practice, the physical properties of materials vary with temperature. To identify the effect of such changes on a typical DTA curve, computations were carried out in which the physical properties were allowed to vary both with the extent of the reaction and the prevailing temperature.

The temperature dependence of each physical property was assumed to follow the relationship

$$N_{\mathrm{T}} = N_0(1 + A'T)$$

where N_0 is the value of the particular property at 0 K, N_{T} is the value of the particular property at T K and A' is a constant.

By comparing computed DTA curves for the situation in which one property was varied with temperature, whilst all other properties were considered to be temperature independent, the effects of the changes in each property were assessed.

As anticipated, if the property changes with temperature and not with the extent of reaction, there arises only a baseline "slope", that is a gradual shift in the DT value either in the endothermal or exothermal direction with temperature. The extent of this movement and its direction is determined by the size and form of A'.

If this temperature dependent property also changes with the extent of reaction, an offset is created during the reaction. Also, the slopes of the baseline before and after the DTA peak are usually different. This difference can lead to difficulties in defining an accurate base line across the recorded peak. This problem makes area measurement subject to significant error and uncertainty when particular baseline construction methods are employed. In this work, it has proved possible to define with greater confidence a baseline for any DTA curve, and so calculate more realistically DTA peak areas. If changes are observed in the measured peak areas for a particular transition, then these variations are a consequence of the temperature dependence of the sample and reference physical properties.

When the sample specific heat is temperature dependent but independent of the extent of reaction, then the baseline construction is straightforward. A simple extrapolation of its shape and position before and after the reaction (i.e. DTA peak) is readily reproduced. The DTA peak area is the same as that for a system in which no specific heat change occurs. The apparent peak temperature observed in the original DTA curve will shift to higher and lower temperatures depending on whether the baseline slope is respectively positive or negative. The size of this shift is normally small unless large baseline gradients are created.

If the sample system conductivity is temperature dependent, then the area is affected and the peak shape is distorted by this change much in the same way as was found earlier when the conductivity was changed as a function of extent of reaction.

The conclusions reached previously [1] still remain valid. Additionally, when in DTA experiments the basic physical properties of either the sample or the reference change during the course of a thermally induced physical transition or chemical reaction within the active sample, specific conclusions can be reached as to their effects on the observed DTA curves.

Here, the influences on the DTA curve of sample and reference changes during a reaction within the sample, are identified as follows:

(a) A change in the sample system conductivity during the reaction (i.e. across the temperature zone within which reaction occurs) results in a different peak area compared with the constant conductivity situation. The extent of change is marked, a 13% increase in area occurs when a 25%

decrease in conductivity occurs between that of the products and the reactants. No noticeable change in peak position arises but there is a distortion of peak shape and in its overall width.

(b) The change in specific peak area (i.e. the area per unit mass of the active sample) due to either density or specific heat changes as a function of the extent of reaction is normally small; a 50% change in either property results in but a 1% change in the area. Again, no noticeable change in peak position arises.

(c) Any change in a physical property during a reaction must result in a difference between the values for the property in the sample and those for the reference material. A change in the DT level (the DTA baseline) will arise. This change can make peak area measurement difficult, as often an accurate assessment of the baseline is not possible. If the peak area is small, uncertainties in the drawing of the "true" baseline can, when area measurements are attempted, result in large errors.

The examinations considered here show that it is possible, with care, to define the optimum baseline for such situations. The practical constructional procedures are described elsewhere [4].

The offset produced by these physical property changes during a reaction is often attributed to a change of specific heat only, whereas it has been demonstrated here and that density and conductivity changes can also play their part. Thus, care must be exercised in quoting specific heat changes as measured by DTA.

(d) If the physical properties of either sample or reference are temperature dependent, then it is the difference between consequences of the relative dependencies at each instant temperature which determines the characteristic form of the overall baseline. Further, the baseline is but rarely horizontal even when no reaction occurs. It is usually sloped, the gradient of which at any given temperature depends on the relative variations with temperature of the physical properties of the sample and reference systems, as well as their changes with extent of reaction. It can be demonstrated that, depending upon the relative temperature coefficients of the sample and reference, the gradient of the baseline can change sign from before compared with after a reaction, i.e. either side of a peak. Again, such a situation creates difficulties for area measurement. Effective and practical constructions under these circumstances are also considered elsewhere [4].

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