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A STUDY OF THE THERMAL EFFECTS OBSERVED IN DTA.

Part 3. The influence of a holder around the sample and reference materials on a typical DTA curve

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ABSTRACT

In this study the thermal effects are reported when the sample and reference materials are held within separate "holders", each heated so that the periphery of each rises at the given rate of heating. The effect of different holder thermal conductivities, of different holder densities and specific heats, of holder radius, of different heating rates, and of differing heats of reaction are all considered, as is the effect on a typical DTA curve of varying sample properties in a holder with constant physical properties. The results suggest that the area of the DTA curve, when the thermocouples are situated between the sample and holder interface, are independent of the sample conductivity but the curve is distorted in shape compared with that drawn using the sample and reference thermocouples placed in the centre of the samples. If these latter thermocouples are used for area measurement then the results vary with sample conductivity. It is apparent that the centre measuring thermocouple system is suitable for qualitative work while a holder–sample interface thermocouple system is best suited for quantitative work.

INTRODUCTION

The first two parts of this series of papers dealt with the theory [1] and the influence of varying physical properties of the sample on a typical DTA curve [2]. In the last part [2] the conductivity of the holder was assumed to be infinite, i.e. the temperature regime was applied directly to the periphery of the cylindrical sample and reference materials. That paper showed how the sample and reference physical properties influence the production of the resulting DTA curve. In practice the holder conductivity will not be infinite, so that there will be a radial temperature profile across the cylindrical holder. This profile will influence the temperature profile within the sample and reference materials and so will affect the shape, position, and size of the resulting DTA peak.

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In this present paper the sample and reference materials are held within separate "holders" each being heated so that the periphery of each rises at the given rate of heating. The more usual cell system having two (or more) containers within a single holder cannot easily be treated mathematically [3]. Thus it will not be possible to study the effect of heat leakage between the two materials. The physical properties of the "holders", whilst identical, will be varied in order to simulate various kinds of practical holder.

Radiation has not been included in the mathematical treatment, because many designs rely mainly on conduction for their operation. Radiation formulae are similar to conduction equations so long as the difference in temperature between the source and recipient surfaces is small [4]. Thus the radiation effect can be considered as a contribution to the thermal conductivity of the sample and reference holders.

In some designs the "holder" consists of a composite, such as a metal block containing cylindrical holes. These holes are sleeved with tubes of a poor conductor. The physical properties of such a holder will lie between those of a good conductor and an insulator. In certain DTA designs the measuring thermocouples are located between the sample pan and the support, modelled in this work by temperatures at the sample–holder and reference–holder interface.

The results presented here will show the effect on a DTA curve of holders around the sample and reference materials and will show how the DTA curve using central thermocouples, and that using sample–holder and reference thermocouples, differ in shape and in the temperature of the DTA maximum (peak) from the curve of dx/dt versus temperature using the reaction equation given in the previous work [1].

SYMBOLS

The term "difference temperature (holders)" refers to the difference between the temperatures on the interface between the holder and sample and that between the holder and reference material. The term "Difference temperature (centres)" refers to the temperatures on the central axis of the cylindrical sample and reference materials.

Temperature

The following six symbols all refer to values (in ° C) at the maximum of a DTA peak:

temperature at sample–holder interface	T_{SH}
temperature at reference–holder interface	T_{RH}
difference temperature (holders)	DT_{HH}

difference temperature (centres)	$\mathrm{DT}_{\mathrm{CC}}$
centre temperature (sample)	T_{SC}
centre temperature (reference)	T_{RC}

Area

Areas (in units of deg s) using the difference in temperature between two thermocouples multiplied by time are,

for the two central thermocouples	A_{C}
for the holder interface thermocouples	A_{H}
due to the sample alone	$A_{\mathrm{S}} = A_{\mathrm{C}} - A_{\mathrm{H}}$

Heating rate

Heating rates (deg min^{-1}) are denoted as follows:

at sample centre	Θ_{C}
at sample–holder interface	Θ_{H}

Standard conditions

Standard values of radius, physical properties, and heating rate will be used for all computations, except where otherwise stated. These "standard" conditions will be as follows:
holder radius, 1.00 cm; sample (and reference) radius, 0.35 cm;
heating rate, 10 deg min^{-1} (ϕ).

Sample and reference physical properties are, conductivity 0.105 W m^{-1} K^{-1}, density 2.5×10^3 kg m^{-3} and specific heat 836 J kg^{-1} K^{-1}.

Heat symbols

The following heat symbols are used in all tables: conductivity (W m^{-1} K^{-1}), k; density (kg m^{-3}), p; specific heat (J kg^{-1} K^{-1}), c; radius (cm), r. Subscripts; S denotes sample material, R denotes reference material and H signifies holder. Thus the combined symbol k_{H} is used for the conductivity of the holder and r_{s} refers to the radius of the sample, etc. Other symbols are referred to above.

RESULTS

Effect of holder properties on a typical DTA curve

Effect of different holder thermal conductivities

As the holder changes from a gaseous space to a solid block its conductivity will increase. In these computations the sample and reference material

TABLE 1

Effect of different holder thermal conductivities

k_H	T_{CC}	DT_{CC}	T_{SH}	DT_{HH}	A_C	A_H	A_S	Θ_C	Θ_H
0.010	523.45	−19.76	536.79	−18.10				6.50	6.60
0.017	525.27	−18.62	540.59	−16.36				7.54	7.66
0.021	525.77	−18.03	542.02	−15.46	34811.6	31749.1	3062.5	8.04	8.16
0.031	526.24	−16.90	543.79	−13.72				8.78	8.91
0.042	526.22	−16.03	544.92	−12.42	18937.1	15874.6	3062.5	9.24	9.30
0.105	523.65	−12.94	542.44	−8.10	9412.3	6349.8	3062.5	9.90	9.90
0.210	520.83	−10.60	538.16	−5.11	6237.4	3174.9	3062.5	10.00	10.00
0.420	518.41	−8.77	533.73	−2.91	4649.96	1587.46	3062.5	10.00	10.00
2.100	516.43	−6.79	527.54	−0.64	3379.99	317.49	3062.5	10.00	10.00
4.180	516.21	−6.50	526.59	−0.32	3221.2	158.75	3062.5	10.00	10.00
Inf.	516.00	−6.21			3062.5	0	3062.5	10.00	10.00

physical properties were kept constant during the reaction. The results are tabulated in Table 1.

The temperatures at the reference–holder interface and the reference centre temperature can be found as follows: reference–holder interface temperature = $T_{sh} - DT_{HH}$; reference centre temperature = $T_{CC} - DT_{CC}$. The areas were computed as described in the previous publication (1).

The following observations are possible. As the holder conductivity decreases both the peak centre temperature (T_{SC}) and the holder interface temperature (T_{SH}) initially increase and then decrease at low conductivities as a consequence of the actual heating rate at both the sample centre and at the holder interface being less than the nominal 10 ° C min^{-1}; this effect was also observed for large radius samples [1]. The difference temperatures (DT_{HH} and DT_{CC}) both increase with decreasing holder conductivity. The area measured at the holder–sample interface A_H is inversely proportional to the holder conductivity and the area A_C measured at the sample centre is that due to the sample and holder combined; the area A_S, being the subtraction of A_H from A_C, is independent of the holder conductivity, and has the value previously found for the sample alone.

One can generalize as follows: as the holder thermal conductity decreases, (a) T_{SC} and T_{SH} increase and then decrease, (b) DT_{CC} and DT_{HH} increase continuously, (c) A_H is proportional to 1/holder conductivity, and (d) A_S is proportional to 1/sample conductivity.

Effects of different holder densities and specific heats

The effects of different holder densities and specific heats are given in Table 2. For increasing density and/or specific heat, T_{SC} increases and then decreases as the heating rate decreases, T_{SH} follows a similar trend but the effect is not so marked, DT_{CC} and DT_{HH} both decrease, and A_H and A_S are both independent of both holder density and specific heat.

TABLE 2

Effect of different holder densities and specific heats

ρ_H	C_H	T_{SC}	DT_{CC}	T_{SH}	DT_{HH}	A_C	A_H	A_S	Θ_C	Θ_H
$k_H = 0.021$ W m^{-1} K^{-1}										
2.5×10^3	836	525.77	−18.05	542.05	−15.46	34811.6	31749.1	3062.5	8.04	8.16
1.0×10^3	836	529.88	−22.92	544.82	−20.22	34811.7	31749.2	3062.5	9.00	9.06
0.5×10^3	836	531.16	−25.63	544.93	−22.90	34811.7	31749.2	3062.5	9.33	9.42
0.1×10^3	836	531.06	−29.14	543.19	−26.28	34811.7	31749.2	3062.5	9.60	9.66
0.03×10^3	836					34811.7	31749.2	3062.5	9.63	9.69
$k_H = 0.21$ W m^{-1} K^{-1}										
5.0×10^3	4100	515.19	−6.77	543.25	−2.35	6237.41	3174.91	3062.5	8.46	8.66
5.0×10^3	836	521.03	−9.90	541.60	−4.49	6237.41	3174.91	3062.5	10.00	10.00
2.5×10^3	836	520.83	−10.60	538.16	−5.11	6237.41	3174.91	3062.5	10.00	10.00
1.0×10^3	836	520.06	−11.10	534.43	−5.52	6237.41	3174.91	3062.5	10.00	10.00
0.5×10^3	836	519.60	−11.25	532.75	−5.64	6237.41	3174.91	3062.5	10.00	10.00

TABLE 3

Effect of holder radius [a]

r_H	T_{SC}	DT_{CC}	T_{SH}	DT_{HH}	A_C	A_H	A_S	Θ_C	Θ_H
0.5	517.18	−8.14	528.65	−2.12	4153.50	1091.00	3062.5	10.0	10.0
0.6	518.06	−9.00	530.83	−3.11	4708.47	1645.97	3062.5	10.0	10.0
0.8	519.64	−10.09	534.77	−4.42	5575.92	2513.42	3062.5	10.0	10.0
1.0	520.88	−10.60	538.16	−5.11	6237.41	3174.35	3062.5	10.0	10.0
1.2	521.56	−10.76	540.50	−5.42	6766.84	3704.35	3062.5	9.99	9.99
1.4	521.82	−10.70	541.95	−5.49					
1.8	521.39	−10.23	543.25	−5.31					
2.5	518.70	−9.11	542.28	−4.66				8.80	8.82
3.0	516.11	−8.13	540.68	−4.17				8.00	8.12

[a] Sample and reference properties: conductivity, 0.015 W m^{-1} K^{-1}; others as standard. Holder properties: conductivity, 0.030 W m^{-1} K^{-1}; others as standard.

Effect of holder radius

The results are given in Table 3. Both the sample centre temperature (T_{SC}) and the holder–sample interface temperature (T_{HS}) increase as the holder radius is increased but then decrease. This is due to the reduction in heating rate as found earlier. A similar effect is observed in the difference temperatures.

The relationship between the peak area as the difference between the two interface temperatures versus time, and $\ln(r_H/r_S)$ (where r_H and r_S are the holder and sample radii respectively) is found to be linear with a slope of $3036 \pm 2\%$. A_S is found to be independent of the holder radius and has a value equivalent to that found for the sample alone.

TABLE 4

Effect of different heating rates on holders [a]

ϕ	T_{SC}	DT_{CC}	T_{SH}	DT_{HH}	Θ_C	Θ_H	A_C	A_H	A_S
Holder conductivity, 0.210 W m^{-1} K^{-1}									
10.0	520.88	−10.60	538.16	−5.11	10.0	10.0	6237.41	3174.91	3062.5
15.0	533.13	−13.92	557.12	−6.47	15.0	15.0	6237.41	3174.91	3062.5
20.0	541.17	−16.60	571.69	−7.43	20.0	20.0	6237.41	3174.91	3062.5
Holder conductivity, 0.021 W m^{-1} K^{-1}									
10.0	525.77	−18.03	542.02	−15.46	8.04	8.16			
15.0	534.34	−20.04	555.48	−16.48	10.89	11.07			
20.0	540.07	−21.54	565.32	−17.75	13.23	13.68			

[a] Holder conductivity, k_H, 0.021 W m^{-1} K^{-1}.

One may summarize as follows: with increasing radius T_{SC} and T_{SH} first increase and then decrease, DT_{CC} and DT_{HH} first increase and then decrease, A_H is proportional to $\ln r_H/r_S$, and A_S is independent of the holder radius.

Effect of different heating rates

The results are shown in Table 4. From the table both peak temperatures (T_{SC} and T_{SH}) and the magnitudes of both difference temperatures (DT_{HH} and DT_{CC}) increase with heating rate, as one would predict from the reaction equation used in the computations. If these results are used in the Kissinger equation [5] a non-linear relationship is apparent. This suggests the non-applicability of the Kissinger equation in practical situations.

Effect of differing heats of reaction

The sample centre temperature (T_{SC}) decreases with increased endothermicity of reaction, whereas the sample–holder interface temperature increases slightly. The areas measured using both interface and centre temperatures against time are directly proportional to the heat of reaction.

Summary of effects of holder properties

The effects of the sample and reference holder characteristics are as follows:

(1) The temperatures measured at the centre of the sample (T_{SC}) are, for all types of holder, higher than those when considering the sample alone (using the same physical properties for the sample).

(2) Temperatures measured at the holder–sample interface (T_{SH}) are always higher than those measured at the sample centre.

(3) Generally a change in a holder physical property has a smaller effect on sample centre temperatures and difference temperatures than a corresponding change in the sample physical property. Low thermal conductivity

TABLE 5

Effect of different sample thermal conductivities

k_S	T_{SC}	DT_{CC}	T_{SH}	DT_{HH}	Θ_C	Θ_H	A_C	A_H	A_S
$k_H = 0.210$ W m^{-1} K^{-1}									
0.053	519.20	−15.09	546.40	−4.71	10.0	10.0	9299.91	3174.91	6125.00
0.105	520.88	−10.60	538.16	−5.11	10.0	10.0	6237.41	3174.91	3062.50
0.157	521.87	−8.94	534.87	−5.24	10.0	10.0	5216.58	3174.91	2041.67
0.210	522.59	−8.07	533.15	−5.29	10.0	10.0	4706.16	3174.91	1531.25
$k_H = 0.021$ W m^{-1} K^{-1}									
0.053	521.29	−20.52	549.80	−14.98	8.0	8.16			
0.105	525.77	−18.03	542.02	−15.46	8.04	8.16			
0.157	528.04	−17.23	539.27	−15.59	8.04	8.10			
0.210	529.29	−16.84	537.96	−15.65	8.04	8.10			

holders can produce distortion of the heating rate during a reaction, leading to erroneous peak temperatures.

(4) The area A_H of a DTA peak measured using the difference between the sample-holder and reference-holder temperatures against time, is
(a) inversely proportional to the holder conductivity,
(b) independent of the holder density and specific heat,
(c) proportional to $\ln(r_H/r_S)$ (where r_H and r_S are the radii of the holder and sample respectively),
(d) independent of the heating rate,
(e) proportional to the heat of reaction.

The temperature T_R of the reference material is considerably higher than that of the sample at the peak. The latter temperature is closer to the peak temperature given by the "standard" reaction equation, so that DTA curves are better plotted with sample temperature (preferably the centre) as abscissa.

Effect of varying sample properties in a holder with constant physical properties on a typical DTA curve

Effect of sample conductivities

The results are given in Table 5 and observations from them give the following indications.

The peak centre temperature of the sample (T_{SC}) increases with sample conductivity, and this effect is more marked as the holder conductivity is reduced. The sample–holder interface temperature (T_{SH}) increases with increasing sample conductivity.

The centre difference temperature (DT_{CC}) decreases as expected with increasing sample conductivity, whilst that of the sample–holder interface increases slightly.

The area (A_H) measured from the DT_{HH}/time curve is independent of the sample conductivity, and thus can be used as a measure of the heat of

TABLE 6

Effect of sample radius within a holder of fixed radius

r_s	T_{SC}	DT_{CC}	T_{SH}	DT_{HH}	Θ_S	Θ_H	A_C	A_{SH}	A_{CS}
$k_H = 0.210$ W m^{-1} K^{-1}									
0.20	521.03	−4.65	530.55	−2.70	10.0	10.0	2552.14	1552.14	1000.0
0.35	520.88	−10.60	538.16	−5.11	10.0	10.0	6237.41	3174.91	3062.5
0.50	519.71	−16.64	545.31	−6.36	10.0	10.0	10560.91	4310.97	6250.0
0.80	516.77	−26.00	554.70	−4.35	10.0	10.0	19568.40	3568.60	15998.0
$k_H = 0.021$ W m^{-1} K^{-1}									
0.20	526.76	−9.76	534.85	−8.84	7.86	7.92			
0.35	525.77	−18.03	542.02	−15.46	8.04	8.16			
0.50	524.34	−25.03	551.48	−19.99	8.25	8.41			
0.80	520.22	−35.41	570.71	−20.83	9.15	9.36			

reaction. This finding is in agreement with the findings of Boersma [6]. Area measured at the centre of the sample is inversely proportional to the conductivity of the sample material as found in an earlier paper [1]. Its numerical value is equal to that found for the sample alone.

Effect of sample density

When the heat of reaction remains constant then the areas (A_S, A_C, and A_H) are all proportional to the sample density. If, however, the heat of reaction is adjusted so as to keep the heat per unit volume constant, then the areas are independent of the sample density. All peak temperatures increase with increasing density, but difference temperatures remain sensibly constant. Similar results are obtained for changes in specific heat.

Effect of sample radius within a holder of fixed radius

The results are given in Table 6. It is seen that the sample temperature (T_{SC}) decreases, and the centre difference temperature (DT_{CC}) increases rapidly as the sample radius increases. Initially T_{SH} increases and DT_{HH} also increases. However, with further increase in sample (and reference) radius, these temperatures decrease due to the reduction in the size of the holder.

The area A_H is found to be proportional to $r_S^2 \ln(r_H/r_S)$, and the area due to the sample A_S is proportional to r_S^2 as found for the sample alone.

Area measurement

These results make it possible to devise a mathematical expression for the area. The area measured as DT_{HH}/time (A_H) is found to be proportional to

$$\frac{DH \rho_S r_S^2 \ln(r_H/r_S)}{k_H}$$

using results gained so far, where DH is the heat (J) per unit mass as defined previously [1]. The constant of proportionality is found on closer inspection to be 1/2 giving the final expression

$$A_H = \frac{\mathrm{DH}p_S r_S^2 \ln(r_H/r_S)}{2k_H}$$

This resulting formula shows that areas measured in this way are independent of the sample physical properties so long as the volume of the sample is kept constant, i.e. $r_S^2 p_S$ must be kept constant. In a holder of fixed radius this means that the depth of the sample must remain constant. Then

$$A_H = K\mathrm{DH}$$

This provides the basis for the achievement of quantitative evaluations from DTA observations. Thus the conditions for quantitative estimations from DTA are that the sample holder should always be filled to a constant volume with the mass of the sample known. As the expression which related peak area to the heat of reaction does not contain terms associated with the physical properties of the sample being studied, then once calibrated the system may be used for widely differing materials.

These results have shown that the area due to the sample alone (A_S) even when within a holder is identical to that found for a sample without a holder [1] namely

$$A_S = \frac{\mathrm{DH}pr_S^2}{4k_S}$$

The area measured at the sample centre is A_C and is equal to the sum of A_H and A_S, that is

$$A_C = \frac{\mathrm{DH}p_S r_S^2\left[\ln\left(\frac{r_H}{r_S}\right)\right]}{2k_H} + \frac{\mathrm{DH}p_S r_S^2}{4k_S} = \left(\frac{\mathrm{DH}p_S r_S^2}{4}\right)\left(\frac{2\ln\left(\frac{r_H}{r_S}\right)}{k_H} + \frac{1}{k_S}\right)$$

Thus, unless $2\ln(r_H/r_S)$ is much greater than $1/k_S$, areas measured using centre sample and reference thermocouples cannot be used for quantitative measurements.

McIntosh [7] has shown theoretically that the equation derived empirically from the computer results for A_H is correct. His reasoning is given here.

The heat input per unit time into the surface of the holder during a reaction will be

$$(\mathrm{d}q/\mathrm{d}t)_H = k_H A\ \mathrm{d}T/\mathrm{d}r$$

where A is the exposed area.

$$(\mathrm{d}q/\mathrm{d}t)_H = k_H 2\pi r_H\ \mathrm{d}T/\mathrm{d}r$$

per unit length. Transposing

$$(\mathrm{d}q/\mathrm{d}t)_\mathrm{H}(\mathrm{d}r/r_\mathrm{H}) = 2\pi k_\mathrm{H}\,\mathrm{d}T$$

and integrating gives

$$q \times \int_{r_\mathrm{S}}^{r_\mathrm{H}} \mathrm{d}r/r = \int_{T_2}^{T_1} 2\pi k_\mathrm{H}\,\mathrm{d}T$$

where q is the heat input per unit time interval, that is

$$q[\ln r]_{r_\mathrm{S}}^{r_\mathrm{H}} = 2\pi k_\mathrm{H}[T]_{T_2}^{T_1}$$

but $T_1 - T_2$ is the temperature difference between the sample–holder interface and the outside of the holder and will be denoted by ΔT. Thus

$$q\ \ln(r_\mathrm{H}/r_\mathrm{S}) = 2\pi k_\mathrm{H}\,\Delta T$$

or

$$q = \frac{2\pi k_\mathrm{H}\,\Delta T}{\ln(r_\mathrm{H}/r_\mathrm{S})}$$

However, the total heat absorbed in is equal to the heat of reaction which, for the sample, will be $Hp_\mathrm{S}\pi \mathrm{r}_\mathrm{S}^2$ which is equal to

$$\frac{2\pi k_\mathrm{H}}{\ln(r_\mathrm{H}/r_\mathrm{S})} \times \int_{t_1}^{t_2} \Delta T\,\mathrm{d}t$$

This last term is the area under the DTA peak so that

$$A_\mathrm{H} = \frac{Hp_\mathrm{S} r_2^2 \ln(r_\mathrm{H}/r_\mathrm{S})}{2k_\mathrm{H}}$$

This formula shows that the area measured in this way is independent of the sample properties other than density. For the equation above to be used, Hp_S must be constant, that is for a sample holder of fixed radius this means that the sample volume must be constant.

GENERAL CONCLUSIONS

A general perusal of the results so far, suggests that for area measurement with the thermocouples situated between the sample and the holder interface, such areas (deg. s) produced are independent of the sample conductivity. This finding is in agreement with the findings of Boersma [6], but further shows that the DTA curve drawn from a plot of the difference between these two thermocouples is distorted in shape compared with that drawn using the sample reference centre thermocouples. Thus shape factors, etc., must be measured using centre thermocouples. However, if these thermocouples are used for area measurement, such results will vary with sample conductivity.

Thus two designs are required for DTA, a centre measuring thermocouple system for qualitative work and a holder–sample interface thermocouple system for quantitative work.

It is evident that DTA peak shape measured with interface thermocouples is increasingly distorted as the holder conductivity decreases. However, the peak area increases so that a compromise must be reached if it is required to measure area with reasonably shaped curves.

Thus the thermocouple position is basically different for quantitative and qualitative work. Indeed there is a need for two independent designs for DTA, one for quantitative work with the thermocouples at the holder–sample and holder–reference interface, the other with thermocouples in the sample directly, for qualitative work. The influence of thermocouple location has been published as a separate paper [8] which also recommends the method of base line construction discussed in the previous paper [2].

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