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HEAT TRANSFER ERRORS IN QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS

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A DTA apparatus has been built to examine some of the errors neglected in present quantitative DTA. The heat transfer characteristics within DTA systems were found to limit in situ measurements of powder thermal conductivity. It was also demonstrated that the negligence of heat lost to the DTA block from the sample cell during an exothermic reaction and heat gained from the DTA block by the sample cell during endothermic reactions lead to large errors in quantitative estimations. A modified double differential thermocouple DTA was designed to take these heat losses into account. The apparatus was calibrated with $CaCO_3$ and kaolinite endotherms and the kaolinite exotherm and tested on the $SrCO_3$ rhombic $\rightleftharpoons$ trigonal inversion endotherm. The result was found to be in good agreement with accepted literature values.

The technique of differential thermal analysis (DTA) is well established. As an absolute quantitative technique for gathering thermodynamic data, however, DTA has not been successful [1]. It was the purpose of this work to experimentally investigate the validity of some of the assumptions made in quantitative DTA techniques and indicate remedial measures to reduce the associated errors.

The differential temperature peak associated with a reaction can be expressed mathematically by comparing total heat contents of the sample and reference cells in the DTA system [2–6]. It can be shown that the area under the differential temperature peak is related to the enthalpy of the associated reaction thus:

$$\int_a^c y dt = \frac{m \Delta H}{g K_s} \tag{1}$$

where g is the geometrical shape factor, t the time, m the sample mass, ΔH the reaction enthalpy, y the differential temperature and K_s the effective thermal conductivity of the sample. The integration limits a and c indicate the time interval over which the reaction occurs.

It should be noted that in deriving this formula and its other modifications, all the authors assume the reference material and the sample to have identical thermal conductivities, specific heats and bulk densities. Furthermore, no account is taken of the variation of the heat of reaction and the change of heat transfer coefficients with temperature. The work here reported is concerned with errors arising from heat transfer coefficient variations (K_s) and heat losses which avoid the sensing DTA thermocouples.

To circumvent some of the problems in quantitative DTA, sample dilution techniques are often used. Up to 70% dilutent is often added to the sample material. The total heat effect is considerably reduced in this manner with the consequent loss of accuracy. Also, as will be demonstrated, the remaining disparity of heat transfer coefficients between the diluted sample and the inert reference is still sufficient to introduce significant errors.

Most attempts at quantitative DTA therefore involve calibration procedures in which the heat of reaction of an unknown sample is calculated from a proportionality equation such as:

$$\Delta H_{\text{unknown}} = (\Delta H_{\text{known}}) \times \left\{\frac{\text{area under the peak for unknown}}{\text{area under the peak for known}}\right\} \qquad (2)$$

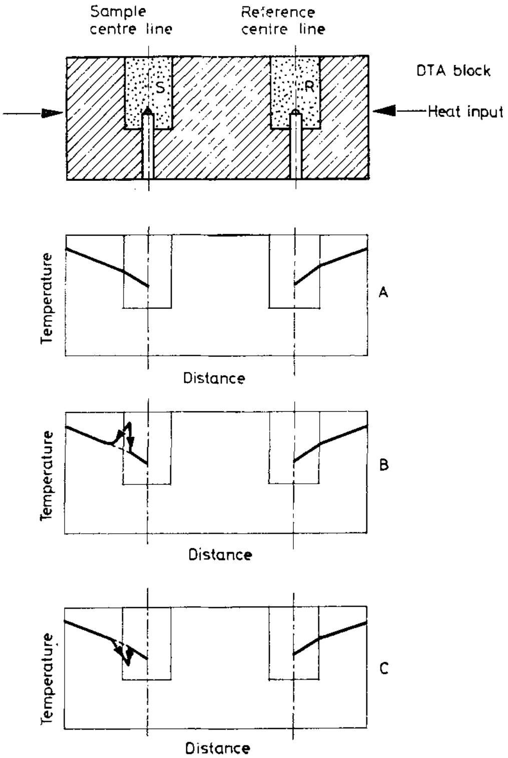

Fig. 1. Temperature profiles associated with initial sample reaction (S — sample cell, R— reference cell); A: temperature profile for no reaction condition; B: temperature profile for exothermic reaction (arrows indicate heat flow direction); C: temperature profile for endothermic reaction (arrows indicate heat flow direction)

Using the relationship (2) involves the difficulty of preparing samples of the same thermal conductivity from different materials. Also, as will be demonstrated, the calibrant reaction must be very carefully chosen to be of the same nature, to evolve the same gases (if gases are evolved) and to occur at about the same temperature as the reaction being investigated. If such measures are not taken, errors can result in the $(\Delta H)_{\text{unknown}}$ values calculated.

A significant source of error in quantitative DTA which has not heretofore been considered is that of reaction heat losses to the DTA monitoring system. Considering the heat flow associated with the initial stages of a reaction, with the aid of Figure 1, it can be seen that a temperature peak will be produced on the system temperature profile. This peak will either be positive or negative depending on whether the reaction is exo- or endothermic. Considering an exotherm first, heat will flow towards the differential couple located in the sample *and* into the sample block. The out-flowing heat (supplied to the DTA block) is not sensed by the differential thermocouple and therefore does not appear on the ΔT vs. time peak. With an endotherm, the flow of heat is reversed and now it flows from the sensing couple environment and the block. The heat supplied to the reaction by the DTA block is not sensed by the differential couple and therefore does not appear on the ΔT vs. time trace. Hence in both cases the ΔT vs. time peak does not indicate the entire heat effect involved in the reaction.

A simple double differential thermocouple technique for eliminating errors due to these heat losses is described in the following pages and it is shown that the errors involved are substantial.

The location of the two differential couples described is also ideal for the study of heat transfer conditions within the cells of the DTA apparatus. By disconnecting each DTA differential thermocouple and reconnecting the four individual thermocouples so created differentially across each cell, the temperature gradients existing in each cell can be continuously monitored. Assuming identical geometries and heat influxes from the environmental furnace for each cell, the measured temperature gradients indicate the relative heat transfer coefficients in each cell. In this way, it is possible to determine the best reference materials to use.

A series of model reactions were chosen to study the heat-loss and heat-transfer errors involved in quantitative DTA. Two cell-block designs were utilised to indicate the influence of the geometric factor and sample mass on these parameters. Dilution and calibration techniques were also investigated.

Apparatus

Two designs of DTA block were used in the investigations. The blocks were fabricated of stabilised-zirconia (ZrO_2) to minimise reaction heat losses from the DTA block and to prevent heat leakage between the sample and reference cells. Each block contained two symmetrically-located cylindrical cavities, the top, bottom and side surfaces of which were covered with platinum foil. The two cell geometries utilised were 1/2″ diameter (*D*) by 1/2″ deep (*L*) and 1/4″ diameter and 1/2″ deep, giving L/D ratios of 1 : 1 and 2 : 1 respectively. As a result of the double differential thermocouple technique utilised, it was possible to use comparatively large samples thereby increasing the total heat effects measured. The platinum foil ensured uniform heat distribution on the peripheries of both cells. Carefully calibrated and balanced platinum/platinum-13% rhodium thermocouples were located in the centre and at the walls of each cell. The wall thermocouples were spot-welded to the platinum cell lining. The complete DTA assembly is shown in Figure 2. A ZrO_2 cover of identical thickness to the bottom section of the particular DTA block was placed on top of the block so locating the cell cavities in a symmetrical ZrO_2 environment. Sample and reference materials were packed to the same relative density in each cell using a powder-packing stencil.

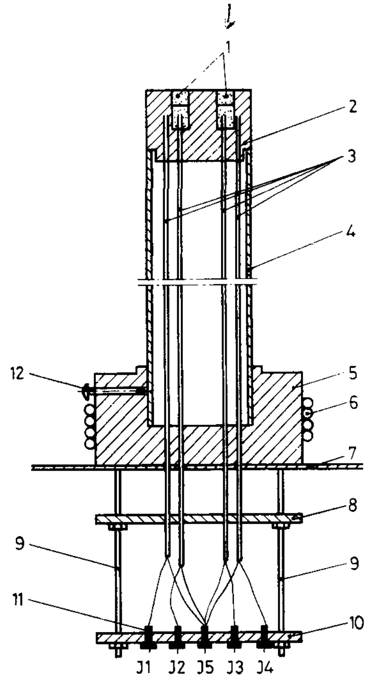

Fig. 2. DTA block and thermocouple assembly. 1. Platinum lined reference and sample cells. 2. ZrO_2 DTA block. 3. Thermocouple sheathing. 4. Al_2O_3 support tube. 5. Aluminium block. 6. Water cooling. 7. Aluminium support plate. 8. Lucite plate with screws to hold T/C sheaths in position. 9. Brass screw rod. 10. Lucite plate with banana jacks. 11. Banana jacks. 12. Set screw to hold (4) in position

The whole DTA assembly was located in a differentially-wound molybdenum furnace with a grounded platinum tube around the DTA block to avoid A. C. pick-up in the differential thermocouple systems. The position of the column could be laterally adjusted inside the furnace from below the furnace. In this way it was possible to ensure the thermal symmetry of the DTA system simply by assuring identical temperatures at the sample and reference cell walls. Such alignment could be checked before and after reaction measurements.

The differential or direct-reading thermocouple connections were made outside the furnace and could be switched at will. The outputs of the two differential thermocouples were passed through separate balanced amplifiers. The amplified signals were plotted on a two-pen recorder giving a maximum sensitivity of 30 μV $\pm 2\%$ full scale deflection.

In order to approach quasi-equilibrium conditions as closely as possible during the investigated reactions, a furnace heating rate of 2°/minute was utilised. An automatic programmer utilising a conducting chart ensured a linear rate of temperature rise for the furnace.

Experimental and results

The experiments were divided into two parts, namely:

1. assessment of the potential of the modified DTA for in situ measurement of sample thermal conductivity, and

2. measurement of the heat loss to the DTA block or heat gain from it during exothermic or endothermic reactions, respectively.

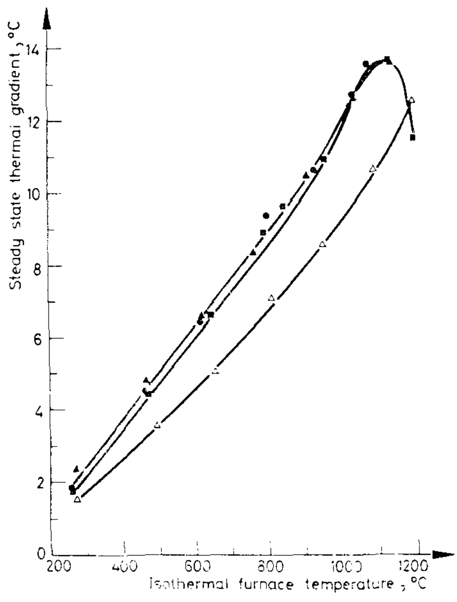

Fig. 3. Kaolinite thermal gradient plot; Kaolinite 48WO230; sample cell; △ thermal gradient for Al_2O_3 standard, ■ thermal gradient for live kaolinite, ● thermal gradient for semi-dead-burnt kaolinite, ▲ thermal gradient for dead-burnt kaolinite

The sample materials used in the thermal conductivity studies were alumina, kaolinite, montmorillonite, semi-dead-burnt and dead-burnt kaolinite and semi-dead-burnt and dead-burnt montmorillonite. The "dead-burnt" minerals were prefired to a temperature above that of the highest-temperature reaction of interest in the raw minerals so rendering them inert. The "semi-dead-burnt" minerals were prefired so as to dehydrate them but the temperature utilised was below that of the high temperature reaction. Alumina powder was used throughout in the reference cell. The temperature gradients across the sample (ΔT_s) and reference (ΔT_r) cells were measured by connecting the wall and central thermocouples of each cell differentially. Measurements were made at temperatures between room temperature and 1150°. Both static (isothermal) and dynamic (constant temperature rise) heating conditions were used.

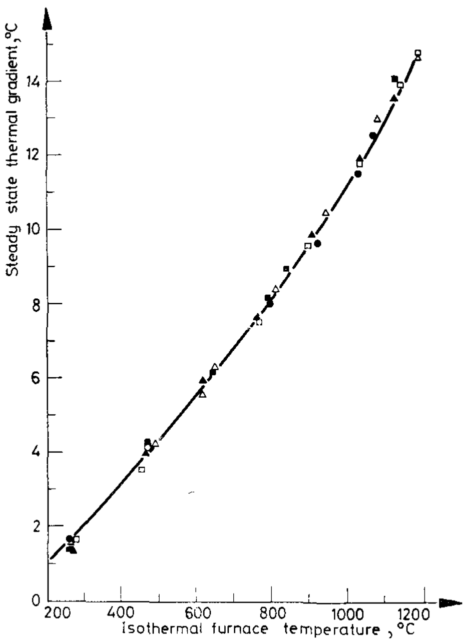

Fig. 4. Thermal gradient reference plot; — thermal gradient reference curve (powder Al_2O_3 in reference cell); △ Al_2O_3 vs. Al_2O_3 powder, ■ Al_2O_3 vs. live kaolinite, ● Al_2O_3 vs. semi-dead-burnt kaolinite, ▲ Al_2O_3 vs. D. B. kaolinite, □ Al_2O_3 vs. montmorillonite

The reference cell was filled with (−325 mesh) Al_2O_3 powder and all the observations were referenced to the differential temperature across this cell. This cell was left intact during all the conductivity experiments. The sample cell was filled with the (−325 mesh) test powder. The DTA column was electrically aligned in the furnace at ≃300° by making sure ΔT_w (the temperature difference between the wall thermocouples of both cells) was 0 ± 3 μV. The ΔT_r and ΔT_s values were measured at seven or eight higher constant temperatures. The procedure was repeated for all the sample materials and the results for kaolinite are shown in Figure 3.

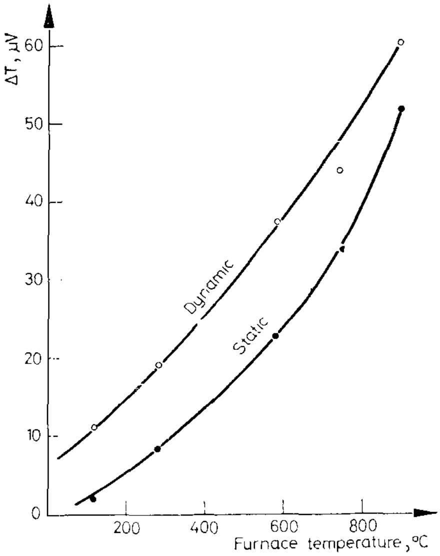

Fig. 5. Thermal gradients across Al_2O_3-loaded sample cell for static and dynamic conditions

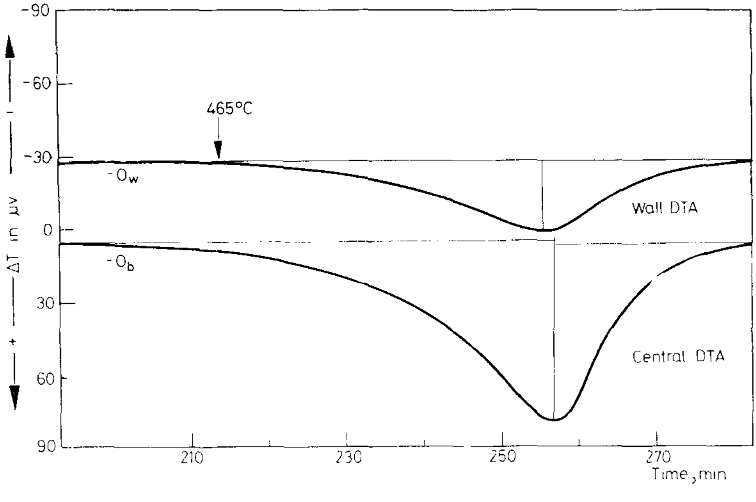

Fig. 6. Kaolinite endotherm (60% dilution)

The steady state thermal gradients increase with increasing temperature (Figure 3) and beyond 1100° the clay samples begin to sinter. The dead-burnt material data and that of the semi-dead-burnt material fall along the same curve. The curve for live kaolin shows slightly lower thermal gradients, but the curve for Al_2O_3 is considerably lower, indicating a higher effective thermal conductivity for Al_2O_3. A similar plot showed that the points for live and dead-burnt montmorillonite fall on the same curve and the Al_2O_3 values a little lower.

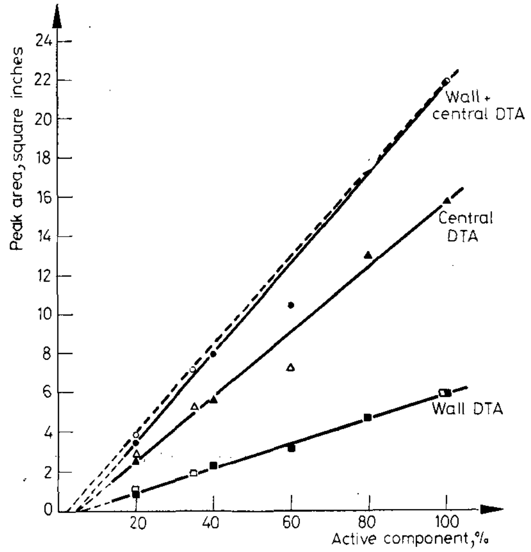

Fig. 7. Effect of change of reference and dilutent substance on peak area (kaolin endotherm); ● ▲ ■ Kaolinite — Al_2O_3 DTA system; ○ △ □ Kaolinite — D. B. Kaolinite DTA system

Comparison of the ΔT_s values at a given temperature for two different samples is a measure of their relative thermal conductivities, provided the heat transfer conditions are identical during the different experimental runs. The equivalence of the runs was checked by continuously monitoring the ΔT_r across the undisturbed Al_2O_3 reference cell which was always the same as shown in Figure 4. The run with Al_2O_3 in both cells checked the heat transfer equivalence of the two cells.

Dynamic temperature gradient measurements were made with Al_2O_3 in both cells. A heating rate of 2°/minute was imposed on the system and the sample cell differential temperature was measured at different furnace temperatures without interrupting the heating cycle. A comparison of the static and dynamic temperature condition results is shown in Figure 5.

To investigate the heat losses incurred by use of the conventional single differential thermocouple DTA, a series of model reactions were chosen. These are as follows:

(a) a solid-state polymorphic reaction

rhombic $\rightleftharpoons$ trigonal $SrCO_3$ (endothermic)

(b) a solid-state crystallisation reaction

metakaolinite $\rightarrow$ mullite + β-quartz (exothermic)

(c) a dehydration reaction

kaolinite $\rightarrow$ metakaolinite (endothermic), and

(d) a decomposition reaction

$CaCO_3 \rightarrow CaO + CO_2$ (endothermic).

The influence of the degree of dilution of the sample with inert material and the nature of the reference material were also studied. The two DTA block geometries previously described were utilised.

The peripheral and central thermocouples of each cell were connected differentially in this case in the usual DTA manner. The areas under the DTA peaks obtained were measured with a polar-compensating planimeter and appropriate corrections made for base-line drift [7]. The cells were manually loaded with a carefully weighed sample in each case. The loss in weight while loading was at the most 0.35%. Identical masses of sample and reference were used in each case and both powders were compressed equally into the cells using the powder packing stencil.

A typical DTA trace obtained is shown in Figure 6 and the data obtained for the various reactions studied are summarised in Table 1. The final column of this table indicates the percentage of the heat effect which eludes the single-couple DTA systems. The influence of the degree of dilution of the sample and the nature of the reference material are plotted in Figures 7 and 8 for the kaolinite endo-

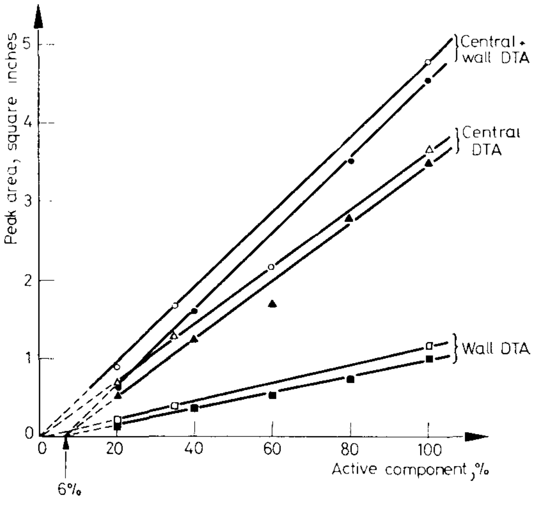

Fig. 8. Effect of change of reference and dilutent substance on peak area (kaolinite exotherm); ● ▲ ■ Kaolinite — Al_2O_3 DTA system; ○ ○ □ Kaolinite — D. B. Kaolinite DTA system

Table 1

Heat loss (ΔT): Type of reactions

Reaction	Active mass of sample, g	DTA peak areas in square inches		$[w/(w+b)]$ % heat lost/gained to/from DTA block
		Central (b)	Wall (w)	
$SrCO_3$	0.54	0.78	0.372	32.1
Kaolinite exotherm	0.652	1.209	0.394	24.8
Kaolinite endotherm	0.652	5.61	2.34	29.4
$CaCO_3$	0.489	8.45	5.31	39.1

Table 2

Effect of change of cell geometry on peak area

Kaolinite endotherm		
Design number	1 $(L/D = 1)$	2 $(L/D = 2)$
Mass of kaolinite, g	1.63	0.371
Central (b)	15.61	4.74
Wall (w)	6.07	2.416
% Heat gained from DTA block (% $w/w + b$)	28%	34%
Kaolinite exotherm		
Design number	1	2
Mass of kaolinite, g	1.63	0.371
Central (b)	3.6	1.12
Wall (w)	1.164	0.484
% Heat lost to the DTA block (% $w/w + b$)	25%	30%

thermic and exothermic reactions utilising Al_2O_3 and dead-burnt kaolinite as dilutent and reference material as indicated. The influence of cell geometry on the peak areas obtained for the conventional and double thermocouple DTA designs are summarised in Table 2 for the two kaolinite reactions.

Discussion

Conventional thermal conductivity measurement apparatuses make thermal gradient measurements across samples interposed between a heat source and an infinite heat sink. In a DTA apparatus under steady-state conditions, the heat arriving at the periphery of the DTA cell (q) is split up into two parts. One part travels through the block, q_b, and the other part, q_c, travels across the cell. The heat travelling across the cell sees as a sink the thermocouple placed in the centre of the cell. This sink is not infinite and the greater the heat supplied, the less its efficiency and a consequent rise in the cell temperature gradient ensues as observed. The "limited sink" renders absolute thermal conductivity measurements difficult, however given reproducible heat transfer conditions, relative thermal conductivity data may be obtained.

It is evident from the data plotted in Figure 3 that, based on heat transfer considerations, the dead-burnt sample material is a better reference.

The imposition of a heating rate of the static-temperature thermal gradients across the sample cell (Figure 5) increases the temperature drop across the cell. In effect, therefore, the heating rate produces the same result as decreasing the sample thermal conductivity.

The results shown in Figure 6 and Tables 1 and 2 clearly indicate that part of the reaction heat evolved or absorbed by the sample is never sensed by the recording thermocouple. It is evident that two such thermocouples are required to record the temperature effects associated with the total reaction heat. The last columns of Table 1 and the bottom rows of Table 2 express the percentage inefficiency of the single-thermocouple system. This percentage should ideally be the same for any reaction. The variation of $\% (w/b + w)$ with different types of reactions can be explained qualitatively. As the sample is hottest at the cell wall periphery, a sample reaction will start at this location. The temperature gradient imposed on the system by the furnace will limit the amount of sample reaction heat which flows into the DTA block during an exotherm (w). This will be further limited by the progress of the reaction front towards the sample centre for the reaction heat source is moving away from the cell wall boundary. A larger portion of the evolved heat will thus be sensed by the centre thermocouple (b) in this case. On the other hand, during an endothermic process initially the main source of heat is the DTA block (which is at a higher temperature than the sample (w'). Even as the reaction front advances, the sample will gather more heat from its reacted component (and so from the block) than from its unreacted portion (b'). Thus it might be expected that:

$$\% \, [w'/(b' + w')] > [w/(b + w)]$$

(endothermic) (exothermic)

The $SrCO_3$ polymorphic endotherm and the kaolinite exotherm are numerically approximately equal and the postulated $(w/w + b)$ ratio inequality is observed.

The evolution of a gas during a reaction will markedly influence the heat transfer characteristics in the sample by changing the gas species in the sample and removing heat from the system as the evolved gas leaves the sample. Both of these processes result in a change in the temperature gradient across the cell and can therefore be considered in terms of the change of overall sample heat transfer coefficient. The relative contribution of the two processes can be tested by comparison of the measured relative heat transfer coefficients for given reacting systems at the same temperature and the calculated heat-content ratios for the two gases involved. Two reactions were investigated involving the evolution of a gas, namely the decomposition of $CaCO_3(CO_2)$ and the dehydroxylation of kaolinite (H_2O). These two reactions occur in approximately the same range of temperature. Comparison of the K value ratios obtained and the heat content ratios for the two gases at these temperatures are shown in Table 3 assuming:

$$\Delta H(CaCO_3 \rightarrow CaO + CO_2) = 40.38 \text{ kcal/mole } (1000^\circ K)$$

$$\Delta H_{(\text{kaolinite} \rightarrow \text{metakaolin} + H_2O)} = 39.0 \text{ kcal/mole } (900^\circ K)$$

Table 3

$\dfrac{K_{CaCO_3}}{K_{\text{kaolinite endotherm}}}$	1.35
$\dfrac{\text{Heat content of } CO_2 \ (1000^\circ K)}{\text{Heat content of } H_2O \ (900^\circ K)}$	1.34

These results indicate that the change in heat transfer conditions in the reacting sample could in large measure be explained by the loss of the evolved gas and its heat content from the sample. When the calibration technique of quantitative DTA is used, therefore, the calibrant reaction should, if possible, evolve the same gaseous species as the unknown sample reaction of interest if a true calibration is to result.

The linear relationship between the peak areas and percentage active component in the sample is evident in Figures 7 and 8. Such plots should extrapolate through the origin as zero peak area should result from zero % active component. Only the (kaolinite-dead-burnt-kaolinite) plots in Figure 8 in fact extrapolate through the origin.

The availability of alternate paths for heat flow in a DTA system means that modification of the heat transfer conditions for one path could lead to an increase in flow along the other paths. The non-origin intercept cases indicate that mixtures containing approximately 6% of active component or less do not produce a differential temperature peak associated with the reaction of this component. A modification of heat transfer conditions within the reacting diluted sample must occur such as to maintain the temperature gradients within the dilute sample and inert reference sensibly equal, i.e.,

$$(\mathrm{d}T/\mathrm{d}x)_{\text{sample}} = (\mathrm{d}T/\mathrm{d}x)_{\text{reference}} \tag{3}$$

where T defines temperature and x is a distance parameter measured within the sample or reference. Assuming the simple conductivity equation then from (3):

$$(q/KA)_{\text{sample}} = (q/KA)_{\text{reference}} \tag{4}$$

where q is the energy input into each system, K the effective thermal conductivity and A the area across which the heat flows. For the 6% active component to react unnoticed, the following inequalities must hold:

$$K_{\text{sample}} > K_{\text{reference}} \text{ for the endotherm}$$

and

$$K_{\text{sample}} < K_{\text{reference}} \text{ for the exotherm}$$

The endothermic "K" inequality is possibly explained by the replacement of the air in the powder by the evolved water vapour and the exothermic inequality by reduction of the effective thermal conductivity of Al_2O_3 by dilution with a lower thermal conductivity component, i.e., kaolinite. It is being suggested, therefore, that as the peak area is a function of both the enthalpy and the heat transfer conditions, a change of K could influence the differential temperature peak area associated with ΔH and in some cases reduce it to zero. These results indicate that choice of the wrong reference material or a gaseous atmosphere different from that evolved by the sample can lead to errors.

The role of the geometry of the system is evident in Table 2. Although the "wall" peak areas in the second design are smaller than the "central" peak areas, the peak area ratio, $\% (w/w + b)$ for the second is higher than in the first design. As the L/D ratio is increased, the wall thermocouple moves toward the central thermocouple and the wall platinum foil contacts more powder area/unit mass of sample. These facts will both increase the proportion of heat sensed by the wall thermocouple.

Table 4

Quantitative estimation

(A) Calibrant: Kaolinite exotherm
(B) Calibrant: Kaolinite endotherm
(C) Calibrant: $CaCO_3$ endotherm

Type of DTA	Heat effect for $SrCO_3$ Rhombic $\rightleftharpoons$ Trigonal Inversion (kcal/mole) (±5%)
Design #1 (this work) (A)	
Peak area: — central DTA	4.16
Design #1 (A)	
Peak area: — (central + wall) DTA	4.63
Literature values for $SrCO_3$ inversion	
Design #1 (B)	4.7
Peak area: — (central + wall) DTA	3.46
Design #1 (C)	
Peak area: — (central + wall) DTA	4.29

The inversion heat for the rhombic ⇌ trigonal transformation in $SrCO_3$ was measured on the experimental DTA both of which had been calibrated with the kaolinite exotherm. Each estimation was performed four times and in each case the calibration and experimental runs were carried out in identical DTA systems. Neither reaction involves a gaseous product and both occur at roughly the same temperature (930° and 975° respectively). The results, together with the accepted literature value [8, 9] are shown in Table 4. Also included in this table are the estimated enthalpies for the inversion based on the kaolinite and calcium carbonate endothermic reactions as calibrants. Both these results are for the double-thermocouple DTA design. The accuracy of the double-differential thermocouple DTA technique is evident. These results also show the influence of the non-identity of the calibrant and investigated reaction types (the endothermic calibrant reactions involve gaseous evolution and occur at different temperatures) and the errors involved indicate the importance of the choice of the proper calibrant reaction.

Conclusions

As a result of the investigations here reported the following conclusions can be made:

1. Absolute thermal conductivity data cannot be measured in DTA apparatuses as the design militates against thermal conductivity measurements which require infinite heat sinks.
2. Relative effective thermal conductivity values as a function of temperature can be checked on a DTA apparatus. It can be concluded also that dead-burnt sample material constitutes a better DTA reference than other inert materials.
3. The imposition of a heating rate on the static-temperature thermal gradient across the sample cell increases the thermal drop across the cell. In effect, therefore, the heating rate produces the same effect as decreasing the sample thermal conductivity.
4. It has been demonstrated that a significant portion of the enthalpy produced in the reacting sample in a single thermocouple differential thermal analyser escapes detection and constitutes an error in quantitative DTA estimations. Double thermocouple techniques can eliminate this source of error.
5. The percentage heat loss associated with the escape of heat is not constant and varies with the type of reaction concerned, the reaction temperature and the reaction products. For valid results based on calibration techniques, therefore, the calibrant reaction should be physically identical to the reaction being investigated.
6. Certain dilution techniques appear to give valid results but care should be taken that the dilutent has the same effective thermal conductivity as the diluted species.
7. It was demonstrated that the correctly calibrated double-couple DTA technique gave more accurate results than the correctly calibrated single-couple technique.

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RÉSUMÉ — On a réalisé un appareil ATD pour étudier certaines erreurs négligées jusqu'à présent en ATD quantitative. On a trouvé ainsi que les caractéristiques du transfert de chaleur limitent la mesure in situ de la conductivité thermique des poudres. On montre également que le fait de négliger les échanges de chaleur entre la cellule renfermant l'échantillon et le bloc ATD (pertes ou gains de chaleur suivant que les réactions sont exothermiques ou endothermiques) conduit à des erreurs considérables dans les dosages. Un double thermocouple différentiel a été conçu pour tenir compte de ces pertes. L'étalonnage de l'appareil a été réalisé à l'aide des réactions endothermiques de $CaCO_3$ et de la kaolinite et contrôlé avec la transition endothermique de $SrCO_3$ (rhomboédrique-trigonal).

ZUSAMMENFASSUNG — Ein DTA-Apparatur wurde gebaut um einige in der gegenwärtig üblichen quantitativen DTA vernachlässigte Fehler zu prüfen. Es wurde gefunden, daß die Wärmeübertragungscharakteristika in DTA-Systemen die in situ Messungen der Wärmeleitfähigkeit von Pulvern begrenzen. Es wurde ebenfalls gezeigt, daß die Vernachlässigung von Wärmeverlusten der Probezelle an den DTA-Block bei exothermen Reaktionen und vom Wärmegewinn der Probezelle vom DTA-Block bei endothermen Reaktionen zu bedeutenden Fehlern in den quantitativen Bestimmungen führt. Ein DTA-Gerät mit doppeltem Differentialthermoelement wurde entworfen um diese Wärmeverluste zu berücksichtigen. Der Apparat wurde mittels der endothermen Reaktionen von $CaCO_3$ und Kaolinit, bzw. mittels der exothermen Reaktion von Kaolinit geeicht und an der Inversion von rhombischem zu trigonalem $SrCO_3$ erprobt.

Резюме — Построен прибор DTA для изучения некоторых ошибок, допускаемых в настоящее время при количественном DTA. Обнаружено, что характеристики теплопередачи внутри систем DTA лимитируются измерениями теплопроводности порошка. Показано, что пренебрежение утечкой тепла, передающегося блоку DTA от ячейки образца при экзотермической реакции и приобретением тепла ячейкой образца от блока DTA при эндотермических реакциях приводит к большим ошибкам в количественных оценках. Использована двойная модифицированная дифференциальная термопара, позволяющая учитывать эти теплопотери. Прибор калиброван $CaCO_3$ и эндотермиками и экзотермикой каолинита и проверен на эндотермике перехода тригональный ромбический $SrCO_3$.