Journal of Thermal Analysis, Vol. 5 (1973) 285—291

INVESTIGATION OF THERMAL CHARACTERISTICS OF A DTA CELL BLOCK

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Prior to evaluating DTA curves a thorough investigation of different types of specimen holders and cell blocks should be made, which means a quantitative appraisal of heat transfer conditions. The empirical approach makes use of the thermal analogue of Ohm's law, where R = thermal resistance. Calculation of R gave a graphical correction of about 1 mm, which stresses the merit of computer calculation. Very small differences of the values for R between platinum and alumina sample holders were observed. R was experimentally determined at 500 °K and 1000 °K by means of UO_2 and $BaCO_3$.

A rigorous comparison of various approaches in investigations of kinetics is needed to clear up the controversy between isothermal versus dynamic experimental methods. DTA methods, which are simple and time-saving, might be of use in such a project. Prior to evaluating DTA curves a thorough investigation of different types of specimen holders and cell blocks must be accomplished. This means that a quantitative appraisal of heat transfer conditions existing in an actual block should be made. A close examination of the total peak area including the exponential tail of a DTA curve, i.e. that part returning from the peak to the baseline, may make it possible to calculate the parameters of the apparatus. Thus the kinetic effects might be separated from the main diffusivity of the system, and the existing theories, (e.g. Piloyan et al.) for kinetic calculations might be tested.

There have been a number of mathematical treatments of DTA curves. The investigation of thermal characteristics of DTA cell blocks has received less attention.

In 1954 the following question was put by the late Dr. Allison [1]: To what extent is the curve influenced by the thermal diffusivity of the system?

The following expressions were developed:

$$\frac{\Delta H}{C_s} \cdot \frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\mathrm{d}y}{\mathrm{d}t} + A(y - y_s) \tag{1}$$

where ΔH = heat of reaction

C_s = heat capacity of the sample + holder

$\frac{\mathrm{d}f}{\mathrm{d}t}$ = rate of fractional transformation of the sample

$y = T_r - T_s$
$A = (K_r + \alpha_r + 2\sigma)/C_s$
K_r = heat transfer coefficient
α_r = heat loss
σ = heat transfer coefficient between the sample holders
$y_s = [(C_s - C_r)\mathrm{d}T_r/\mathrm{d}t]/(K_r + \alpha_r + 2\sigma)$.

When the reaction is complete, $\frac{\mathrm{d}f}{\mathrm{d}t}$ is zero.

Integration is possible, if

$\mathrm{d}T_r/\mathrm{d}t$ = constant
$T_w - T_s$ = constant
$T_s - T_0$ = constant
T_w = furnace temperature
T_0 = sample environment temperature.

Limits being put, $y = y$, $y = y_1$, $t = t$, and $t = t_1$, one gets

$$y = y_s[1 - e^{-A(t-t_1)}] + y_1 e^{-A(t-t_1)} \tag{2}$$

When t approaches infinity, y approaches y_s. A plot of $\ln(y - y_s)$ against t gives a straight line of slope A.

Allison stated that the end-point of the reaction is obtained by plotting the logarithm of the differential temperature against time starting at the apex of the peak. The end-point of the reaction is given by the deviation from a linear relationship.

The slope A is also said to represent a measure of the mean thermal diffusivity of the system.

The calculation of Eq. (1), however, makes use of a known value for C_s, which is somewhat complicated to evaluate, especially during a transformation. The same remark is valid for y_s.

This method gave lower heat of reaction data than those determined by other methods. Kinetic data, however, were in fair agreement with isothermal data.

Similar ideas were presented some 16 years later [2]. The use of expression (3) makes it possible to determine the time constant (thermal lag) of the sample holder

$$\frac{L}{K_1} = S = S_1 + S_2 = \frac{a\tau^2}{2} + a\tau\Theta_1 \tag{3}$$

where S = peak area (S_1 = from start to apex, S_2 = from apex to baseline)
L = heat of reaction
K_1 = heat transfer coefficient
a = linear rise of the slope of the differential signal
τ = time from the start of the reaction to the apex
Θ_1 = "time constant" $= \frac{C_1}{K_1}$.

There are several possibilities to evaluate the peak areas. We have chosen the method mentioned above, treating the area in two parts.

In order to eliminate tedious manual plotting of thermal data, the recorder should be computerized. Equipment is now available and the methods have been discussed [3].

The empirical approach (4) makes use of the thermal analogue of Ohm's law

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{T_p - T_s}{R} \tag{4}$$

where R = thermal resistance.

By rearranging Eq. (4) and introducing the heat generation by the sample, we obtain

$$\frac{R\,\mathrm{d}h}{\mathrm{d}t} = (T_s - T_r) + R(C_s - C_r)\frac{\mathrm{d}T_r}{\mathrm{d}t} + RC_s\frac{\mathrm{d}(T_s - T_r)}{\mathrm{d}t} \tag{5}$$

RC_s is the thermal time constant of the system. The recorded signal $T_s - T_r$ is proportional to R.

After the thermal event, the signal decays exponentially from the peak to the baseline. By solving Eq. (5) with $\frac{\mathrm{d}h}{\mathrm{d}t} = 0$ and $T_s - T_r = \Delta T_{\max}$, one obtains

$$\Delta T = \Delta T_{\max}\, e^{-t/RC_s} \tag{6}$$

Prior to $T_{\max}$, the displacement from the baseline at any time should be proportional to the reaction rate. The fraction of the total area up to that time must be proportional to the fraction of the sample which has reacted. This value, however, is superimposed by R, which might be temperature-dependent. Hence, the need for calibration with well-characterized samples over a temperature range still exists. The evaluation of R, however, makes it possible to compare different sample holders and correction factors.

The area under the peak is given by $R \cdot \Delta h$. From the measurement of a known heat effect, the value of R can thus be calculated.

The fundamental theory is similar in fact to that given in [2]. As stated earlier, "time constant" has been defined by $\Theta = \frac{C}{K} \sim (RC)$. C can be calculated with sufficient accuracy.

Experimental

The tentative evaluation of R was made by means of two different substances, UO_2 and $BaCO_3$. For UO_2, the heat of the reaction $UO_2 \rightarrow U_3O_7$, 13.5 kcal · mole^{-1} [5] is used. For $BaCO_3$, the heat of transition at 1083 °K, 4.5 kcal · mole^{-1} [7] is applied.

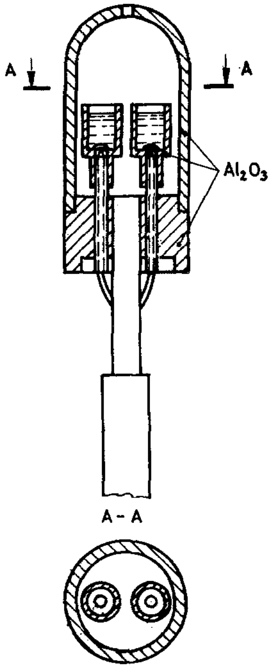

Fig. 1. The DTA cell applied

The DTA cell can be seen in Fig. 1. The sample holders were made of alumina and platinum, respectively. Different data [5–7] used in the calculation are given in Table 1.

The contribution of the heat capacity of the sample will be omitted in the following. The curves denoted by A and C were obtained with alumina specimen holders.

Table 1

Material data

Material	Curve	Weight, g	Heat capacity, cal · degree^{-1}
Al_2O_3	(A)	1.0770	26.9×10^{-2}
Pt	(B)	3.0651	10.0×10^{-2}
U_3O_7	(A)	0.1019	66.2×10^{-4}
U_3O_7	(B)	0.1034	67.0×10^{-4}
$BaCO_3$	(C)	0.1509	–
$BaCO_3$	(D)	0.1523	–

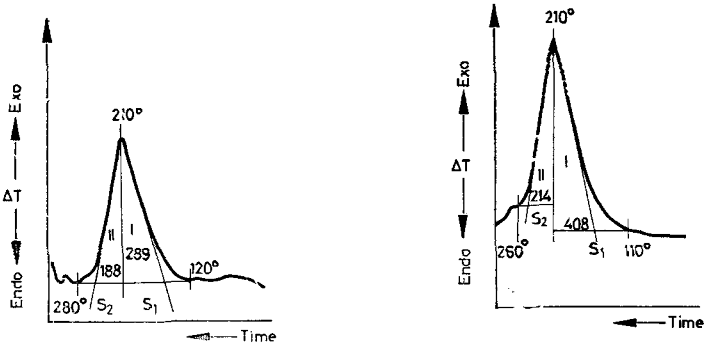

Fig. 2. DTA curves for $UO_2 \rightarrow U_3O_7$

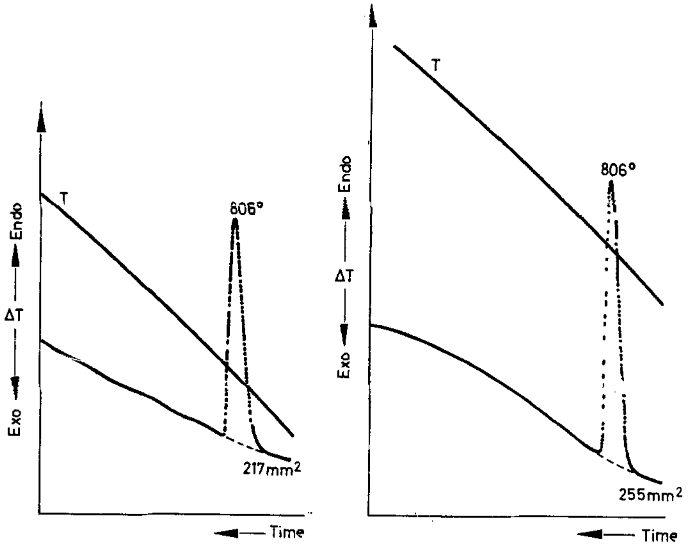

Fig. 3. DTA curves on heat of reaction of $BaCO_3$

Table 2

Conversion

Area A = 474 mm^2 = 711 degree · sec
Area B = 622 mm^2 = 933 degree · sec
Area C = 217 mm^2 = 221 degree · sec
Area D = 255 mm^2 = 260 degree · sec

Calibration

Area A (cal · mm^{-2}) = 1.05×10^{-2}
Area B (cal · mm^{-2}) = 0.82×10^{-2}
Area C (cal · mm^{-2}) = 1.58×10^{-2}
Area D (cal · mm^{-2}) = 1.36×10^{-2}

The DTA curves are given in Figs 2 and 3. The heating rate was 10 °C · min^{-1}. Pt/10RhPt thermocouples were used. Paper speed was 120 mm · h^{-1}, and ΔT-scale: 100 μV = 250 mm. The measured peak areas were converted to degree · · seconds (at 500 °K and at 1000 °K), and the heat effects to cal · mm^{-2}. The conversion factor was 1 degree · sec = 0.67 mm^2 (at 500 °K) and 0.97 mm^2 (at 1000 °K). The results are given in Table 2.

Calculation of R gave 142 degree · sec · cal^{-1} for the alumina sample holder, and 184 degree · sec · cal^{-1} for platinum sample holder at 500 °K. The corresponding figures were 64 and 74 at 1000 °K.

Discussion

The "time constant" RC was 38 and 18 sec, respectively. The construction of the correction is simple. RC_s is drawn horizontally from a tangent. The distance where the perpendicular meets the tangent is added to the actual point. *In this case the correction is approx. 1 mm which makes graphical construction difficult to use. The merit of computer calculation is evident.*

When using Eq. (3) for a similar evaluation, the values obtained for Θ are $-$ 59.4 sec and $-$ 161 sec, respectively. In this case, the term for heat transfer coefficient is involved instead of a more general term of heat resistance.

The correction was also applied at 1000 °K. Again it was found that the correction term is less than 1 mm in the present case. It is quite evident that the use of computerized scanning and calculation would give more exact figures.

As a result we have found that calculation of R represents a suitable means for the evaluation of a DTA cell. The investigation of the exponential tail by graphical correction must be omitted for practical reasons. The type of DTA cell in our case gives a very swift return to the baseline (exponential tail).

Some other observations may be mentioned, namely the very small differences of the values for R between platinum and alumina specimen holders. The difference is more accentuated when heat transfer (Θ) is involved. Small R : *s*, however, give reproducible curves with a high resolution.

The fact that R is temperature-dependent makes calibration of a DTA cell necessary. The total area of the peak must be used for the calibration of the apparatus. Various types of reactions in different temperature intervals are also needed to give a more exhaustive determination of R.

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RÉSUMÉ — L'exploitation des courbes ATD devrait être précédée d'une étude approfondie de l'influence des divers types de supports d'échantillon et de cellules, c'est-à-dire d'un examen quantitatif des conditions du transfert de chaleur. L'approximation empirique utilise l'analogie thermique de la loi d'Ohm où R est la résistance thermique. Le calcul de R donne une correction graphique d'environ 1 mm, ce qui met en relief les mérites du calcul à l'ordinateur. On n'a observé que de très petites différences entre les creusets en platine ou en aluminium contenant les échantillons. On a déterminé R expérimentalement à 500 °K et à 1000 °K en utilisant UO_2 et $BaCO_3$.

ZUSAMMENFASSUNG — Vor der Auswertung von DTA-Kurven sollte eine gründliche Prüfung der verschiedenen Typen von Probebehältern und Zellenblöcken erfolgen, was für die quantitative Abschätzung der Wärmeübertragungsverhältnisse von Bedeutung ist. Die empirische Annäherung macht von dem thermischen Analogen des Ohmschen Gesetzes Gebrauch, wobei R der thermische Widerstand ist. Die Berechnung von R ergab eine graphische Korrektion von etwa 1 mm, was die Vorteile der Komputerberechnung betont. Sehr kleine Unterschiede der Werte für R wurden bei Platin-, bzw. Aluminium-Probebehältern beobachtet. R wurde bei 500 °K und 1000 °K mittels UO_2 und $BaCO_3$ auf dem Versuchswege bestimmt.

Резюме — Перед обработкой кривых ДТА следует провести тщательное исследование различных типов держателей образцов и блоков, в целях количественной оценки условий передачи тепла. Эмпирическое приближение использует термическую аналогию закона Ома где R — термическое сопротивление. Расчет величины R дал графическую коррекцию около 1 мм, что подчеркивает значение расчета на вычислительной машине. Установлено, что для платиновых и алюминиевых держателей образцов разница в величине R весьма незначительна. Величина R экспериментально определена при 500°К и 1000°К с помощью UO_2 и $BaCO_3$.