A SIMPLE METHOD OF DETERMINING THE ACTIVATION ENERGY OF AN ISOTHERMAL SOLID-STATE DECOMPOSITION REACTION

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(Received April 16, 1979)

A simple approach to determine the activation energy (E) of solid-state decomposition reactions is described. The activation energy is calculated from the slope of the logarithm of the maximum peak height of the isothermal DTA trace versus the reciprocal of the absolute temperature. The proposed method is applied in the study of the kinetics of thermal decomposition of cadmium carbonate. The activation energy calculated from this method (90.8 ± 2.2 kJ mole^{-1}) is in very good agreement with the value (87.5 ± 2.5 kJ mole^{-1}) obtained by the conventional method.

In the study of solid-state decomposition kinetics using thermal analysis, the activation energy is one parameter that is generally calculated. The normal practice is to assume or determine an appropriate integral rate expression $g(\alpha)$, and then evaluate the activation energy [1]. In a previous communication [2], we have shown that to determine the proper $g(\alpha)$ function, in addition to the data from dynamic techniques such as TG and DTA, at least one set of isothermal measurements is necessary. Several investigators have shown the difficulties in calculating meaningful activation energies from the dynamic method alone [1 – 4]. Even with isothermal TG or DTA data, the evaluation of E by any of the standard techniques is rather tedious. It involves determining the proper mechanism of the reaction and then evaluating the appropriate $g(\alpha)$ and specific reaction rates. In the literature, the use of the induction period [5], the time of completion of the reaction [6] or the completion of a given fraction of the reaction [7], have been suggested as alternatives to determine the specific reaction rates. However, in all of these techniques, an accurate knowledge of the time of inception of the reaction is necessary. This is difficult to obtain in practice. Young [5] has suggested without any comments or examples that, in isothermal TG or DTA, the plot of the logarithm of the maximum slope of (α vs. t) curves against $\dfrac{1}{T}$ could be used as an alternative method of obtaining E in a decomposition process. No detailed study utilizing his suggestion of calculating the E of a decomposition reaction by isothermal DTA has so far been reported. In the present communication, we report our results of such an analysis of an isothermal DTA study of the decomposition of $CdCO_3$.

Experimental

Cadmium carbonate powder (99% purity, $-$ 200 to $+$ 240 BSS mesh) was used in all DTA experiments. A scheme of the controlled gas atmosphere DTA apparatus used is shown in Fig. 1. In each experiment about 100 mg of the sample and about an equal amount of calcined alumina (calcined at 1720 K for 3 hours) were taken in platinum cups [8], and a controlled flow of about 2.5 dm^3/hr of the
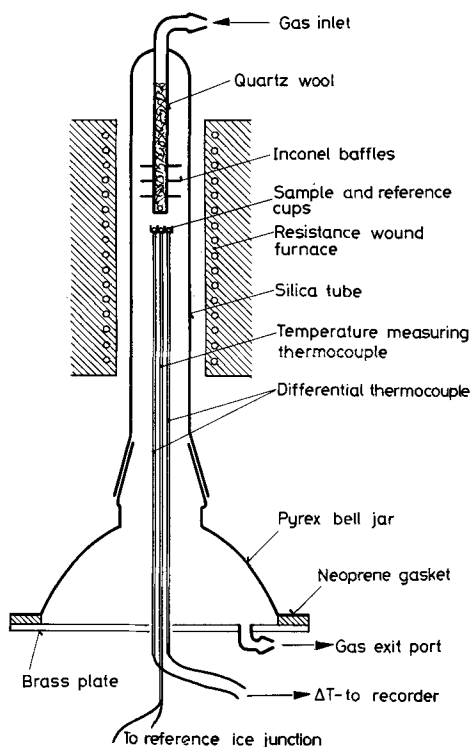

Fig. 1. Scheme of the apparatus for controlled atmosphere DTA

desired gas was maintained through the apparatus. Provision was also made to preheat the gases before they entered the reaction zone. All temperatures were measured with calibrated thermocouples, with the ice-point as the reference. Temperatures were controlled to ± 0.5 K.

In preliminary experiments the DTA curves were recorded at 5 K/min heating rate in air or in carbon dioxide. The decomposition began in air atmosphere at 650 K, and in carbon dioxide at 760 K. Based on these results, the isothermal DTA runs were conducted as follows. The CdCO$_3$ and the reference were heated at 5 K/min in one atmosphere of CO$_2$ (flow rate $= 2.5$ dm^3/hr) to a predetermined

temperature below 760 K. After the attainment of thermal equilibrium, CO_2 was replaced by air flowing at the same rate. The DTA trace was then recorded as a function of time. A few typical isothermal DTA curves are shown in Fig. 2.
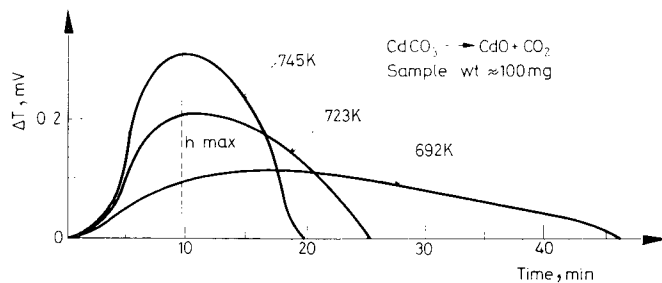

Fig. 2. Isothermal DTA curves for the thermal decomposition of $CdCO_3$ in air

Results and discussion

It was observed that the total area under each ΔT vs. t curve is nearly constant for samples of equal mass (for ~ 100 mg samples the areas were 27.0, 25.5 and 26.0 cm²), indicating that this area at any 't' is proportional to α, the fraction of the sample decomposed by that time. Thus, the height, h, of the DTA peak at any given time is proportional to the rate $\left(\dfrac{d\alpha}{dt}\right)$ at that time.

The time, t_{max}, at which the maximum height occurred in these isothermal DTA curves decreased with increasing temperature (Fig. 2). When log h_{max} was plotted against $1/T$, a linear plot was obtained (Fig. 3). Since (as seen above) $\left(\dfrac{d\alpha}{dt}\right)_{max}$ is proportional to h_{max}, the slope of the log h_{max} vs. $\dfrac{1}{T}$ plot would yield the activation energy for the decomposition reaction [5]. The activation energy E, calculated from the slope of the line in Fig. 3, was found to be 90.8 ± 2.2 kJ mole^{-1}. When the area under the $h(\Delta T)$ vs. t plot from $t = 0$ to $t = t_{max}$ was calculated from the experimentally obtained isothermal curves, in every case this area was found to be $40.8 \pm 1.5\%$ of the total area (Table 1). This confirms that the fraction α decomposed at t_{max} was independent of the temperature at which the decomposition was studied.

It was previously shown [2] that the isothermal decomposition of $CdCO_3$ followed the Avrami – Erofeyev [9, 10] equation

$$[- \log (1 - \alpha)]^{1/3} = kt \tag{1}$$

where k is the specific reaction rate. The specific reaction rates were evaluated from measured α's. From the plot of log K vs. $\dfrac{1}{T}$ (Fig. 3), an activation energy of

Table 1

Values of h_{max} and α_{max} at

T, K	661	665	673	675	681	685	701
h_{max}, cm	1.10	1.20	1.45	1.50	1.70	1.90	2.60
α_{max}, %	37.9	38.5	40.4	39.7	42.6	42.6	38.9

87.5 ± 2.5 kJ mole^{-1} was obtained. It can be seen that the value of 90.8 ± 2.2 kJ mole^{-1} calculated from the simple plot of log h_{max} vs. $\frac{1}{T}$ is in very good agreement with the E of 87.2 ± 2.5 kJ mole^{-1} calculated using the standard method.

The reason for this agreement is that, in general, the rate of a solid-state decomposition is

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (2)$$

where α is the fraction of the sample decomposed at time t, k is the specific reaction rate, and $f(\alpha)$ is a characteristic function that depends upon the mechanism of the
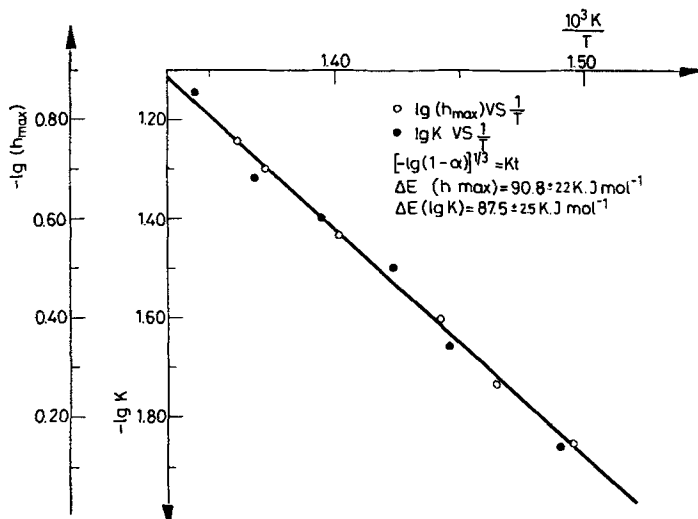

Fig. 3. Plots of log K vs. $\frac{1}{T}$ and log (h_{max}) vs. $\frac{1}{T}$ for the thermal decomposition of CdCO$_3$ in air

different temperatures

703	712	718	723	725	734	740	745
3.00	3.30	3.70	4.25	4.30	5.10	5.80	6.10
41.5	40.4	41.5	41.2	40.4	42.6	41.3	42.6

$\alpha_{max} = 40.8 \pm 1.5\%$.

decomposition process. The specific reaction rate is usually expressed as

$$k(T) = Z \exp(-E/RT) \tag{3}$$

where E is the overall activation energy, and Z the pre-exponential factor. Substituting (3) in (2) and rearranging, we have

$$\log \frac{\left(\dfrac{d\alpha}{dt}\right)}{f(\alpha)} = -\frac{E}{2.303RT} + \log Z \tag{4}$$

If $f(\alpha)$ is independent of temperature, which is true if the mechanism of the reaction does not undergo a change in the temperature interval of the investigation, then according to (4) a plot of $\log\left(\dfrac{d\alpha}{dt}\right)$ vs. $\dfrac{1}{T}$ for a fixed value of α would yield the activation energy. This is true when the chosen value of α corresponds to the maximum rate of reaction, provided the α_{max} is independent of temperature.

As found experimentally, this α_{max} was constant and equal to $40.8 \pm 1.5\%$ in the temperature range of the present study. There are other reports [6, 11, 12] where this α_{max} was shown to be temperature-independent. Hence, the activation energy could be calculated from the plot of $\log\left(\dfrac{d\alpha}{dt}\right)_{max}$ vs. $1/T$. However, in practice this involves the calculation of the α vs. t curve from the experimentally measured DTA trace, and then evaluating the slope at the inflection point. Besides being time-consuming, both steps introduce additional uncertainties in E. In the present investigation, we have shown that the same activation energy is obtained when the log of the maximum height, h_{max}, of the DTA trace is plotted against $\dfrac{1}{T}$.

The errors involved in the measurement of h_{max} are relatively smaller, thus improving the accuracy of the value of E.

There have been no reports in the literature where this simple method has been used, though there are reports [6, 11, 12] in which the data have shown that a plot

of the logarithm of the maximum reaction rate as a function of $\frac{1}{T}$ is linear and *the slope yields the activation energy.*

The analysis of the isothermal DTA data of decomposition reactions for the calculation of activation energies by the present method is not only simple and time-saving, but also yields more reliable values. One other advantage of the present method is that it does not require an a priori knowledge of the form of the $g(\alpha)$ function for the reaction.

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RÉSUMÉ — On décrit une méthode simple d'approximation pour déterminer l'énergie d'activation (E) des réactions de décomposition en phase solide. Le calcul de l'énergie d'activation s'effectue à partir de la pente du logarithme de la hauteur maximale du pic de la courbe d'ATD isotherme en fonction de l'inverse de la température absolue. On a appliqué la méthode proposée lors de l'étude de la cinétique de la décomposition thermique du carbonate de cadmium. L'énergie d'activation calculée à partir de cette méthode (90.8 $\pm$ 2.2 kJ mole^{-1}) est en bon accord avec la valeur (87.5 $\pm$ 2.5 kJ mole^{-1}) obtenue par la méthode conventionnelle.

ZUSAMMENFASSUNG — Eine einfache Annäherung zur Bestimmung der Aktivierungsenergie (E) von Festphasenzersetzungsreaktionen wird beschrieben. Die Aktivierungsenergie wird aus dem Anstieg des Logarithmus der maximalen Peakhöhe der isothermen DTA-Kurve als Funktion der reziproken absoluten Temperatur errechnet. Die vorgeschlagene Methode

wird zur Untersuchung der Zersetzungskinetik von Cadmiumcarbonat eingesetzt. Die hiernach berechnete Aktivierungsenergie (90.8 ± 2.2 kJ mol^{-1}) ist in guter Übereinstimmung mit dem durch die konventionelle Methode erhaltenen Wert (87.5 ± 2.5 kJ mol^{-1}).

Резюме — Описано простое приближение для определения энергии активации твердотельных реакций разложения. Энергия активации вычислялась их наклона кривой в координатах логарифм максимума высоты пика и обратной абсолютной температуры. Предложенный метод был применен для изучения кинетики термического разложения карбоната кадмия. Вычисленная по этому методу энергия активация ($90.8 + 2.2$ кдж.моль$^{-1}$) находится в хорошем согласии со значением 87.5 ± 2.5 кдж.моль$^{-1}$, полученным обычным методом.