preferentially etched out during the thinning process before examination.

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CHEMISTRY

Determination of Activation Energies of Chemical Reactions by Differential Thermal Analysis

A NUMBER of articles have been published dealing with the differential thermal analysis (DTA) of chemical reaction kinetics[1-5]. Only one of these, however, gives a direct method for determining the activation energy (E) of the chemical reaction[4]. In this method, DTA curves are recorded at several different rates of heating. The results are then plotted as $\ln b/T_m^2$ against $1/T_m$, where T_m is the peak temperature in $°$ K (the temperature of point B, Fig. 1), and b is the rate of heating. The magnitude of E is calculated from the angle between this straight line and the abscissa. This procedure has two principal shortcomings: (1) it is necessary to record several DTA curves with various rates of heating; and (2) it is necessary to use a special programming device to control the temperature. This device must be capable of providing linear heating at a number of rates of heating. The latter condition imposes serious technical difficulties, because all the DTA apparatuses at present available are adjusted for only one rate of heating.
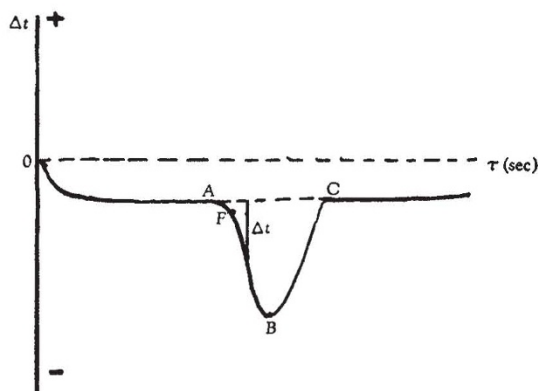

Fig. 1. Formalized differential thermal curve, showing the various attributes of the thermal effect. For explanation see text.

The present communication puts forward a method for determining E from a single DTA curve recorded at an arbitrary rate of heating.

Let us consider this method applied to the decomposition reactions of solids. The given substance dissociates over a particular range of temperature and gives rise to the thermal effect ABC on the DTA curve (Fig. 1). It is well known[2,6] that the deviation from the baseline (Fig. 1) in the initial stages of the reaction is satisfactorily described by

$$\Delta t = S \frac{d\alpha}{d\tau} \qquad (1)$$

where Δt is the deviation from baseline ($°$ C); S is the area of the thermal effect ($°$ C × sec); $d\alpha/d\tau$ is the rate of the reaction; and α is the extent of the reaction.

The rate of a chemical reaction is usually described by

$$\frac{d\alpha}{d\tau} = A_0 f(\alpha) \exp(-E/RT) \qquad (2)$$

where A_0 is a constant, $f(\alpha)$ is a function of the extent of reaction (it is often assumed that $f(\alpha) = (1-\alpha)^n$, where n is the order of reaction; but in more general cases $f(\alpha) = \alpha^m (1-\alpha)^n$, where m and n are the constants).

Substituting equation (1) into equation (2), and taking logarithms, the following equation can be obtained

$$\ln \Delta t = C - \ln f(\alpha) - \frac{E}{RT} \qquad (3)$$

where C is a constant which combines all the constants of equations (1) and (2), and T is the temperature in $°$ K corresponding to a given value of Δt.

Under normal isothermal conditions, the only variable determining the reaction rate is α. In DTA, however, the temperature also varies. It can easily be shown that when the value of α lies between 0·05 and 0·8 (approximately up to the peak of the thermal effect) at the usual heating rates the change in temperature has a greater effect on Δt than the change in α at the normal rates of heating (10°–40° C/min). To an approximation, therefore, the term $\ln f(\alpha)$ can be neglected and equation (3) written in the following form*

$$\ln \Delta t = C^1 - \frac{E}{RT} \qquad (4)$$

The values of Δt are taken directly from the DTA curve in units of length (cm or mm) as is shown in Fig. 1.

Table 1. ACTIVATION ENERGIES FOR SOME REACTIONS

Substance	Type of reaction	E (experimental)	E (from the literature)	Ref.
$CuSO_4.5H_2O$	Dehydration	17·9	18·0	7
$CaCO_3$	Dissociation	35·4	35–48	7
$MgCO_3$	,,	32·0	32·4	5
$CaC_2O_4.H_2O$	Dehydration	21·0	20–22	8

The errors of these determinations are estimated at between 15 and 20 per cent.

The interval measured is approximately represented by the portion FB of the curve in Fig. 1. The measurements are taken not from the point at which the thermal effect begins (point A, Fig. 1), but at some distance from it (approximately from the point of maximum curvature, F). Table 1 gives values of E determined for the decomposition reactions of various substances.

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* Under the conditions indicated, equation (4) also comprises processes obeying the equations of diffusion kinetics.

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Microwave Rotation Spectra of Ethyl Acetylene and Ethyl Isocyanide

THE rotation spectra of ethyl derivatives continue to be of interest for determining structure parameters and the force field of these molecules[1-5]. We have measured the rotation spectra of two further members of this series, ethyl acetylene and ethyl isocyanide.