

Note

A METHOD FOR THE DETERMINATION OF KINETIC PARAMETERS
BY DTA

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Differential thermal analysis (DTA) is a useful tool for the determination of kinetic parameters of solid thermal reactions. At present, several methods [1–4] are available for obtaining kinetic parameters from DTA curves. Unfortunately, parameter values calculated by these methods not only differ from an established value, but also disagree amongst themselves. This situation raises doubt about the validity of kinetic analysis by non-isothermal methods and has created a flurry of controversy [5,6].

A close examination of a DTA curve, shown in Fig. 1, will reveal that the first step of a process for obtaining kinetic parameters by the use of this curve is to relate ΔT with the fraction, α , of materials reacted in time t . This can be done by an energy balance as Borchardt and Daniels [1] did under some assumptions, which could be fulfilled by a careful design of experiments, to obtain the equation

$$\alpha = \frac{1}{A} \left[\frac{C}{K} \Delta T + a \right] \quad (1)$$

where a is that part of the total area, A , in a DTA curve up to time t as shown by the shaded part of Fig. 1, C is the heat capacity of the sample and standard, and ΔT is the temperature difference between the sample and

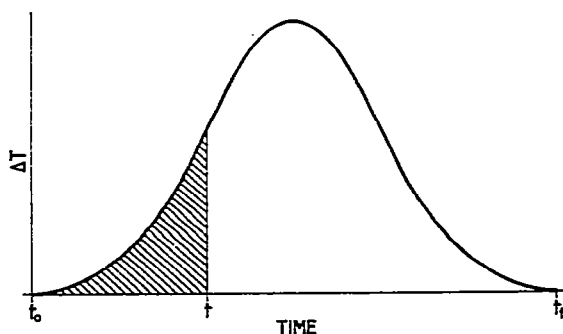


Fig. 1. Simple DTA curve.

standard at t . K is a constant relating A and the enthalpy change of a reaction.

In eqn. (1), $C\Delta T/K$ is very small compared with α and can be neglected to relate α with ΔT through a .

$$\alpha = \frac{a}{A} \quad (2)$$

The area a is given by

$$a = \int_0^t \Delta T dt \quad (3)$$

and α can be expressed by

$$\alpha = \int_0^t Q dt \quad (4)$$

where $Q = d\alpha/dt = \Delta T/A$.

Following Erofeyev [7], $d\alpha/dt$ can be described by

$$\frac{d\alpha}{dt} = p(1 - \alpha) \quad (5)$$

in which p stands for the probability of the reaction of an individual molecule and is a function of temperature and time.

In a recent note [8], it is shown that p can be expressed by

$$p = \left(\frac{\beta}{\gamma}\right) \left(\frac{t}{\gamma}\right)^{\beta-1} \quad (6)$$

with parametric constants β and γ representing the effect of temperature on the reaction. After substitution for p , eqn. (5) gives

$$\frac{d\alpha}{dt} = \left(\frac{\beta}{\gamma}\right) \left(\frac{t}{\gamma}\right)^{\beta-1} (1 - \alpha) \quad (7)$$

In eqn. (7), (β/γ) represents the specific rate constant and with this, the activation energy, E , and pre-exponential factor, k_0 , can be obtained from the Arrhenius law, expressed by

$$\ln \left(\frac{\beta}{\gamma}\right) = \frac{-E}{RT_{0.63}} + \ln k_0 \quad (8)$$

where R is the gas constant and $T_{0.63}$ is the Kelvin temperature determined at $\alpha = 0.63$. At this value of α , t equals γ and the term $(t/\gamma)^{\beta-1}$ in eqn. (7) becomes unity for all values of β . This term also becomes one when $\beta = 1$, bringing eqn. (7) in the line with the first-order decay law. In that case, eqn.

(8) can be written as

$$\ln\left(\frac{1}{\gamma}\right) = \frac{-E}{RT_{0.63}} + \ln k_0 \quad (9)$$

For the first-order law, some methods [9,10] have used T , the temperature corresponding to t of a DTA curve, in place of $T_{0.63}$ to calculate E by the use of the Arrhenius law. This procedure appears to be erroneous as the left-hand side of eqn. (9) remains constant for a DTA curve.

For the determination of E and k_0 by the use of eqn. (8), β and γ are required and these can be found from the integrated form of eqn. (7). After the integration and converting the resulting equation into a logarithmic form, eqn. (7) gives

$$\log \ln[1/(1 - \alpha)] = \beta \log t - \beta \log \gamma \quad (10)$$

In agreement with this equation, α values calculated by eqn. (2), when plotted as $\ln[1/(1 - \alpha)]$ vs. t in a log-log plot should yield a straight line with slope β and, in this plot, γ is located by the t axis, as $t = \gamma$ at $\ln[1/(1 - \alpha)] = 1.0$. Since only one set of β and γ values can be obtained from one DTA curve, more curves at different heating rates are required to obtain E and k_0 for a reaction.

For the complete analysis of solid state reactions, it is also required to know the mechanism of the reactions. Previous methods have been based on the concept of the order of reaction, although its significance in thermal decomposition is limited. However, in this method, β , being the slope of $\alpha-t$ relation, carries significance towards the mechanism of reactions, and solid state reactions can be classified by means of β as reported in a previous note [8].

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