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Note

DETERMINATION OF KINETIC PARAMETERS BY THERMOANALYTICAL TECHNIQUES

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In the present method for finding kinetic parameters through thermoanalytical techniques kinetic data obtained under isothermal and dynamic temperature conditions are analysed by a rate equation of the form

$$d\alpha/dt = kg(\alpha) \qquad (1)$$

where k is the specific rate constant and $g(\alpha)$ is a function of the fraction α of materials reacted in time t. The functional form of $g(\alpha)$ is derived by a trial-and-error procedure in which α is fitted into a set of functions developed on the concept of some model mechanisms of solid state reactions and if a linear relation is obtained between a function and the rate of reaction, the function is accepted as the true function. The activation energy, E and the pre-exponential factor k_0 are determined by the Arrhenius law,

$$k = k_0 \exp(-E/RT) \qquad (2)$$

in which R is the gas constant and T is the Kelvin temperature.

This procedure for finding the kinetic parameters has been the subject of varied criticism [1]. A major objection is that an individual model function can describe a particular reaction occurring under the actions of a specific number of variables, while thermal decomposition reactions occur under the influence of many interrelated factors.

A generalized rate equation was found most suitable to describe decomposition reactions. A method for finding kinetic parameters through thermoanalytical techniques is demonstrated through the use of this equation.

It was found that the equation developed on the basis of the probability of an elementary event by Erofeev could be expanded to describe the rate of solid-state reactions. The basic equation can be expressed in the form

$$d\alpha/dt = \rho(1 - \alpha) \qquad (3)$$

where ρ is the mean probability for reaction of an individual molecule. For a decomposition process ρ is found to be a function of temperature and time, and if ρ can be expressed by

$$\rho = (\beta/\gamma)\,(t/\gamma)^{\beta-1} \qquad (4)$$

the rate of decomposition is given by

$$d\alpha/dt = (\beta/\gamma)\,(t/\gamma)^{\beta-1}\,(1-\alpha) \qquad (5)$$

in which γ and β are functions of temperature. These parameters may also depend upon the particle size of solid materials, defects in the crystal lattice, preliminary thermal treatment and reaction pressure. For a given system these factors are expected to remain constant, allowing γ and β to vary with temperature only. Integrating eqn. (5) leads to

$$\alpha = 1 - \exp(-(t/\gamma)^{\beta}) \qquad (6)$$

A logarithmic form of eqn. (6) is specially convenient in the treatment of thermal decomposition data. Expressing eqn. (6) in a log form gives

$$\ln \ln (1/(1-\alpha)) = \beta \ln t - \beta \ln \gamma \qquad (7)$$

This shows that data plotted as $\ln \ln (1/1-\alpha)$ vs. $\ln t$, should yield a straight line with a slope β and intercept $\beta \ln \gamma$, from which γ can be determined.

From eqn. (6) it can be shown that at $\alpha = 0.632$, $t = \gamma$, and at this condition eqn. (5) becomes

$$d\alpha/dt = (\beta/\gamma)\,(1-\alpha) \qquad (8)$$

Since (β/γ) is a function of temperature alone, eqn. (8) gives a first-order decay law with the specific rate constant (β/γ).

With the use of the Arrhenius law, the activation energy E and the pre-exponential factor k_0 can be obtained from (β/γ) by

$$\ln(\beta/\gamma) = -E/RT_{0.63} + \ln k_0 \qquad (9)$$

where $T_{0.63}$ is the Kelvin temperature evaluated at $\alpha = 0.63$.

$T_{0.63}$ is essentially the same as the temperature of decomposition occurring under isothermal conditions. For decompositions carried out under dynamic temperature conditions the temperature is allowed to vary following temperature—time relations. Assuming a linear relation between temperature and time

$$T = T_0 + \theta t \qquad (10)$$

$t = (T - T_0)/\theta$, as at $\alpha = 0.632$, $t = \gamma$, $\gamma = (T_{0.63} - T_0)/\theta$. In this case β can be obtained as the slope of a straight line resulting from $\ln \ln [1/(1-\alpha)]$ vs. $\ln (T - T_0)/\theta$ plot. The activation energy and pre-exponential factor can be calculated from eqn. (9). T_0 in eqn. (10) is the temperature at $t = 0$, and θ is the fixed rate of increase of temperature.

APPLICATION OF EQUATION (6)

The Avrami and Erofeev equations, which have been used to describe decomposition kinetics [2,3], are the offshoots of eqn. (6), although the specific rate constant is represented by $(1/\gamma)$, not (β/γ), the true constant. Equation (6) was also found to describe the functions [4] developed on the basis of model reaction mechanisms, with the β values representing these mechanisms. From the analysis it was found that when $\beta = 1$, decomposition follows the first-order decay law; $1 < \beta \leqslant 3$, decomposition occurs at the phase boundary of the products; $\beta > 3$, nucleation and the growth of nuclei control decomposition; and $\beta < 1$, the diffusion of gaseous products is the controlling factor in the decomposition process.

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