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Note

A SIMPLE KINETIC RELATION OF DERIVATIVE THERMOANALYTICAL CURVES

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In a previous paper [1], kinetic relations for derivative curves of thermal analysis, such as evolved gas analysis, were elucidated, and methods for their kinetic analysis were proposed. These methods were applied, for example, to thermal decompositions of poly(methyl methacrylate) [2,3] and poly(ethylene terephthalate) [4] and also to the thermal volatilization of hydrogen chloride from epoxide resin [5]. Another simple relation of derivative thermoanalytical curves has recently been derived, which is described below.

The following equations are the prerequisites in this paper

$$C = \mathrm{f}(\alpha) \tag{1}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A \exp\left(-\frac{\Delta E}{RT}\right)\mathrm{g}(\alpha) \tag{2}$$

where α, t, A, ΔE, R and T are the fractional reacting species, the time, the pre-exponential factor, the activation energy, the gas constant and the absolute temperature, respectively. The conversion, C, is defined as follows

$$C = \frac{P_t - P_\mathrm{i}}{P_\mathrm{f} - P_\mathrm{i}} \tag{3}$$

where P_i, P_f and P_t are the properties measured in this thermoanalytical technique at beginning of the process, the end, and at the time t, respectively. Thus, the process is assumed to proceed by a single elementary reaction.

In the derivative thermoanalytical curve, $\mathrm{d}C/\mathrm{d}t$ is recorded, and

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{\mathrm{d}C}{\mathrm{d}\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{4}$$

$$= A \exp\left(-\frac{\Delta E}{RT}\right)\psi(\alpha) \tag{5}$$

where $\psi(\alpha)$ is equal to $\mathrm{g}(\alpha)\,\mathrm{d}(\mathrm{f}(\alpha))/\mathrm{d}\alpha$. Thus

$$\exp\left(\frac{\Delta E}{RT}\right)\frac{\mathrm{d}C}{\mathrm{d}t} = A\psi(\alpha) \tag{6}$$

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As previously shown in another paper [6], integral thermoanalytical curves, such as thermogravimetric curves, obtained at different linear heating rates can be superposed upon each other by lateral shift, when the curves are plotted against the reciprocal absolute temperature. At a given conversion, values of exp $(\Delta E/RT)(\mathrm{d}C/\mathrm{d}t)$ at different rates are also equal to each other, because values of $\psi(\alpha)$ are also equal to each other at a given conversion, as mentioned above. Therefore, values of exp $(\Delta E/RT)(\mathrm{d}C/\mathrm{d}t)$ can also be superposed on each other by the same lateral shift, when plotted against the reciprocal absolute temperature.

Because the activation energy can easily be estimated by plotting the logarithms of the heating rate vs. the reciprocal absolute temperature at the peak of the derivative curves [1], the above-mentioned plot can easily be performed and, confirming the superposition, we can conclude that the process proceeds by a single elementary reaction, and that eqns. (1) and (2) hold. The distance of the lateral shift for the superposition can also be used to estimate the activation energy, because the following equation holds at a given conversion

$$\log \phi + 0.4567\left(\frac{\Delta E}{RT}\right) = \text{constant} \tag{7}$$

where ϕ is a heating rate, and therefore

$$\log \phi - \log \phi_{\mathrm{s}} = 0.4567\left(\frac{\Delta E}{R}\right)\left(\frac{1}{T_{\mathrm{s}}} - \frac{1}{T}\right) \tag{8}$$

where the suffix s means the standard curve, on which the superposition of the other curves is made. When we plot the left side of eqn. (8) against the distance of the lateral shift, i.e., the difference in the reciprocal absolute temperature, we get a straight line, whose slope is $0.4567(\Delta E/R)$.

By using the activation energy and the reciprocal absolute temperature, we can calculate reduced time θ, which is a generalized time for the reaction [1,6,7], and the experimental master curve of exp $(\Delta E/RT)(\mathrm{d}C/\mathrm{d}t)$ vs. $1/T$ can easily be converted to a curve of exp $(\Delta E/RT)$ $(\mathrm{d}C/\mathrm{d}t)$ vs. the logarithms of the reduced time by using the following approximate equation

$$\log \theta = \log \Delta E - \log \phi - \log R - 2.315 - 0.4567\left(\frac{\Delta E}{RT}\right) \tag{9}$$

and

$$\exp\left(\frac{\Delta E}{RT}\right)\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{\mathrm{d}C}{\mathrm{d}\theta} \tag{10}$$

This curve can be used for prediction under various conditions other than the experimental conditions, because the actual time can be calculated from the reduced time and $\mathrm{d}C/\mathrm{d}t$ can also be calculated by using the activation energy and the temperature. Moreover, further kinetic analysis, such as elucidation of the mechanism, can be made by using the above superposed curve and by utilizing kinetic relations derived preciously [1,6,7].

This method for kinetic analysis of derivative thermoanalytical curves is preferable to the other methods hitherto proposed for kinetic analysis of the derivative thermoanalytical curves in simplicity and reliability, and the kinetic method based on superposition is effective in illustrating the process, especially when the mechanism changes along with the conversion.

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