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Note

Semi-empirical description of sigmoidal and other decomposition curves

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If it may be assumed in the case of a heterogeneous reaction that it will correspond to an Arrhenius type of kinetic temperature dependence, then the fraction of decomposition α as a function of time, t, and temperature, T, may at least be partially described by the following differential equation

$$\frac{d\alpha}{dt}=\left(\frac{d\alpha}{dt}\right)_{\alpha=\frac{1}{2}}\cdot[1-2\Delta\alpha]^n\cdot\exp\left(\frac{1}{R}\Delta\frac{E_a}{T}\right) \tag{1}$$

with $\Delta\alpha=|\alpha-\frac{1}{2}|$ (1a)

and $\Delta\frac{E_a}{T}=\left(\frac{E_a}{T}\right)_{\alpha=\frac{1}{2}}-\frac{E_a}{T}$ (1b)

In eqn (1) the descriptive exponent n is equal to the order of reaction only for $\alpha>\frac{1}{2}$. Equation (1) is especially useful in evaluating sigmoidal, thermogravimetric records of the decomposition of solid samples, in which α, $d\alpha/dt$ and T can easily be determined, and in which the decomposition rate at half-way level $(d\alpha/dt)_{\alpha=\frac{1}{2}}$ approaches the maximum value $(d\alpha/dt)_{max}$.

Provided that T and the activation energy, E_a, are constant, the temperature-dependent factor in eqn (1) can be cancelled, and evaluation of n is considerably simplified.

Under non-isothermal conditions ($dT/dt\neq 0$), the temperature-dependent factor, related to $\alpha=\frac{1}{2}$, can be calculated from $E_a=E_a(\alpha)$, $T=T(\alpha)$ and the gas constant R.

Without using a specific kinetic model, E_a can be evaluated from different thermogravimetric records read at a fixed level of completion (e.g., $\alpha=\frac{1}{2}$), assuming that E_a is at least independent of time and temperature[1].

In an Arrhenius type of temperature dependence, E_a and n should be independent not only of time but also of temperature. They are usually independent of T in the entire temperature region of interest. E_a may also be considered to be practically independent of α in certain regions of α. Using the evaluation method mentioned above this can be checked.

Sometimes it is advisible to consider two different values of E_a, one in the acceleratory period, and another in the decay period, of a decomposition curve[2]. However, this is obviously not always sufficient or even necessary[*].

It is well known that the reaction order can be constant in the decay period[**]. In these special cases, eqn (1) should be modified to

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha=\frac{1}{2}} \cdot [2-2\alpha]^n \cdot \exp\left(\frac{1}{R}\,\Delta\,\frac{E_a}{T}\right) \tag{2}$$

at least for $\alpha < \frac{1}{2}$. In general, n has to be considered as a function of α. This function $n = n(\alpha)$ can suddenly change from one α region to another, if different E_a values in these regions are accepted. If, under isothermal conditions, the decomposition curve is a symmetrical sigmoid, n will be a single-valued function of $\Delta\alpha$.

In describing sigmoidal decomposition curves according to eqn (1), n can, in certain special cases, remain constant during the whole reaction for kinematic reasons.

EXAMPLES

(i) If a reaction zone of unchanged dimensions travels from one side of a homogeneous sample to the other at constant speed under isothermal conditions, then $n = 0$.

(ii) In the case of a flat, diamond-shaped crystal, if the reaction starts in a corner and continues from one structural layer to the next at constant speed under isothermal conditions in the direction of the opposite corner, then $n = \frac{1}{2}$.

(iii) In the case of a bipyramidal-shaped crystal, if the reaction starts in one peak and continues with constant speed under isothermal conditions from one structural layer to the next until it reaches the other peak. the reaction zone being always parallel to the basic plane, then $n = \frac{2}{3}$.

Isothermal decomposition curves, corresponding to the special cases just mentioned, are shown in Fig. 1. Plotting $\mathrm{d}\alpha/\mathrm{d}t$ against $(1-2\Delta\alpha)$ from these curves on a double logarithmic scale will result in straight lines.

Normally slightly curved lines with two different values for each $\Delta\alpha$ can be expected from such double logarithmic plots of experimental data. Under isothermal conditions, n-values can be graphically determined directly from the slope of these lines.

It is more accurate to determine n numerically from

$$n = \left[\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha\neq\frac{1}{2}} - \ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha=\frac{1}{2}} - \frac{1}{R}\,\Delta\,\frac{E_a}{T}\right] \cdot [\ln(1-2\Delta\alpha)]^{-1} \tag{3}$$

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[*] E.g., if there is only one reaction zone in a solid, originally homogeneous material with relatively rapid transport of volatile reactants through the decomposed, outer phases, it can be assumed that $\mathrm{d}\alpha/\mathrm{d}t$ will be proportional to the surface of the reaction zone, which might go through a maximum. E_a will then remain fairly constant during the whole reaction.

[**] E.g., $n = \frac{2}{3}$, if the reaction zone is a congruent, contracting, 3-dimensional envelope. (For further conditions, see the former footnote.)

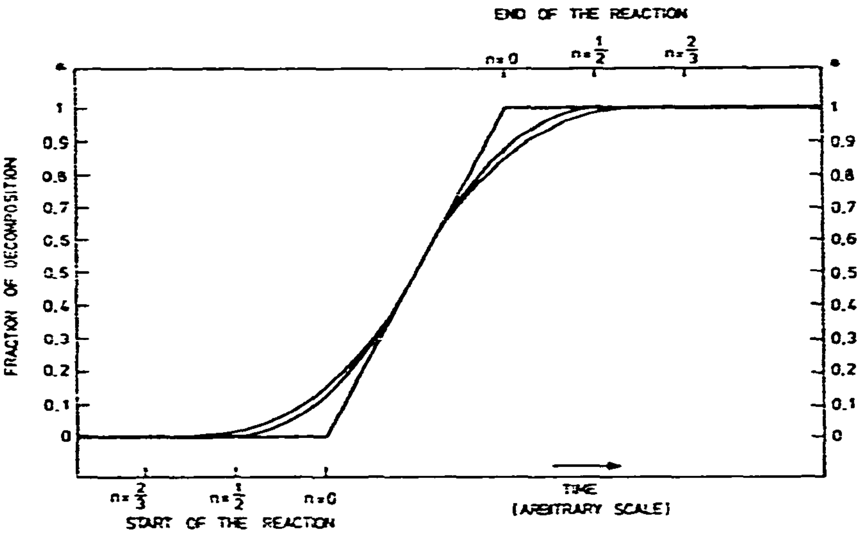

Fig. 1. Isothermal decomposition curves.

for $\alpha \neq \frac{1}{2}$. Provided E_a is the same as for $\alpha = \frac{1}{2}$, eqn (3) is simplified to

$$n = \left[\log\left(\frac{d\alpha}{dt}\right)_{\alpha\neq\frac{1}{2}} - \log\left(\frac{d\alpha}{dt}\right)_{\alpha=\frac{1}{2}}\right]\cdot[\log(1-2\Delta\alpha)]^{-1} \qquad (4)$$

under isothermal conditions. Similar explicit formulas for n can be derived from eqn (2).

A kinetic model may be chosen to fit experimental n values. This choice may be purely empirical, or may be restricted by theory, e.g., for kinematic reasons.

$n<1$ can usually be expected, unless a diffusion process is the rate-determining step in the reaction mechanism. In the latter case the reaction order is initially very high (i.e., according to eqn (2): $n \gg 1$), with a continuous decrease, e.g., to first order ($n \to 1$) for mass diffusion at the end of the reaction.

The relationship

$$\left(\frac{d\alpha}{dt}\right)_{\alpha=\frac{1}{2}} = \lim_{T\to\infty}\left(\frac{d\alpha}{dt}\right)_{\alpha=\frac{1}{2}}\cdot\exp\left(\frac{-E_a}{RT}\right)_{\alpha=\frac{1}{2}} \qquad (5)$$

is normally valid in the whole temperature region of interest. The extrapolated value $\lim_{T\to\infty}(d\alpha/dt)_{\alpha=\frac{1}{2}}$ should not be regarded strictly as a theoretical limit. It may well be that there is no actual limit for $d\alpha/dt$.

If eqn (5) is valid and E_a practically independent of α in its region of interest, it is sufficient to determine the 'constants' E_a, $\lim_{T\to\infty}(d\alpha/dt)_{\alpha=\frac{1}{2}}$, and additionally some $n = n(\alpha)$ values, according to eqns (1) or (2), in order to describe an experimental set of decomposition curves. However, an interpolated value $(d\alpha/dt)_{\alpha=\frac{1}{2},T=T_i}$ (T_i being a characteristic temperature inside the experimental region) can be determined with more precision than the extrapolated value $\lim_{T\to\infty}(d\alpha/dt)_{\alpha=\frac{1}{2}}$.

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