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Note

The rapid estimation of reaction order from thermogravimetric traces

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Numerous methods have been reported for the determination of reaction order from thermogravimetric traces. Most of these are based on the Arrhenius equation, but a few utilize only the shape characteristics of the thermogravimetric curve[1,2].

These latter methods have the advantage of enabling the user to establish the reaction order in a separate procedure which requires no prior knowledge of the intrinsic parameters such as activation energy and pre-exponential factor.

Reaction orders determined independently in this way are useful in kinetic analysis procedures which require a value for this parameter to be assumed before the activation energy and pre-exponential factor can be calculated.

In this note a very simple and rapid method is suggested for the estimation of the reaction order. This method utilizes the shape characteristics of a differential thermogravimetric curve and is derived as follows.

If a reaction can be characterised by a single activation energy (E), pre-exponential factor (A), and reaction order (n), related by the Arrhenius equation:

$$\frac{dx}{dt} = Ae^{\frac{-E}{RT}}(1-x)^n \tag{1}$$

the following expression can be derived for the conversion (x) corresponding to the maximum point of a differential thermogravimetric curve:

$$x_M = 1 - \left(\frac{a}{A}\cdot\frac{E}{RT_M^2}\cdot e^{\frac{E}{RT_M}}\cdot\frac{1}{n}\right)^{1/(n-1)} \tag{2}$$

where a is the constant heating rate, dT/dt, and the subscript M indicates values corresponding to the maximum point.

Kissinger[1] has pointed out that the product

$$\frac{a}{A}\cdot\frac{E}{RT_M^2}\cdot e^{\frac{E}{RT_M}}$$

is usually very near to unity. If this is so, it follows from eqn. (2) that x_M is primarily a function of the reaction order. Flynn and Wall[3] have suggested the following approximation, which expresses this deduction in the form of an equation:

$$x_M \approx 1 - n^{1/(1-n)} \tag{3}$$

However, it can be shown that x_M increases gradually with increasing activation energy and decreasing a/A ratio. We have calculated values of x_M for reaction orders in the range 0.1 to 3, with values of a/A ranging from 10^{-8} to 10^{-20} K, and of E ranging from 10 to 100 kcal/mole, thus covering the usual range of values of the kinetic constants.

The calculations, which were carried out with the aid of a computer, were based upon the maximum conditions of eqn. (1) and on the following relationship:

$$\int_0^{x_M} \frac{dx}{(1-x)^n} = \frac{A}{a}\int_0^{T_M} e^{\frac{-E}{RT}} \cdot dT \tag{4}$$

Curves A and B in Fig. 1 show the relationship between x_M and n for the extreme values $E = 10$ kcal/mole; $a/A = 10^{-8}$ K and $E = 100$ kcal/mole; $a/A = 10^{-20}$ K, respectively.

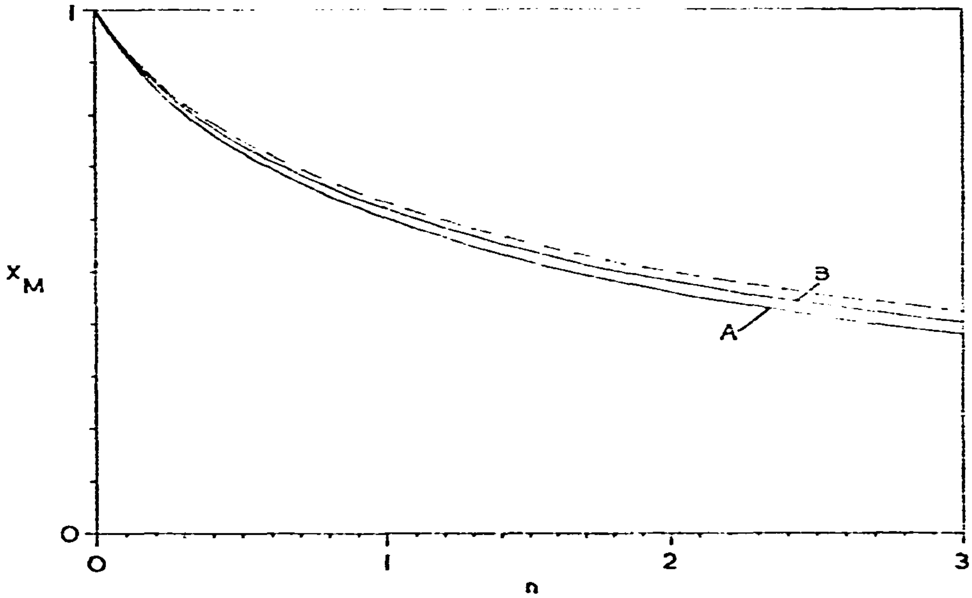

Fig. 1. The determination of reaction order from the conversion at the maximum decomposition rate. n, reaction order; x_M, conversion at the maximum decomposition rate. Curve A: E, 10 kcal/mole; a/A, 10^{-8} K. Curve B: E, 100 kcal/mole; a/A, 10^{-20} K. Broken line: curve calculated on the basis of eqn. (3).

The reaction order can be estimated from Fig. 1 by laying a straight line parallel to the abscissa at the altitude of x_M. The intersection of this line with curves A and B defines a reaction order range whose width is approximately 10% of the corresponding order values. If the order is taken as the central value of this range, the maximum error of the determination becomes approximately ±5%, provided that a/A and E lie between the specified limits—a condition which is fulfilled in most practical cases. The error increases only moderately if either or both of the above parameters are outside the specified limits.

The curve expressed by eqn. (3), also shown in Fig. 1, corresponds to very high values of the activation energy and/or pre-exponential factor. If the actual kinetic parameters lie in the middle of the specified range, and eqn. (3) is used for the determination of order, the error will reach approximately 12–15%. The curve representing the mean of curves A and B, which gives the more accurate estimation of reaction order, can be represented in the form of eqn (3) by the following approximation:

$$x_M \simeq 1 - 1.062 \cdot n^{1/(1-n)} \tag{5}$$

1 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
2 L. Reich and D. W. Levi, *J. Polym. Sci.*, 2B (1964) 1109.
3 J. H. Flynn and L. A. Wall, *J. Res. Nat. Bur. Stand.*, 70A (1966) 487.

Notice

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As a result of a recent election of its members, the officers for 1973 are as follows:

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