Journal of Thermal Analysis, Vol. 23 (1982) 235—237

CAN A RATE CONSTANT INDEPENDENT OF SAMPLE SIZE BE OBTAINED FROM THE RATE EQUATION GENERALLY USED IN THERMAL ANALYSIS?

GY. POKOL

Institute for General and Analytical Chemistry,
Technical University, Budapest, 1521 Hungary

(Received September 25, 1981)

Some consequences of using the rate equation $d\alpha/dt = k_t f(\alpha)$ are shown on a simple example. It is demonstrated that k_t usually depends on the sample size, and that it is usually incorrect to assume that if mass and heat transport effects are avoided both α and $d\alpha/dt$ — as functions of time — are independent of the initial mass. Rate equations should be based on real local quantities.

Criado recently published remarks [1] on the application of Chatterjee's method [2] for the kinetic analysis of TG data. The discussion is based on the comparison of two rate equations: the one used by Chatterjee

$$-\frac{dW}{dt} = k \cdot W^n \tag{1}$$

(where W is the active weight of the material at time t, and n and k are the order of reaction and the rate constant, respectively), and the formula most commonly used in thermal analysis:

$$\frac{d\alpha}{dt} = k_t \cdot (1 - \alpha)^n \tag{2}$$

Equation (2), said to be valid for the "thermal decompositions of solids following n-order kinetics", contains the reacted fraction α and k_t, "the 'true' rate constant of the reaction", assumed to be independent of sample mass.

After a correct mathematical treatment, Criado reaches the conclusion that k of Eq. (1) depends on the initial mass and that Chatterjee's procedure to determine the n value (based on TG curves of samples of different initial mass) cannot be used at all. The same conclusions were drawn by Székely [3] several years ago.

The conclusions — in the form written above — are correct. However, it is necessary to discuss the assumption that, for decompositions of solids, k_t in Eq. 2 or in the more general form

$$\frac{d\alpha}{dt} = k_t \cdot f(\alpha) \tag{3}$$

is independent of the initial mass. Of course, this assumption, which can be encountered in practically any kinetic study in the field of thermal analysis, should not be attributed to Criado, whose activity in the clarification of problems of kinetics is rated highly by the present author.

As a simple example, let us consider an irreversible solid – gas decomposition where the time derivative of the reactant mass (m) divided by the area of the reacting surface (A) depends on the temperature only (mass and heat transport do not affect the rate of the process):

$$-\frac{1}{A}\cdot\frac{\mathrm{d}m}{\mathrm{d}t}=k'_{\mathrm{T}} \tag{4}$$

If this is applied to the isothermal reaction of a compact spherical sample of initial radius R, the rate of mass change will be

$$-\frac{\mathrm{d}m}{\mathrm{d}t}=k'_{\mathrm{T}}\cdot 4\,r^2\,\pi \tag{5}$$

where r represents the radius at time t. Taking into account

$$1-\alpha=\frac{m}{M}=\frac{r^3}{R^3} \tag{6}$$

M being the initial mass), we can write

$$-\frac{\mathrm{d}m}{\mathrm{d}t}=k'_{\mathrm{T}}\cdot 4\cdot[(1-\alpha)\cdot R^3]^{2/3}\cdot\pi \tag{7}$$

Expressing M in terms of the initial radius and the density (ϱ) yields

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=-\frac{1}{M}\cdot\frac{\mathrm{d}m}{\mathrm{d}t}=\frac{3\,k'_{\mathrm{T}}}{\varrho R}\cdot(1-\alpha)^{2/3} \tag{8}$$

If this equation is compared to Eq. (2) containing an n value of 2/3, we get

$$k_{\mathrm{t}}=\frac{3\,k'_{\mathrm{T}}}{\varrho R} \tag{9}$$

showing that the rate constant of Eq. (2) depends on the initial size. Had the contrary been true, the time required for total decomposition of spheres of any size should have been identical in this example – which is physical nonsense.

As a consequence, the other common assumption does not hold either, that "provided that mass and heat transfer effects have been avoided, both α and ($\mathrm{d}\alpha/\mathrm{d}t$) are quite independent of W_{i}", the initial weight [1].

Generally speaking, as previously discussed in detail [4, 5], in heterogeneous reactions occurring on a moving phase boundary or in a narrow reacting zone, the fraction reacted is an average value for the whole sample, not a local (intensive) quantity, and Eq. (2) should be used for kinetic analysis of these reactions only if

(a) the initial mass, the particle size distribution and the geometry of the samples are identical, or

(b) the particle size (distribution) is identical and the process advances uniformly in each particle, or

(c) the particle size (distribution) is identical and the rate is governed by nucleation only (first-order kinetics).

Even in these cases, k_t will be characteristic of the sample size.

In order to overcome the difficulties arising from the application of Eq. (3), we suggested a new mode of description for the rate of heterogeneous processes [4, 5], based on real local quantities. (The treatment of the example presented above can in fact be regarded as a simple application of that description, without mentioning general quantities.) A detailed discussion of the suggested new forms of the rate equation can be found in [5].

References

1. J. M. Criado, J. Thermal Anal., 20 (1981) 487.
2. P. K. Chatterjee, J. Polymer Sci. A, 3 (1965) 4253.
3. T. Székely: The application of thermogravimetric methods in the kinetic description of thermal decomposition reactions of polymers, in "A kémia újabb eredményei" (Recent results of chemistry); vol. 12, ed.: B. Csákvári, Akadémiai Kiadó, Budapest 1973, p. 148 (in Hungarian).
4. Gy. Pokol, S. Gál, J. Sztatisz, L. Domokos and E. Pungor, in Reactivity of Solids, Proc. 8th ISRS, Göteborg 1976, ed.: J. Wood, O. Lindqvist, C. Helgesson, N. G. Vannerberg, Plenum Press, New York 1977, p. 209.
5. Gy. Pokol, S. Gál and E. Pungor, Thermochim. Acta 33 (1979) 259.