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Note

ON THE USE OF THE DEGREE OF CONVERSION IN THE RATE EQUATIONS. II

D. FĂTU and E. SEGAL

Department of Physical Chemistry and Electrochemical Technology, Polytechnic Institute of Bucharest, Bd. Republicii 13, Bucharest (Romania)

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In a previous note [1] we discussed the advantages as well as the disadvantages of using the degree of conversion in the rate equations of heterogeneous reactions. A relatively recent comment of our statements reveals a certain misunderstanding [2]. We have pointed out that for the decomposition of a crystalline granule whose kinetics is described by a rate equation corresponding to the contracting sphere model

$$\frac{d\alpha}{dt} = k_\alpha (1-\alpha)^{2/3} \tag{1}$$

the rate constant is given by

$$k_\alpha = \frac{3k_i}{r_0} \tag{2}$$

where k_i is the constant decrease rate of the radius of the spherical interface between the solid reactant and product, whose initial value is r_0. Relationship (2) shows an obvious dependence of k_α on the initial radius and hence on the initial weight of the granule. For this reason we consider that the values $k_{\alpha 1}$ and $k_{\alpha 2}$ measured at the temperatures T_1 and T_2 cannot be used to evaluate the activation energy unless samples with the same initial radii or weights are used. To justify this statement let us suppose that the Arrhenius equation is valid for k_α, i.e.,

$$k_\alpha = A_\alpha e^{-E/RT} \tag{3}$$

From two isothermal measurements at temperatures T_1 and T_2, the apparent activation energy is given by the known relationship which can be derived from eqn. (3),

$$E_a = \frac{R \ln(k_{\alpha 2}/k_{\alpha 1})}{(1/T_1) + (1/T_2)} \quad T_2 > T_1 \tag{4}$$

Let us suppose that at the temperatures T_1 and T_2, the intial radii and weights of the samples are $r_{0,1}$, $w_{0,1}$, $r_{0,2}$ and $w_{0,2}$. Apparently due to the dimensionless character of the variable α the values of the kinetic parameters are not sensitive to the differences in the initial radii and weights. To demonstrate the erroneous nature of such a statement let us reconsider relationship (2) where k_α depends on temperature through the dependence of k_i on temperature which is given by,

$$k_i = A_i e^{-E/RT} \tag{5}$$

Taking into account the meaning of k_i, it follows that E is the true activation energy. From relationships (2) and (5) one obtains

$$\ln k_{\alpha 1} = \ln 3A - \ln r_{0,1} = \frac{E}{RT_1}$$

$$\ln k_{\alpha 2} = \ln 3A - \ln r_{0,2} = \frac{E}{RT_2}$$

The solution of this system with respect to E, is

$$E = \frac{R[\ln(k_{\alpha 2}/k_{\alpha 1}) - \ln(r_{0,1}/r_{0,2})]}{(1/T_1) - (1/T_2)} \tag{6}$$

Relationship (6) shows that for only $\mathrm{r}_{0,1} = \mathrm{r}_{0,2}$ does the apparent activation energy equal the true one ($E_\alpha = E$).

Let us now express the reaction rate as a function of weight, w_A of the undecomposed core of the contracting sphere

$$w_\mathrm{A} = \frac{4\pi r^3}{3}\rho \tag{7}$$

By taking the derivative with respect to time one obtains:

$$\frac{\mathrm{d}w_\mathrm{A}}{\mathrm{d}t} = 4\pi\rho r^2 \frac{\mathrm{d}r}{\mathrm{d}t} \tag{8}$$

As

$$r = r_0 + k_i t, \tag{9}$$

or

$$\frac{\mathrm{d}r}{\mathrm{d}t} = -k_i \tag{10}$$

by expressing, r from eqn. (7),

$$r = \left(\frac{3w_\mathrm{A}}{4\pi\rho}\right)^{1/3} \tag{11}$$

and introducing eqns. (10) and (11) in eqn. (8) results in

$$-\frac{\mathrm{d}w_\mathrm{A}}{\mathrm{d}t} = k_w w_\mathrm{A}^{2/3} \tag{12}$$

where

$$k_w = (36\pi\rho)^{1/3} k_i \tag{13}$$

Thus k_w does not depend on the initial radius of the granule if the kinetic variable is the weight of the unreacted core.

All these statements should not be considered as a reason for the replacement of the degree of conversion with the extensive variable, w. Like many other researchers we use the degree of conversion as a kinetic variable in our experimental and theoretical work. We want only to point out the necessity of constant sizes and even weights of the sample for the study of (k_α, T) dependence. Moreover, the history of the samples i.e., their previous treatment should be the same.

Relationship (1) can be writen in a universal form by introducing the dimensionless reduced time τ according to the relationship:

$$\tau = \frac{t}{t_\mathrm{f}} \quad 0 \leq \tau \leq 1 \tag{14}$$

where t_f, is the time necessary for the interface between the reactant and product to reach the center of the "spherical" granule, or the time necessary for completion of the reaction.

Taking into account that in eqn. (9) for $t = t_\mathrm{f}$, $r = 0$, one obtains:

$$t_\mathrm{f} = \frac{r_0}{k_i} \tag{15}$$

and eqn. (14) becomes:

$$\tau = t\frac{k_i}{r_0} \tag{16}$$

By introducing this new variable in the expression of the reaction rate it results that:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}\tau} \cdot \frac{\mathrm{d}\tau}{\mathrm{t}d} \tag{17}$$

or taking into account relationship (16)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{d}\alpha}{\mathrm{d}\tau}\frac{k_i}{r_0} \tag{18}$$

By comparing this result with eqn. (1) where k_α is given by eqn. (2) it results that:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\tau} = 3(1-\alpha)^{2/3} \tag{19}$$

or in the integrated form:

$$1 - (1-\alpha)^{1/3} = \tau \tag{20}$$

The dimensionless kinetic equations are independent on the radius of the granule and on the material constants. The reduced reaction rate $\mathrm{d}\alpha/\mathrm{d}\tau$ is independent of temperature. Thus, the reduced kinetic equations allow an elegant checking of the reaction mechanism but cannot be used to determine the activation energy.

If the plot $[1-(1-\alpha)^{1/3}, \tau]$ gives a straight line independent of the granule radius or the constant temperature at which the isothermal measurement is carried out, one can conclude that the reaction is described by a contracting sphere mechanism.

Thus, taking into account the results obtained for this particular mechanism, one can state that any of the variables w, α or r (the radius of the unreacted core) associated with t or τ can be used in heterogeneous kinetics. The use of the extensive variable w and of the time leads to a rate constant which depends on k_i and ρ (material constants). When using α and t, k_α depends on k_i and r. The use of α and τ leads to a rate constant $k_\tau = 3$ which does not depend on material constants.

As far as the criticism of Chaterjee's method [3] is concerned, this should not be done starting from the statement according to which the constant k_w depends on the sample weight [4] as this statement cannot be supported by relationships from formal kinetics. The factors which influence a kinetic constant can be established only if the mechanism is known and carefully taken into account.

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