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Note

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

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In terms of the degree of conversion the rate equations are to a certain extent advantageous, due to the dimensionless character of α $(0 \leqslant \alpha \leqslant 1)$. Nevertheless, to avoid misunderstandings, the degree of conversion should be used carefully. As an example an n order reaction is considered whose rate equation in terms of α is

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

where k_α is the rate constant. Integration of eqn. (1) gives

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = k_\alpha t \tag{2}$$

For $t = \tau_{1/2}$ (where $\tau_{1/2}$ is the half time) $\alpha = 1/2$ and eqn. (2) leads to

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

At first glance, according to eqn. (3) the half time does not depend on the initial concentration of the reactant. To show the relationship between the half time and the initial concentration of the reactant eqns. (1)–(3) must be written in terms of concentration, c, as

$$-\frac{dc}{dt} = k_c c^n \tag{4}$$

$$\frac{c_0^{1-n} - c^{1-n}}{1-n} = k_c t \tag{5}$$

$$\tau_{1/2} = \frac{1-2^{n-1}}{k_c c_0^{n-1}(1-n)} \tag{6}$$

where k_c is the rate constant in terms of concentration and the subscript 0 denotes the initial value. From a comparison of eqns. (3) and (6)

$$k_\alpha = k_c c_0^{n-1} \tag{7}$$

This result shows that in relationship (3) the half time depends on the initial concentration through k_α. Thus, the use of α in homogeneous kinetics could lead to erroneous results if relationship (7) is not taken into account. Equation (1) cannot be used to determine the reaction order using the initial rates method [1] unless k_α given by eqn. (7) is considered. Indeed, for the initial moment, as $\alpha_0 = 0$, from (1) and (7)

$$\log\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_0 = \log k_c + (n-1)\log c^0 \tag{8}$$

Equation (8) for two different initial concentrations c_1^0 and c_2^0 leads to

$$n = 1 + \frac{\log\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_1^0 - \log\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_2^0}{\log c_1^0 - c_2^0} \tag{9}$$

Relationship (9) is equivalent to

$$n = \frac{\log\left(-\frac{\mathrm{d}c}{\mathrm{d}t}\right)_1^0 - \log\left(\frac{\mathrm{d}c}{\mathrm{d}t}\right)_2^0}{\log c_1^0 - \log c_2^0} \tag{10}$$

which can be derived from (4).

The above relationships are also used in heterogeneous kinetics to describe thermal decompositions of solids as

$$\mathrm{A(s)} \rightarrow \mathrm{B(s)} + \mathrm{C(g)} \tag{11}$$

under isothermal and nonisothermal conditions. These reactions are frequently followed by measuring the weights of the volatile component evolved (or of the solid residue) at various moments. In such conditions the rate equation and reaction order take, respectively, the forms

$$-\frac{\mathrm{d}w}{\mathrm{d}t} = k_w w^n \tag{12}$$

$$n = \frac{\log\left(-\frac{\mathrm{d}w}{\mathrm{d}t}\right)_1 - \log\left(-\frac{\mathrm{d}w}{\mathrm{d}t}\right)_2}{\log w_1 - \log w_2} \tag{13}$$

where w is the residual weight of the volatile component at moment t. Relationship (13) was used by Chaterjee [2] to evaluate the reaction order from two thermogravimetric curves recorded for two samples with different weights at the same temperature.

In a recent paper Criado [3] states that relationship (13) is not correct as k_w depends on the system's weight and cannot be eliminated using samples with different weights. He recommends the use of relationship (1) which is more correct as k_α is independent of sample weight. As far as we are concerned, we consider relationships (1) and (2) as equivalent as one can pass from one to the other by means of a change of variable. The previous considerations concerning the homogeneous kinetics show that, contrary to Criado's statement, k_c is independent of the initial concentration and k_α depends on it. The same conclusion can be drawn from the analysis of a heterogeneous decomposition reaction such as (11). Taking into account the contracting sphere model [4,5]

$$\frac{d\alpha}{dt} = k_\alpha(1-\alpha)^{2/3} \tag{14}$$

with

$$k_\alpha = \frac{3k_i}{r_0} \tag{15}$$

where k_i is the constant decrease rate of the spherical interface radius between the solid reactant A and the solid product B, and γ_0 is the initial radius of the sphere. Relationship (15) can be easily put under its equivalent form

$$k_\alpha = (36\pi\rho)^{1/3} k_i w_0^{-1/3} \tag{16}$$

where ρ is the density of the parent compound A. Relationship (16) shows that k_α depends on the initial weight of the sample w_0. On the other hand

$$w_A = \frac{4\pi r^3}{3}\rho \tag{17}$$

By differentiation

$$\frac{dw_A}{dt} = (36\pi\rho)^{1/3} k_i w_A^{2/3} \tag{18}$$

where

$$k_w = (36\pi\rho)^{1/3} k_i \tag{19}$$

i.e. k_w does not depend on the initial weight. From (16) and (19)

$$k_\alpha = k_w w_0^{-1/3} \tag{20}$$

Formally this result can be obtained from (7), for $c_0 = w_0$ and $n = 2/3$.

CONCLUSIONS

(a) For a kinetic control of the reaction, the rate constants k_c and k_w are independent of the initial values of concentration or weight.

(b) The kinetic constant k_α depends on the initial concentration or weight for $n \neq 1$.

(c) The k_α values for different temperatures should not be used to evaluate the activation energy unless samples with the same weight are considered.

(d) Using only relationships (7) or (20) one cannot establish which of the rate constants k_c, k_α, k_w is dependent on the initial weight or concentration. In order to do that, the particular kinetic equations describing the system must be taken into account.

(e) Taking into account the above statements, Criado's criticism concerning Chaterjee's method for evaluating the reaction order appears to be inconsistent.

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