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Note

The kinetic equation under linear temperature increase conditions

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Descriptions of the kinetics of chemical reactions are very often based on the use of the same form of equation with no regard to whether or not the reaction is investigated under isothermal conditions. There is no agreement as to whether dealing with the subject in this way would be correct[1] or not[2]. In many cases this problem is not particularly discussed, for the opinion is held that the possible errors resulting from this procedure are not very significant in comparison with those arising during experimental work.

In the case where the progress of a certain chemical reaction merely depends on time and temperature,

$$x = x(T, t) \tag{1}$$

and thus

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \left(\frac{\partial x}{\partial t}\right)_T + \left(\frac{\partial x}{\partial T}\right)_t \left(\frac{\partial T}{\partial t}\right)_x \tag{2}$$

where x is the ratio of the amount of reacted substrate to initial amount of substrate, T is the absolute temperature and t stands for time. According to eqn. (1), a given value $x = \mathrm{b}$ may be achieved in two different ways, either as a result of the isothermal course of the reaction, or during a non-isothermal reaction run. There is only one value $x = \mathrm{b}$ for each point $P(T_\mathrm{b}, t_\mathrm{b})$.

The differential equation describing the kinetics of a given chemical reaction under isothermal conditions is often presented in the form

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \mathrm{f}(x) \cdot \mathrm{g}(T) \tag{3}$$

where

$$\mathrm{f}(x) = (1 - x)^n, \text{ or } \mathrm{f}(x) = x^n, \text{ etc.} \tag{4}$$

$\mathrm{g}(T)$ is usually given in the form of the Arrhenius equation

$$g(T) = \mathrm{A}\exp\left(-\frac{E}{RT}\right) \tag{5}$$

where n is the constant (order of reaction), A is the pre-exponential constant, E is the activation energy and R the gas constant.

Integrating eqn. (3) on both sides for isothermal conditions, one obtains

$$\int_0^x \frac{\mathrm{d}x}{\mathrm{f}(x)} = g(T)\int_0^t \mathrm{d}t \tag{6}$$

The introduction of the designation

$$\mathrm{F}(x) = \int_0^x \frac{\mathrm{d}x}{\mathrm{f}(x)} \tag{7}$$

results in an equation analogous to eqn. (1), namely,

$$x = \mathrm{h}[g(T)\cdot t] \tag{8}$$

where $\mathrm{h}(x)$ is the anti-function to $\mathrm{F}(x)$. Differentiation of eqn. (8) with respect to T gives

$$\left(\frac{\partial x}{\partial T}\right) = h'[g(T)\cdot t]\cdot t\cdot g'(T) \tag{9}$$

As, for continuous and monotonous functions, relation (10) applies,

$$\mathrm{F}'(x) = \frac{1}{\mathrm{h}'(x)} \tag{10}$$

the following expression can be written, when eqn. (7) is considered:

$$\left(\frac{\partial x}{\partial T}\right)_t = \mathrm{f}(x)\cdot t\cdot g'(T) \tag{11}$$

Substituting eqns. (11) and (3) into eqn. (2), one obtains

$$\frac{\mathrm{d}x}{\mathrm{d}t} = [g(T) + a\cdot t\cdot g'(T)]\cdot \mathrm{f}(x) \tag{12}$$

where a is the heating rate.

For the Arrhenius equation (5), eqn. (12) has the form

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \mathrm{A}\left[1 + \frac{atE}{RT^2}\right]\exp(-E/RT)\cdot \mathrm{f}(x) \tag{13}$$

Because

$$T = at + T_0 \tag{14}$$

where T_0 the initial temperature, we have

$$\frac{dx}{dt} = A \exp(-E/RT)\left[1 + \frac{E}{RT}\left(1 - \frac{T_0}{T}\right)\right] f(x) \tag{15}$$

Comparing eqns. (3) and (15), it must be stated that a given chemical reaction will appear to proceed faster, under conditions of linear temperature increase, than predicted if eqn. (3) is used for non-isothermal reactions. Depending on the method of elaboration of the experimental data, the resulting error may influence the value of kinetic equation constants evaluated from experimental data in various ways. These constants include the activation energy E, the order of reaction n, and the pre-exponential constant A. This however, presents a separate problem.

REFERENCES

1 E. L. Simmons and W. W. Wendlandt, *Thermochim Acta*, 3 (1972) 498.
2 J. P. MacCallum and J. Tanner, *Nature*, 225 (1970) 1127.