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Note

The role of constitutive equations in chemical kinetics

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Recent articles on the non-isothermal rate equation[1–3] have initiated a rather extensive discussion[4–13]. Misunderstanding arose mainly about the meaning of the partial derivatives of the function f in the equation for the fractional conversion α, (a kinetic variable conventionally normalized $\alpha = 0$ at $t = 0$ and $\alpha = 1$ at $t \to \infty$):

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

$$d\alpha = \left(\frac{\partial f}{\partial T}\right)_t dt + \left(\frac{\partial f}{\partial t}\right)_T dT \tag{2}$$

where T and t represent temperature and time, respectively. Some authors claimed that only the partial derivative $(\partial f/\partial t)_T$ can be used so that the function f is appropriate for the description of an isothermally measured rate of a chemical reaction[1–3], while others proposed that it may describe non-isothermal kinetics as well if either the partial derivative $(\partial f/\partial T)_t$[4] or the total differential $d\alpha$[5] are equal to zero. Another suggestion[6] related this problem to the non-uniform temperature within a solid sample. Although some useful criticism on these incorrect ideas was already given[7–13] and the path function character of f in eqn (1) emphasized[8,9] there still remain certain confusions. Therefore we would like to clarify this question from a more unifying viewpoint.

We will mention two different ways in which the relation (1) may be understood:

(A) If eqn (1) represents an equation of state (called "the constitutive equation") of a chemical system under consideration then eqn (1) implies that the value α at t depends on the time t, and the instantaneous value of the temperature T at t regardless of its previous temperature history. The constitutive equation of type (1) would describe the behaviour of a system controlled by an independent "internal clock". Such an equation is *e.g.* the constitutive equation for the pressure p of a gas which is evolved by a radioactive decay. The number of molecules produced is controlled by the radioactive mechanism and is not affected by the temperature. The pressure p is expressed by a function P of the number of molecules, i.e. a function of time t, and the temperature T at t only, $p = P(T, t)$.

It seems that ordinary chemical systems treated so far by the standard methods of chemical kinetics[14] do not represent the case of systems with an "internal clock". The controversy concerning the total differential $d\alpha$ and the partial derivatives $(\partial f/\partial T)_t$ and/or $(\partial f/\partial t)_T$ which appears in some preceding papers[1-5] is a consequence of the application of the described non-adequate interpretation of eqn (1) for ordinary chemical systems.

(B) We are convinced that the constitutive equation for the fractional conversion α determined in a chemical system is

$$\dot{\alpha} = F(\alpha, T) \tag{3}$$

or in a more general form

$$\dot{\alpha} = G(\alpha, T, \dot{T}, \ddot{T}, \ldots) \tag{4}$$

Equations of the eqn (3) type are well established in isothermal kinetics[7,11,14]. Equation (4) which has the form known for non-equilibrium situations could be more appropriate in the case of highly non-isothermal kinetics.

Based on eqn (3) or (4) eqn (1) may be interpreted as follows. For the initial conditions ($\alpha = 0$ and $T = T_0$ at $t = 0$) and a specified temperature regime, $T = \Phi(t)$, we denote the solution of eqn (3) or (4) as

$$\alpha = \alpha_\Phi(t). \tag{5}$$

Note that the subscript Φ indicates that the solution depends on the temperature regime $\Phi(t)$, i.e. α is path dependent. In mathematical terms it means that α is a functional of Φ.

For some special instances of "temperature" kinetics solution (5) can be converted into the form (1). We illustrate this for a simple case of the "linear" non-isothermal kinetics, where

$$T = \Phi(t) = \phi t + T_0 \tag{6}$$

and where ϕ is the constant temperature rate. When substituting eqn (6) into eqn (3) we obtain $\dot{\alpha} = F(\alpha, \phi t + T_0)$ or similarly from eqn (4) $\dot{\alpha} = G(\alpha, \phi t + T_0, \phi, 0, \ldots)$. The solution (5) can then be written in the form $\alpha = g_0(\phi, T_0, t)$. It means that the functional dependence (5) is reduced to the function dependence of α on two parameters ϕ and T_0 which specify the temperature regime Φ. If we compare the evolution of the fractional conversion α for multiple runs accomplished at different ϕ holding the initial temperature T_0 fixed, we can write

$$\alpha = g_0(\phi, T_0, t) \equiv g(\phi, t) = g((T - T_0)/t, t) \equiv f_0(T, T_0, t) = f(T, t) \tag{7}$$

If we understand eqn (1) in the described sense, which is illustrated by eqn (7), then the interpretation of the total differential $d\alpha$ and the partial derivatives, namely $(\partial f/\partial T)_t$, represents no principal difficulty. For a specified class of temperature regimes eqn (6) the eqn (7) can be properly represented as a surface in a three-dimensional diagram α–t–ϕ. Then it is easy to realize that within this specified class of temperature regimes Φ the isochronal derivative $(\partial g/\partial \phi)_t$ indicates the change of α measured at the same time t between two infinitesimally close regimes differing by $\mathrm{d}\phi$, i.e. between two parallel α–t curves which are the sections of the surface taken at ϕ and $\phi+\mathrm{d}\phi$. Similarly we can interpret the derivative $(\partial f/\partial T)_t$ using the α–t–T diagram. A more comprehensive discussion of the meaning of the partial derivatives was dealt with in our previous paper[13].

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