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RELATIONSHIP BETWEEN THE KINETICS OF TRANSFORMATIONS WITH LINEAR TEMPERATURE PROGRAMMING AND THE KINETICS OF TRANSFORMATIONS WITH EXPONENTIAL AND HYPERBOLIC TEMPERATURE PROGRAMMING

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An analytical relationship between the kinetics of non-isothermal transformations with linear, exponential and hyperbolic temperature programming is demonstrated.

A transformation process under non-isothermal conditions is in fact controlled by the transfer of heat to or from the reacting system, or by the correspondingly regulated heating or cooling rate. Under such circumstances it may be assumed that the conversion α is some function of time and of the reaction-controlling action, namely the heating or cooling rate:

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

where $q = \frac{\mathrm{d}T}{\mathrm{d}t}$. The full derivative of this function is

$$\mathrm{d}\alpha = \left(\frac{\partial\alpha}{\partial t}\right)_q \mathrm{d}t + \left(\frac{\partial\alpha}{\partial q}\right)_t dq \tag{2}$$

or

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial\alpha}{\partial t}\right)_q + \left(\frac{\partial\alpha}{\partial q}\right)_t \frac{\mathrm{d}q}{\mathrm{d}t} \tag{3}$$

Let us use the symbol β for $\left(\frac{\partial\alpha}{\partial q}\right)_t$, which presumably reflects certain properties of the reacting system, namely its sensitivity towards the controlling factor q. Equation (3) can then be written in the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \left(\frac{\partial\alpha}{\partial t}\right)_q + \beta\frac{\mathrm{d}q}{\mathrm{d}t} \tag{4}$$

Equation (4) will be the basic equation for investigation of the essence of the interrelation between the different variants of non-isothermal kinetics.

Let us consider three well-known types of temperature programming:

(i) Linear programming: $T = T_0 + at$; $q = a$; $\frac{\mathrm{d}q}{\mathrm{d}t} = 0$.

(ii) Exponential programming: $T = T_0 \exp bt$; $q = bt$; $\dfrac{dq}{dt} = b$.

(iii) Hyperbolic programming: $\dfrac{1}{T} = \dfrac{1}{T_0} - ct$; $q = cT^2$; $\dfrac{dq}{dt} = cT$.

For these three types of temperature programming the basic equation (4) will yield:

$$\frac{d\alpha}{dt} = \left(\frac{\partial\alpha}{\partial t}\right)_q \tag{5}$$

$$\frac{d\alpha}{dt} = \left(\frac{\partial\alpha}{\partial t}\right)_q + \beta b \tag{6}$$

$$\frac{d\alpha}{dt} = \left(\frac{\partial\alpha}{\partial t}\right)_q + \beta cT. \tag{7}$$

Equations (5), (6) and (7) demonstrate that the kinetics of the non-isothermal transformation with exponential and hyperbolic temperature programming are not identical with the kinetics with linear temperature programming.

Next, one should consider the relationship of isothermal and non-isothermal kinetics from the view of McCallum and Tanner's concept [1], which continues to be of interest [2–4]. We have expressed our opinion regarding this concept in an earlier paper [5]. By the mathematical analysis of the implicit function $\psi(\alpha, T, t) = 0$, it could be demonstrated that (at least for irreversible chemical transformations) the kinetic characteristics (activation energy E and pre-exponential factor A_0 in the Arrhenius equation) with linear temperature programming are identical with the kinetic parameters determined from isothermal experiments. A similar statement cannot, however, be made for reversible non-isothermal transformations, since the kinetic parameters of such processes may depend on variations in the rate of temperature increase, and further the compensation effect is observed as a rule. The data cited in [6] serve as a clear illustration of this phenomenon. It is obvious that in the general aspect, isothermal kinetics can be treated as a particular, extreme case of non-isothermal kinetics under the condition $\dfrac{dT}{dt} \rightarrow 0$. If one considers that each chemical act is being accompanied by some sort of thermal effect, the non-isothermal state in the reaction zone proper is an unconditional property of the system. In addition, from the view of the general theory of systems, the non-isothermal transformation possesses priority as compared to the simpler isothermal process. As a consequence, the notion "isothermal kinetics" may be considered as some model concept that to a larger degree corresponds to the gaseous state of matter, and to a lesser degree to the condensed state.

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