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SOME PROBLEMS CONCERNING THE MATHEMATICAL THEORY OF NON-ISOTHERMAL KINETICS. II. PRIMARY ISOTHERMAL DIFFERENTIAL KINETIC EQUATIONS (PIDKEs)

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ABSTRACT

Following earlier work, this paper deals with some new aspects concerning the mathematical theory of non-isothermal kinetics. After a short introduction which emphasizes that in non-isothermal kinetics the temperature T and time t are dependent variables, one of the main problems of non-isothermal kinetics, which involves the derivation of adequate non-isothermal differential kinetic equations, is discussed. The derivation of such equations from isothermal differential kinetic equations using the "classical" transformation (change), i.e. expressing T as a function of t or vice versa is shown to be equivalent to the postulation of some "primary isothermal differential kinetic equations" (PIDKEs). After a discussion concerning the model of infinitesimal isothermal portions (MIIP) in connection with PIDKEs, a non-isothermal kinetic treatment of the nucleation and nuclei growth is suggested. A short discussion of the non-isothermal integration of the Johanson–Mehl–Avrami–Yerofeyev–Kolmogorov (JMAYK) equation completes the paper.

INTRODUCTION

Non-isothermal investigations of physical and chemical systems are done by monitoring the continuous change in temperature with time [1–7]. In this paper, only systems with a uniform space distribution of temperature, i.e. without heat transfer will be considered.

Generally, in non-isothermal conditions, the temperature T and time t are related through an implicit functional relationship of the form

$$\psi(t, T) = 0 \tag{1}$$

which tells us that T and t are dependent variables [1]. From the relationship (1) one can obtain in principle the following two relationships:

$$T = \theta(t) \tag{2}$$

$$t = \varphi(T) \tag{3}$$

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The derivative of the temperature with respect to time is called the heating rate and is given by

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \theta'(t) = \beta_1(t) \tag{4}$$

or by

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{1}{\varphi'(T)} = \beta_2(T) \tag{5}$$

The most usual case is that with a constant value of the heating rate, i.e.

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \beta = \mathrm{const} \tag{6}$$

On integration of relationship (6) one obtains

$$T = T_0 + \beta t \tag{7}$$

or

$$t = (T - T_0)/\beta \tag{8}$$

where T_0 is the initial temperature of the system.

A FUNDAMENTAL PROBLEM OF NON-ISOTHERMAL KINETICS

The problem is to find a differential kinetic equation valid for non-isothermal conditions and describing adequately the physical or chemical changes undergone by the system investigated.

In most cases this is done starting from the differential kinetic equation which is valid in isothermal conditions. This method of obtaining non-isothermal kinetic equations is discussed below. The derivation of a non-isothermal differential kinetic equation without using differential isothermal equations remains an open question. Thus, let us consider the change with time of a characteristic property x of the system given by the following isothermal rate equation:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \mathrm{F}(x, T, t, v) \tag{9}$$

where v represents other variables, which for the moment will not be taken into account ($v = \mathrm{const}$). As far as the variable t is concerned, its presence in the right-hand side of eqn. (9) is not obligatory.

The classical way to derive the non-isothermal kinetic equation makes use of the fact that under non-isothermal conditions T and t are dependent variables. There are two possibilities:

(a) The substitution of T with $\theta(t)$ according to eqn. (2) in eqn. (9) leads to the equation

$$\frac{\mathrm{d}x_\mathrm{N}}{\mathrm{d}t} = \mathrm{F}[x_\mathrm{N}, \theta(t), t] \tag{10}$$

which expresses x_N as a function of t.

(b) The substitution of t with $\varphi(T)$ according to eqn. (3) in eqn. (9) and considering relationship (5) gives

$$\frac{\mathrm{d}x_N}{\mathrm{d}T} = \frac{1}{\beta_2(T)} \mathrm{F}[x_N, T, \varphi(T)] \tag{11}$$

which equation expresses x_N as a function of T.

In eqns. (10) and (11) the subscript N means non-isothermal. Equations (10) and (11) have been obtained by most interested researchers [1–7,11,12].

As will be shown later, the classical way to derive non-isothermal differential kinetic equations from isothermal ones does not always lead to correct results.

Relationships (10) and (11) are equivalent from the standpoint of information about the system investigated. This equivalency is due to the fact that T and t are dependent variables. The question is whether eqns. (10) and (11) are in principle correct or not.

To illustrate these problems we shall consider a very simple physical system, namely, the non-isothermal mathematical pendulum.

THE NON-ISOTHERMAL MATHEMATICAL PENDULUM

It is known that the mathematical isothermal pendulum consists of a punctiform mass suspended from a fixed point through an inextensible rod of constant length l at a variable angle z with respect to the vertical (Fig. 1). The non-isothermal variant of the mathematical pendulum is obtained by a gradual heating of the system, the only effect being the change in the length l with temperature.

$$l = l(T) = l[\theta(t)] = l_N \tag{12}$$

In order to derive the differential equations for the isothermal mathematical pendulum as well as for the non-isothermal one, we shall use the Lagrange equations [8,9] for a system with s degrees of freedom

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0 \qquad i = 1,2,\ldots s \tag{13}$$

where $L(q, \dot{q}, t)$ is the Lagrange function which depends on the generalized

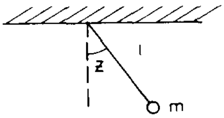

Fig. 1. Isothermal mathematical pendulum.

position coordinates q, the velocities $\dot{q}$ and the time t. For the mathematical pendulum the function L is given by [8]

$$L = T - V \tag{14}$$

where T is the kinetic energy and V is the potential energy. Taking into account the fact that for the mathematical pendulum

$$T = (m/2)l^2\dot{z}^2$$

and

$$V = -mgl \cos z \tag{15}$$

relationship (14) becomes

$$L = (m/2)l^2\dot{z}^2 + mgl \cos z \tag{16}$$

The system has only one degree of freedom, the angle z ($q_1 = z$, $\dot{q}_1 = \dot{z}$, $s = 1$) and from eqn. (13) one obtains

$$l\ddot{z} = -g \sin z \tag{17}$$

which is a differential equation describing the motion of the isothermal pendulum.

The classical way to obtain the differential equation describing the motion of the non-isothermal pendulum is to replace $l = \text{const}$ by l_N, a variable with time, in the isothermal eqn. (17). Thus, the following equation is obtained:

$$l_N\ddot{z}_N = -g \sin z_N \tag{18}$$

Using as a starting point the Lagrange function for the non-isothermal pendulum

$$L_N = \frac{m}{2}\left(\dot{l}_N^2 + l_N^2\dot{z}_N^2\right) + mgl_N \cos z_N \tag{19}$$

another differential equation may be derived. In this case the system has two degrees of freedom. Taking into account the known dependence $l_N = l[\theta(t)] = l(T)$, we shall apply eqn. (13) to the other degree of freedom of the system, namely z_N. After performing the detailed calculations one obtains the following correct differential equation for the non-isothermal pendulum:

$$l_N\ddot{z}_N + 2\dot{l}_N\dot{z}_N = -g \sin z_N \tag{20}$$

A comparison between eqn. (18) for the isothermal case and (20) for the non-isothermal shows that the latter contains the additional term $2\dot{l}_N\dot{z}_N$. Thus eqn. (18) is not valid.

This result leads to the following questions. If in such a simple case the classical way to derive the non-isothermal differential equations is questionable, what happens when dealing with more complicated systems such as chemical systems? Is the classical procedure valid or not for such systems?

SOME GENERAL CONSIDERATIONS CONCERNING THE PROCEDURES TO DERIVE NON-ISOTHERMAL DIFFERENTIAL KINETIC EQUATIONS

The following considerations suppose that the reader is familiar with the fundamentals of both isothermal and non-isothermal kinetics [1–7,10–13].

(1) The classical change of the isothermal differential kinetic equation into the non-isothermal one as shown by eqns. (10) and (11) is not generally valid. The existence of some isothermal differential kinetic equations for which the classical change is correct remains an open question. If such equations exist they will be called primary isothermal differential kinetic equations (PIDKEs).

(2) For the non-isothermal kinetic investigation of complex phenomena it is necessary to postulate at least one isothermal differential kinetic equation as PIDKE. This is called a postulated primary isothermal differential kinetic equation (P-PIDKE). The P-PIDKE should be chosen in such a way that it has not undergone previous mathematical operations such as integration in isothermal conditions.

(3) Taking into account the mathematical complications connected with the derivation of the non-isothermal differential kinetic equation the P-PIDKE cannot always be introduced from the very beginning. Actually there are three possibilities.

(a) Beginning postulated-PIDKE (BP-PIDKE). In this case the existence of a PIDKE is postulated from the very beginning so that all the calculations should be performed in non-isothermal conditions. In this case one has to face considerable mathematical complications.

(b) Finally postulated-PIDKE (FP-PIDKE). In this case all the calculations to derive the rate equation are performed in isothermal conditions, the classical change being made in the final equation. This is the case of the classic non-isothermal kinetics [1–7, 11,12].

(c) Intermediary postulated-PIDKE (IP-PIDKE). In this case, after performing some calculations in isothermal conditions, the classical change is made in an intermediary isothermal differential kinetic equation, the rest of the calculations being performed in non-isothermal conditions.

It is obvious that the correct procedure for a non-isothermal kinetic investigation is BP-PIDKE in spite of the mathematical difficulties. Using the other two procedures the calculations are simpler but the results are quite far from a real description of the system in non-isothermal conditions. These procedures lead to the axiomatic form of classical non-isothermal kinetics.

(4) It should be emphasized that all the considerations from our previous paper [1] are valid for the hypothesis of the axiomatic acceptance of the isothermal differential kinetic equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A\mathrm{f}(x)k(T) \qquad (21)$$

as P-PIDKE. The particular form of eqn. (21) for $x = \alpha$, i.e.

$$\frac{d\alpha}{dt} = A f(\alpha) \exp(-E/RT) \tag{22}$$

where α is the degree of conversion, A is the pre-exponential factor and E is the activation energy, is also axiomatically accepted as FP-PIDKE.

(5) An isothermal differential kinetic equation of the form

$$\frac{dx}{dt} = F(x, T, t) \tag{23}$$

is not acceptable as a P-PIDKE because of the presence of t on the right-hand side of the equation. This implies at least one integration without taking into account the non-isothermal evolution of the system.

THE MODEL OF INFINITESIMAL ISOTHERMAL PORTIONS (MIIP) IN CONNECTION WITH P-PIDKEs

MIIP (Fig. 2) appeared in connection with the integration of the non-isothermal differential kinetic equations [1]. This integration allows: (a) the evaluation of the non-isothermal kinetic parameters; (b) the determination of the dependences $x_N(T)$ or $x_N(t)$ for known non-isothermal kinetic parameters.

Now we shall apply MIIP for a P-PIDKE with a more general form than (21), namely,

$$\frac{dx}{dt} = A f(x) k(T) h(x, t) \tag{24}$$

where $A = \text{const}$ and $h(x, t)$ a function of two inseparable variables. A particular case of eqn. (24) was found in the kinetics of the non-isothermal

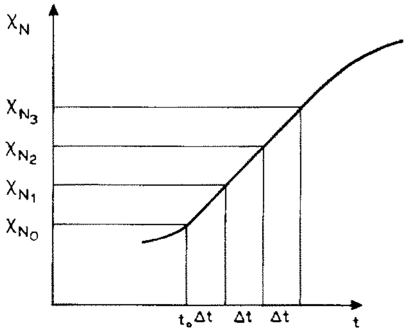

Fig. 2. Infinitesimal isothermal portions on a non-isothermal curve.

heterogeneous decomposition of solids when the activation energy changes linearly with the degree of conversion α [14]. For this case

$$h(\alpha, T) = \exp(-E_1\alpha/RT) \quad E_1 \in R \tag{25}$$

In ref. 15 two other equations which can be reduced to the form (24) have been suggested. Introducing the notation

$$x_{\mathrm{N}} = y \tag{26}$$

and applying the classical change (relationship (10)) in eqn. (24) one obtains

$$\frac{\mathrm{d}y}{\mathrm{d}t} = A\mathrm{f}(y)k[\theta(t)]h[y, \theta(t)] \tag{27}$$

According to the method of separation of variables for the integration of eqn. (27) in non-isothermal conditions, one can distinguish two cases:

(1) It is supposed that an analytical dependence of the form

$$T = u(x_{\mathrm{N}}) = u(y) \tag{28}$$

such as an interpolation polynomial is known. In such conditions the variable separation in eqn. (27) leads to

$$\frac{\mathrm{d}y}{\mathrm{f}(y)h[y, u(y)]} = Ak[\theta(t)]\ \mathrm{d}t \tag{29}$$

On integration, eqn. (29) becomes

$$\int_{y_0}^{y} \frac{\mathrm{d}y}{\mathrm{f}(y)h[y, u(y)]} = A\int_{t_0}^{t} k[\theta(t)]\ \mathrm{d}t \tag{30}$$

By applying MIIP [1] one obtains

$$\left.\begin{aligned}
&\int_{y_0}^{y_1} \frac{\mathrm{d}y}{\mathrm{f}(y)h[y, u(y)]} = Ak[\theta(t_0)]\ \Delta t\\
&\int_{y_1}^{y_2} \frac{\mathrm{d}y}{\mathrm{f}(y)h[y, u(y)]} = Ak[\theta(t_0 + \Delta t)]\ \Delta t\\
&\int_{y_{n-1}}^{y_n} \frac{\mathrm{d}y}{\mathrm{f}(y)h[y, u(y)]} = Ak\{\theta[t_0 + (n-1)\ \Delta t]\}\ \Delta t
\end{aligned}\right\} \tag{31}$$

The summation of relationships (31) leads to

$$\int_{y_0}^{y_n} \frac{\mathrm{d}y}{\mathrm{f}(y)h[y, u(y)]} = A\sum_{i=1}^{n} k\{\theta[t_0 + (i-1)\ \Delta t]\}\ \Delta t = s \tag{32}$$

As in ref. 1, the sum S is given by

$$\int_{y_0}^{y_n} \frac{\mathrm{d}y}{\mathrm{f}(y)h[y, u(y)]} = A\sum_{j=1}^{n} k[\theta(t_0 + j\ \Delta t)]\ \Delta t = S \tag{33}$$

For $n \to \infty$ and $\Delta t \to 0$

$$\lim_{n \to \infty} y_n = y \tag{34}$$

$$\lim_{\substack{n \to \infty \\ \Delta t \to 0}} n \, \Delta t = t - t_0 \tag{35}$$

The sums s and S (Darboux's sums) have the same finite limit which equals the integral $A\int_{t_0}^{t} k[\theta(t)] \, \mathrm{d}t$. Thus for $n \to \infty$ relationships (32) and (33) become

$$\int_{y_0}^{y} \frac{\mathrm{d}y}{\mathrm{f}(y) h[y, u(y)]} = A \int_{t_0}^{t} k[\theta(t)] \, \mathrm{d}t \tag{36}$$

i.e. relationship (30).

(2) In this case a functional dependence of the form

$$x_\mathrm{N} = y = v(T) = v[\theta(t)] \tag{37}$$

is assumed to be known. On variable separation eqn. (27) leads to:

$$\frac{\mathrm{d}y}{\mathrm{f}(y)} = Ak[\theta(t)] h\{v[\theta(t)], \theta(t)\} \tag{38}$$

On integration of eqn. (38) one obtains

$$\int_{y_0}^{y} \frac{\mathrm{d}y}{\mathrm{f}(y)} = A \int_{t_0}^{t} k[\theta(t)] h\{v[\theta(t)], \theta(t)\} \, \mathrm{d}t \tag{39}$$

By applying MIIP the sums s and S are obtained:

$$\int_{y_0}^{y_n} \frac{\mathrm{d}y}{\mathrm{f}(y)} = A \sum_{i=1}^{n} k\{\theta[t_0 + (i-1) \, \Delta t]\} \times$$

$$h\big(v\{\theta[t_0 + (i-1) \, \Delta t]\}, \theta[t_0 + (i-1) \, \Delta t]\big) = s \tag{40}$$

$$\int_{y_0}^{y_n} \frac{\mathrm{d}y}{\mathrm{f}(y)} = A \sum_{j=1}^{n} k[\theta(t_0 + j \, \Delta t)] h\{v[\theta(t_0 + j \, \Delta t)], \theta(t_0 + j \, \Delta t)\} = S \tag{41}$$

For $n \to \infty$, relationships (40) and (41) turn into

$$\int_{y_0}^{y_n} \frac{\mathrm{d}y}{\mathrm{f}(y)} = A \int_{t_0}^{t} k[\theta(t)] h\{v[\theta(t)], \theta(t)\} \, \mathrm{d}t \tag{42}$$

i.e. relationship (39). The equalites of the two pairs of integrals (30)–(36) and (39)–(42) demonstrate that by applying MIIP one obtains in fact the same result as by the classical change of a P-PIDKE followed by variable separation and integration. Thus MIIP gives mathematical support for the classical change of the isothermal differential kinetic equation but it does not help in the derivation of a PIDKE or a P-PIDKE. As we have seen, if PIDKE gives a real description of a non-isothermal system (after the classical change), MIIP gives an equivalent result.

To be aware of the "in principle" mathematical complications which appear in the derivation of non-isothermal kinetic equations, the classical sequence of two consecutive reactions (11) A → B → C will be considered. The differential kinetic equations describing this sequence are

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -k_1 x \tag{43}$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = k_1 x - k_2 y \tag{44}$$

$$\frac{\mathrm{d}z}{\mathrm{d}t} = k_2 y \tag{45}$$

where x, y and z are the time-variable concentrations of A, B and C respectively. By applying the classical change to eqns. (43), (44) and (45) and considering them as BP-PIDKE, it turns out that

$$\frac{\mathrm{d}x_\mathrm{N}}{\mathrm{d}t} = -k_1[\theta(t)]\, x_\mathrm{N} \tag{46}$$

$$\frac{\mathrm{d}y_\mathrm{N}}{\mathrm{d}t} = k_1[\theta(t)]\, x_\mathrm{N} - k_2[\theta(t)]\, y_\mathrm{N} \tag{47}$$

$$\frac{\mathrm{d}z_\mathrm{N}}{\mathrm{d}t} = k_2[\theta(t)]\, y_\mathrm{N} \tag{48}$$

Fortunately eqn. (46), after variable separation, is easy to integrate, i.e.

$$\int_{x_0}^{x_\mathrm{N}} \frac{\mathrm{d}x_\mathrm{N}}{x_\mathrm{N}} = -\int_0^t k_1[\theta(t')]\ \mathrm{d}t' \tag{49}$$

or expressing x_N after integration

$$x_\mathrm{N} = x_0 \exp\left\{-\int_0^t k_1[\theta(t')]\ \mathrm{d}t\right\} \tag{50}$$

Taking into account this result, eqn. (47) becomes

$$\frac{\mathrm{d}y_\mathrm{N}}{\mathrm{d}t} + k_2[\theta(t)]\, y_\mathrm{N} = k_1[\theta(t)]\, x_0 \cdot \exp\left\{-\int_0^t k_1[\theta(t')]\ \mathrm{d}t'\right\} \tag{51}$$

This is a differential kinetic equation valid for non-isothermal conditions whose solution (if there is any exact solution) is very difficult. Introducing, in principle, this solution into eqn. (48), z_N can be obtained. Without considering eqns. (43), (44) and (45) as BP-PIDKE, even these results could not be obtained.

One-stage nucleation

The isothermal differential kinetic equation of the one-stage nucleation is [7,10,11]

$$\frac{\mathrm{d}N}{\mathrm{d}t} = k_1(N_0 - N) \tag{52}$$

where N_0 is the number of energetically favourable sites and N the number of nuclei at the moment t. We shall consider eqn. (52) as BP-PIDKE. Through variable separation and integration in isothermal and non-isothermal conditions, eqn. (52) leads to

$$\ln\frac{N_0}{N_0 - N} = k_1 t \quad \text{(isothermal)} \tag{53}$$

$$\ln\frac{N_0}{N_0 - N_\mathrm{N}} = \int_0^t k_1[\theta(t')]\,\mathrm{d}t' \quad \text{(non-isothermal)} \tag{54}$$

and

$$N = N_0[1 - \exp(-k_1 t)] \tag{55}$$

$$N_\mathrm{N} = N_0\left(1 - \exp\left\{-\int_0^t k_1[\theta(t')]\,\mathrm{d}t'\right\}\right) \tag{56}$$

Taking the derivatives with respect to time of eqns. (55) and (56) one obtains

$$\frac{\mathrm{d}N}{\mathrm{d}t} = N_0 \exp(-k_1 t) k_1 \tag{57}$$

$$\frac{\mathrm{d}N_\mathrm{N}}{\mathrm{d}t} = N_0 \exp\left\{-\int_0^t k_1[\theta(t')]\,\mathrm{d}t'\right\} k_1[\theta(t)] \tag{58}$$

From a mathematical standpoint, it is obvious that even in this very simple case

$$\left(\frac{\mathrm{d}N}{\mathrm{d}t}\right)_\mathrm{N} \neq \frac{\mathrm{d}N_\mathrm{N}}{\mathrm{d}t} \tag{59}$$

where $(\mathrm{d}N/\mathrm{d}t)_\mathrm{N}$ is the expression obtained after the classical change of eqn. (57). For small values of k_1 and $\int_0^t k_1[\theta(t')]\,\mathrm{d}t'$, taking only two terms from the exponentials in (55) and (56) one obtains the following equations:

$$N = N_0 k_1 t \tag{60}$$

$$N_\mathrm{N} = N_0 \int_0^t k_1[\theta(t')]\,\mathrm{d}t' \tag{61}$$

The derivatives of these equations with respect to time are

$$\frac{\mathrm{d}N}{\mathrm{d}t} = N_0 k_1 \tag{62}$$

$$\frac{\mathrm{d}N_\mathrm{N}}{\mathrm{d}t} = N_0 k_1[\theta(t)] \tag{63}$$

In this case $(\mathrm{d}N/\mathrm{d}t)_\mathrm{N} = \mathrm{d}N_\mathrm{N}/\mathrm{d}t$, where $(\mathrm{d}N/\mathrm{d}t)_\mathrm{N}$ is the expression obtained after the classical change of eqn. (62). Thus, while the classical change of eqn. (57) does not lead to eqn. (58), the same change to eqn. (62) leads to eqn. (63).

Two-stage nucleation

In this case the following systems of isothermal differential kinetic equations are valid [10,11]:

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = N_0 k_1 \tag{64}$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = N_1 k_2\ . \tag{65}$$

From eqns. (64) and (65) it is easy to obtain

$$N_1 = N_0 k_1 t \tag{66}$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = N_0 k_1 k_2 t \tag{67}$$

To obtain the non-isothermal differential kinetic equation, one has to consider eqns. (64) and (65) as BP-PIDKE. Thus, integration of eqn. (64) in non-isothermal conditions leads to

$$N_{1\mathrm{N}} = N_0 \int_0^t k_1[\theta(t_1)]\ \mathrm{d}t_1 \tag{68}$$

Introducing this result into eqn. (65) one obtains

$$\frac{\mathrm{d}N_{2\mathrm{N}}}{\mathrm{d}t} = N_0 k_2[\theta(t)] \int_0^t k_1[\theta(t_1)]\ \mathrm{d}t_1 \tag{69}$$

This is an integro-differential equation whose integrated form is

$$N_{2\mathrm{N}} = N_0 \int_0^t \left(k_2[\theta(t_2)] \left\{ \int_0^{t_2} k_1[\theta(t_1)]\ \mathrm{d}t_1 \right\} \right) \mathrm{d}t_2 \tag{70}$$

By comparing eqns. (67) and (69) it is obvious that

$$\left(\frac{\mathrm{d}N_2}{\mathrm{d}t}\right)_\mathrm{N} \neq \frac{\mathrm{d}N_{2\mathrm{N}}}{\mathrm{d}t} \tag{71}$$

where $(\mathrm{d}N_2/\mathrm{d}t)_\mathrm{N}$ is the expression obtained after the classical change of eqn. (67), and that eqn. (67) cannot be considered as a P-PIDKE as it has in its right-hand side the factor t which comes from an isothermal integration.

In isothermal kinetics the total volume of the solid reaction product at the time t is given by the nucleation-growth equation [7,10,11]

$$V(t) = \int_0^t \tau \left[\int_y^t G_{\mathrm{I}}\, \mathrm{d}x \right]^{\lambda} \left(\frac{\mathrm{d}N}{\mathrm{d}t} \right)_{t=y} \mathrm{d}y \tag{72}$$

where τ is a so-called form factor, G_{I} is the growth rate of the nuclei, λ is an exponent which equals 1, 2 or 3 according to the unidimensional, two-dimensional or three-dimensional growth of the nuclei. To make the change of the isothermal eqn. (72) into its non-isothermal variant one has to take into account that G_{N} can be temperature dependent and that $\mathrm{d}N/\mathrm{d}t$ should be replaced by $\mathrm{d}N_{\mathrm{N}}/\mathrm{d}t$, i.e.

$$V_{\mathrm{N}}(t) = \int_0^t \tau \left\{ \int_y^t G_{\mathrm{N}}[\theta(x)]\, \mathrm{d}x \right\}^{\lambda} \left(\frac{\mathrm{d}N_{\mathrm{N}}}{\mathrm{d}t} \right)_{t=y} \mathrm{d}y \tag{73}$$

This result was obtained earlier by Kemeny and Šesták [13]. The use of relationship (73) requires difficult calculations. Indeed the evaluation of the factor $\mathrm{d}N_{\mathrm{N}}/\mathrm{d}t$ from (73) needs, in many cases, solutions of non-isothermal kinetic equations which are very difficult to obtain. Taking into account these difficulties one has to accept FP-PIDKEs.

Another problem raised by the use of relationship (73) is the calculation of the integrals on the right-hand side. Indeed, for $\mathrm{d}N_{\mathrm{N}}/\mathrm{d}t$ given by eqn. (58) and G_{N} given by [13]

$$G_{\mathrm{N}} = G_0 \exp(-E_g/RT\, \mathrm{d}t) \tag{74}$$

relationship (73) turns into

$$V_{\mathrm{N}}(t) = \int_0^t \tau \left(G_0 \int_y^t \exp\left\{ -\frac{E_g}{R[\theta(x)]} \right\} \mathrm{d}x \right)^{\lambda} N_0$$
$$\times \exp\left\{ -\int_0^y k_1[\theta(t')]\, \mathrm{d}t' \right\} k_1[\theta(y)]\, \mathrm{d}y \tag{75}$$

where k_1 is most usually given by [1–8,10–13]

$$k_1 = A_1 \exp\left(-\frac{E_1}{RT} \right) \tag{76}$$

The difficulties in the calculations in eqn. (75) are obvious. Once again one has to emphasize that for systems of complex reactions even $\mathrm{d}N_{\mathrm{N}}/\mathrm{d}t$ cannot be obtained, so until the appearance of new standpoints one has to prefer the axiomatic form, type FP-PIDKE of the classical non-isothermal kinetics.

The axiomatic formulation type FP-PIDKE of the non-isothermal kinetics

This formulation accepts as FP-PIDKE the following general differential kinetic equation [12]:

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p \tag{77}$$

where

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{78}$$

With regard to the classical change of eqn. (77), as shown by a rich literature, its mathematical determination is one of the major concerns of the many people involved in non-isothermal kinetics.

The JMAYK equations

The integral and differential forms of the JMAYK equation are respectively

$$-\ln(1-\alpha) = kt^n \tag{79}$$

$$\frac{d\alpha}{dt} = kn(1-\alpha)t^{n-1} \tag{80}$$

As shown by Kemeny and Šesták [13] a classical change cannot be performed on eqn. (80) as it contains the factor t^{n-1} on the right-hand side.

CONCLUSIONS

The notion of PIDKE introduced in this article proves itself to be useful for the derivation of the non-isothermal kinetic equations from isothermal ones.

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