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SOME MATHEMATICAL ASPECTS OF NONISOTHERMAL KINETICS

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The results of an attempt to derive correct nonisothermal kinetic equations from isothermal ones through the classical nonisothermal change (CNC) of the postulated primary kinetic equations are presented. An alternative possibility through use of the model of infinitesimal isothermal portions (MIIP) is discussed.

In nonisothermal kinetics, the temperature T changes in time t according to a relationship of the form:

$$T = \theta(t) \tag{1}$$

or, in particular for a linear heating program:

$$T = T_o + \beta t \tag{2}$$

Relationships of the forms (1) or (2) show that in nonisothermal kinetics t and T are dependent variables, while in isothermal kinetics they can be regarded as independent [1].

This paper deals with systems characterized by a uniform space temperature (which equals the programmed one), whose change in time is not limited by mass transfer phenomena (i. e. kinetically limited).

A fundamental problem of nonisothermal kinetics. Suggested solution

The problem consists in deriving kinetic equations which adequately describe the evolution of the investigated systems under nonisothermal conditions. Due to the lack of an advanced theory, such a derivation has to be performed by using isothermal kinetic equations. Obviously, under such conditions one has to assume:

a) the validity of the Maxwell–Boltzmann distribution law,

b) the equality between the values of the nonisothermal kinetic parameters and the corresponding values of the isothermal kinetic parameters.

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The derivation of a nonisothermal kinetic equation consists in operating a classical nonisothermal change (CNC), i.e. in the substitution of $T =$ const. in the corresponding isothermal kinetic equation with $T = \theta(t)$. The isothermal kinetic equation (differential or integral) for which the CNC is valid will be called primary. Thus, we have:

– a primary isothermal differential kinetic equation (PIDKE):

– a primary isothermal integral kinetic equation (PIIKE). As shown elsewhere [2], in the case of a complex system it is not possible to decide whether an isothermal kinetic equation is primary or not so, we have to postulate the primary character, i.e. we can distinguish between postulated PIDKE (P-PIDKE) and a postulated PIIKE (P-PIIKE).

To illustrate the above considerations, we may start from the known isothermal kinetic equation:

$$\frac{d\alpha}{dt} = Af(\alpha)\, e^{-\frac{E}{RT}} \quad (T = \text{const}) \tag{3}$$

($A =$ const, $f(\alpha)$ does not change its form in time and ($E =$ const).

From Eq. (3), through integration we obtain:

$$\int_o^\alpha \frac{d\alpha}{f(\alpha)} = Ae^{-\frac{E}{RT}} \cdot dt \; (T = \text{const}) \tag{4}$$

Let us accept Eq. (3) as a P-PIDKE and Eq. (4) as a P-PIIKE. Our main purpose is to show that:

– it cannot be accepted that Eqs (3) and (4) are concomitantly primary;

– it is correct to consider Eq. (3) as a P-PIDKE, but not Eq. (4) as a P-PIIKE.

Operating the CNC in Eq. (3) and taking Eq. (2) into account, we obtain;

$$(N) \quad \frac{d\alpha}{dt} = Af(\alpha)\, e^{-\frac{E}{R(T_o+\beta t)}} \tag{5}$$

where (N) means nonisothermal, the other notations having the usual meanings, or through integration:

$$(N) \quad \int_o^\alpha \frac{d\alpha}{f(\alpha)} = A \int_o^t e^{-\frac{E}{R(T_o+\beta t)\, dt}} \tag{6}$$

which we consider as correct.

The CNC of Eq. (4) leads to:

$$(N) \quad \int_o^\alpha \frac{d\alpha}{f(\alpha)} = A \int_o^t e^{-\frac{E}{R(T_o+\beta t)\, t}} \tag{7}$$

Taking the derivative of Eq. (7) with respect to t, it turns out that:

$$(N) \qquad \frac{d\alpha}{dt} = A\, f(\alpha)\, e^{-\frac{E}{R(T_o+\beta t)}} \left(1 + \frac{E}{R(T_o+\beta t)^2}\right) \tag{8}$$

the result obviously being different from that given by Eq. (5). Thus, Eqs (7) and (8) do not lead to an adequate description of nonisothermal kinetics, whereas the correct Eqs (5) and (6) do. This is easy to understand, considering as primary an equation on which a minimal number of mathematical operations for isothermal conditions was carried out. This requirement is fulfilled by Eq. (3), but not by Eq. (4), obtained from Eq. (3) through an integration for isothermal conditions, which is incompatible with the nonisothermal character of the system [2]. From these considerations, it can be concluded that the isothermal differential kinetic equations should be preferred for postulation as primary.This conclusion in supported by applying the model of infinitesimal isothermal portions (MIIP), which will be briefly presented below.

Model of infinitesimal isothermal portions (MIIP)

The model consists in the division of the nonisothermal curve $\alpha(t)$ into infinitesimally small portions, in which we will consider (axiomatically) that the system is described by the integral kinetic Eq. (4) derived directly from (3). The temperature is considered as corresponding to the middle of the chosen interval [3]. We shall analyse the MIIP corresponding to the division t axis into infinitesimally small portions Δt.

For the n-th interval we have:

$$T = \theta\left(\frac{n-1\,\Delta t + n\Delta t}{2}\right) = \theta\left(\frac{2n-1\,\Delta t}{2}\right) \tag{9}$$

$$(N) \qquad \int_{\alpha_{n-1}}^{\alpha_n} \frac{d\alpha}{f(\alpha)} = A\, e^{-\frac{E}{R\theta\,\left(\frac{2n-1\,\Delta t}{2}\right)}}\,\Delta t \tag{10}$$

By summing the n relationship of the form (10) and taking the limits for $n \to \infty$:

$$(N) \quad \lim_{\substack{n \to \infty \\ \Delta t \to 0}} n\,\Delta t = t \tag{11}$$

$$(N) \quad \lim_{n \to \infty} \alpha_n = \alpha \tag{12}$$

and t being current points:

$$T = \sum_{i=1}^{n} A e^{-\frac{E}{R\theta\left(\frac{2i-1}{2}\Delta t\right)}} \Delta t \tag{13}$$

$$\lim_{\substack{n \to \infty \\ \Delta t \to 0}} T = \int_0^t A e^{-\frac{E}{R\theta(t)}} \mathrm{d}t \tag{14}$$

Taking into account relationship (2), we obtain Eq. (6), which correctly describes the evolution of nonisothermal systems. Thus, the use of MIIP if equivalent to a CNC of Eq. (3) accepted as a P-PIDKE.

On the existence of the total differential $\mathrm{d}\alpha = \left(\frac{\partial \alpha}{\partial t}\right)_T \mathrm{d}t + \left(\frac{\partial \alpha}{\partial T}\right)_t \mathrm{d}T$ in isothermal kinetics.

The discussion concerning this problem was initiated by MacCallum and Tanner [4]. In our opinion such a discussion is meaningless. The mistake of the above-mentioned authors consists in the assumption that in nonisothermal kinetics a relationship of the form:

$$\alpha = u_N\,(T,t) \tag{15}$$

with T and t independent variables, is valid. From Eq. (15), through differentiation, we obtain:

$$\mathrm{d}\alpha = \left(\frac{\partial u_N}{\partial T}\right)_t \mathrm{d}T + \left(\frac{\partial u_N}{\partial t}\right)_T \mathrm{d}t \tag{16}$$

a relationship containing the partial derivative $\left(\frac{\partial u_N}{\partial T}\right)_t$ at t = const, which is meaningless. To solve the problem, one has to consider $\theta(t)$ instead of T in Eq. (15), i.e.

$$\alpha = u_N\ (\theta(t),t) \tag{17}$$

whose differential

$$\mathrm{d}\alpha = \frac{\partial u_N}{\partial t}\,\mathrm{d}t + \frac{\partial u_N}{\partial \theta}\cdot\frac{\mathrm{d}\theta(t)}{\mathrm{d}t}\,\mathrm{d}t \tag{18}$$

does not contain any term at $t = \text{const}$ [3].

Conclusions

1 The authors define the classical nonisothermal change of primary isothermal kinetic equations.

2 The classical nonisothermal change is shown to be equivalent to the use of the model of infinitesimal isothermal portions.

References

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Zusammenfassung — Die Autoren stellen die Ergebnisse eines Versuchs vor, korrekte Gleichungen für die nicht-isotherme Kinetik durch den klassischen nichtisothermen Übergang aus den als primär postulierten isothermen kinetischen Gleichungen abzuleiten. Als alternative Möglichkeit wird das Modell der infinitesimalen isothermen Abschnitte diskutiert.

РЕЗЮМЕ — Представлены результаты некоторых попыток вывести корректные неизотермические кинетические уравнения из изотермических посредством классического неизотермического изменения принятых без доказательств первичных кинетических уравнений. Обсуждена альтернативная возможность использования модели бесконечно малых изотермических величин.