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Note

IS CLASSICAL NON-ISOTHERMAL KINETICS WITH CONSTANT HEATING RATE ACTUALLY NON-ISOTHERMAL KINETICS WITH QUASI-CONSTANT HEATING RATE?

E. URBANOVICI

Research Institute for Electrotechnics (ICPE), Sfîntu Gheorghe Branch, Sfîntu Gheorghe 4000, Str. Jozsef Attila 4, Jud. Covasna (Romania)

E. SEGAL

Department of Physical Chemistry and Electrochemical Technology, Faculty of Chemical Technology, Polytechnic Institute of Bucharest, Bulevardul Republicii 13, Bucharest (Romania)

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ABSTRACT

In thermal analysis equipment, differences between the true temperature of the sample and the programmed one can give rise to errors in the evaluation of non-isothermal kinetic parameters if a strictly constant heating rate is used in the calculations. This paper describes a means of overcoming this shortcoming by applying methods which use integration over small intervals of variable change and thus local heating rates.

Current non-isothermal kinetic methods use linear heating programmes with the variable temperature given by

$$T = T_0 + \beta t \tag{1}$$

where T_0 is the initial temperature (at $t = t_0$) and β is the constant heating rate.

Owing to thermal effects which accompany the change of the sample during heating, the true temperature differs from the programmed one, being given not by eqn. (1) but by

$$T = T_0 + \beta t + \gamma(t) \tag{2}$$

where $\gamma(t)$ is the deviation from linearity.

In principle, $\gamma(t)$ could be determined by interpolation from the temperature and time values corresponding to a certain number of points on the curve (T, t).

As it will be shown, the use of integration over small intervals of variables renders knowledge of the form of the function $\gamma(t)$ unnecessary.

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Considering the isothermal differential kinetic equation

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

with the classical conditions

$$A = \text{const},\ E = \text{const} \tag{4}$$

$$f(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^p \tag{5}$$

(where m, n and p are constants) as the postulated primary isothermal differential kinetic equation (P-PIDKE), and applying classical non-isothermal change (CNC) with the temperature given by eqn. (1), we obtain [1–4]

$$\frac{d\alpha}{dt} = Af(\alpha)\ e^{-E/R(T_0+\beta t)} \tag{6}$$

Taking into account the fact that $dT = \beta dt$, eqn. (6) becomes

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha)\ e^{-E/RT} \tag{7}$$

From eqn. (7), through variable separation and integration, we obtain

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T e^{-E/RT}\, dT \tag{8}$$

In what follows we shall try to derive, in place of eqn. (8) for constant heating rate, a different equation which takes into account the deviation of the temperature from linearity. By applying a CNC in eqn. (3) with the temperature given by eqn. (2), we obtain

$$\frac{d\alpha}{dt} = Af(\alpha)\ e^{-E/R(T_0+\beta t+\gamma(t))} \tag{9}$$

For the change of variable $t \to T$ in eqn. (9), we shall suppose that

$$t = \rho(T) \tag{10}$$

From eqn. (2), through differentiation, we obtain

$$dT = \beta\ dt + \dot{\gamma}(t)\ dt \tag{11}$$

or

$$dt = \frac{dT}{\beta + \dot{\gamma}(t)} \tag{12}$$

Taking into account eqns. (10) and (12), eqn. (9) becomes

$$\frac{d\alpha}{dt} = \frac{A}{\beta + \dot{\gamma}(\rho(T))} f(\alpha)\ e^{-E/RT} \tag{13}$$

which is the corrected non-isothermal kinetic differential equation for a heating rate which is not strictly constant. Nevertheless, its use in an integral equation of the form

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = A \int_0^{T} \frac{\mathrm{e}^{-E/RT}}{\beta + (\dot{\gamma}(\rho(T))} \, \mathrm{d}T \tag{14}$$

is quite tedious, the functions $\gamma(t)$ and $\rho(T)$ being unknown.

It can be shown that eqn. (13) can be used without special complications for integration over small intervals of variable change.

Thus by integrating eqn. (13) for $\alpha \in [\alpha_i, \alpha_k]$, we obtain

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{f(\alpha)} = A \int_{T_i}^{T_k} \frac{\mathrm{e}^{-E/RT}}{\beta + \dot{\gamma}(\rho(T))} \, \mathrm{d}T \tag{15}$$

For

$$T_k - T_i \leqslant 15 \text{ K} \tag{16}$$

the integral from the right side of eqn. (15) can be approximated by using the second mean value theorem [5–7]. Thus

$$\int_{T_i}^{T_k} \frac{\mathrm{e}^{-E/RT}}{\beta + \dot{\gamma}(\rho(T))} \, \mathrm{d}T \frac{1}{\beta + \dot{\gamma}(\rho(T_\lambda))} \int_{T_i}^{T_k} \mathrm{e}^{-E/RT} \, \mathrm{d}T \tag{17}$$

where $T_\lambda \in (T_i, T_k)$.

As a very good approximation, we suggest [6,7]

$$T_\lambda = T_{ik} = \frac{T_i + T_k}{2} \tag{18}$$

In such conditions

$$\beta + \dot{\gamma}[\rho(T_{ik})] = \beta + \dot{\gamma}(t_{ik}) \tag{19}$$

where t_{ik} is the time corresponding to T_{ik}. For small intervals the variables change as follows,

$$\beta + \dot{\gamma}(t_{ik}) \simeq \frac{T_0 + \beta t_k + \gamma(t_k) - (T_0 + \beta t_i + \gamma(t_i))}{t_k - t_i} \tag{20}$$

Hence

$$\beta + \dot{\gamma}(t_{ik}) \simeq \beta_{ik} \tag{21}$$

which corresponds to

$$\dot{\gamma}(t_{ik}) \simeq \frac{\gamma(t_k) - \gamma(t_i)}{t_k - t_i} \tag{22}$$

Taking into account eqns. (18), (19) and (21), eqn. (17) becomes

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta_{ik}} \int_{T_i}^{T_k} \mathrm{e}^{-E/RT} \, \mathrm{d}T \tag{23}$$

This is a general equation which allows for variability of heating rate. We have used it in various methods for the evaluation of non-isothermal kinetic parameters [8–13].

A similar equation, derived for non-classical non-isothermal kinetics [14], has the form

$$\int_{\alpha_i}^{\alpha_k} \frac{\mathrm{d}\alpha}{f^*(\alpha)} = \frac{1}{\beta_{ik}} \int_{T_i}^{T_k} A(v)\, \mathrm{e}^{-E(v)/RT}\, \mathrm{d}T \tag{24}$$

where $f^*(\alpha)$ is a conversion function with $n(\alpha)$, $m(\alpha)$, $p(\alpha)$, and v is a variable (usually α).

CONCLUSIONS

An integral non-isothermal kinetic equation which allows for variability of heating rate has been derived. The equation has been used to work up methods for the evaluation of non-isothermal kinetic parameters.

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