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NON-STEADY-STATE DIFFUSION IN PROGRAMMED HEATING

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The utilization, for programmed heating, of Fick's second equation concerning non-steady-state diffusion is discussed. Methods for calculating the activation energy of the diffusion process and the factor D_0 of the Arrhenius equation from a single non-isothermal experiment are suggested.

It is well known that Fick's second equation is the mathematical model for non-steady-state diffusion under isothermal conditions. For the case when the diffusion coefficient is independent of concentration, this equation has the following shape:

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} \tag{1}$$

However, for a wide range of practical tasks in isotropic media, Eq. (1) may be considered along a single coordinate x:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{2}$$

In the general case, it is assumed that the diffusion coefficient D is related to temperature according to the Arrhenius law:

$$D = D_0 \exp\left(\frac{-E}{RT}\right)$$

The basic differential equation (2) is of great scientific and practical interest in programmed heating following the three most accepted systems:

1. Linear heating: $T = T_0 + at$ or $\frac{dT}{dt} = a$.

2. Exponential heating: $T = T_0 \exp(bt)$ or $\frac{dT}{dt} = bT$.

3. Hyperbolic heating: $\frac{1}{T} = \frac{1}{T_0} - ct$ or $\frac{dT}{dt} = cT^2$.

Let us write the basic equation (2) in the following form:

$$\frac{1}{\exp\left(\frac{-E}{RT}\right)} \cdot \frac{\partial c}{\partial t} = D_0 \frac{\partial^2 c}{\partial x^2} . \tag{3}$$

Introducing a new variable $d\Theta = \exp\left(\frac{-E}{RT}\right)dt$, Eq. (3) may be written in the accepted form

$$\frac{\partial c}{\partial \Theta} = D_0 \frac{\partial^2 c}{\partial x^2} . \tag{4}$$

It should be considered that, when choosing the characteristics for temperature programming, one will always be able to find a starting temperature T_0 for which $\exp\left(\frac{-E}{RT}\right) \gg \exp\left(\frac{-E}{RT_0}\right)$. Then, to simplify the mathematical solution of the task without causing a significant error, one may assume that for the initial boundary conditions $C = C_0$, $x = 0$ and $t = 0$, the value Θ will also be close to zero. In this case, analogously to the classical solution of Fick's second equation under isothermal conditions [1], the following solution will be obtained for Eq. (4):

$$C(x, T) = C_0\left[1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy\right] . \tag{5}$$

where $\int e^{-y^2} dy$ is the probability integral, and $y^2 = \frac{x^2}{4D_0\Theta}$. Eq. (5) can also be written in the shape

$$Z = \frac{C_0 - C(x, T)}{C_0} = \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy = \phi(y) . \tag{6}$$

The numerical value of y can be found in statistical probability calculus handbooks for an experimentally determined value of Z. Knowing the value of y, it is then easy to establish the value $D_0\Theta$ for a known depth of diffusion x in the given moment.

In an earlier paper [2] we reported a simpler solution for Fick's second equation:

$$\frac{C_0 - C(x, t)}{C_0} = \frac{x^2}{2Dt} . \tag{7}$$

Analogously, taking into account the above assumptions, the solution of Fick's second equation for programmed heating is

$$\frac{C_0 - C(x, T)}{C_0} = \frac{x^2}{2D_0\Theta} . \tag{8}$$

Thus, from a corresponding non-isothermal experiment, one will be able to determine the value $D_0\Theta$, which – for the different temperature-programming systems – by integration according to [3, (Eq. 12)] will yield

$$D_0\Theta_a = \frac{D_0}{a}\int_{T_0}^{T} \exp\left(\frac{-E}{RT}\right) dT \simeq \frac{D_0RT^2}{a(E+2RT)} \exp\left(\frac{-E}{RT}\right) \quad (9)$$

$$D_0\Theta_b = \frac{D_0}{b}\int_{T_0}^{T} \frac{\exp\left(\frac{-E}{RT}\right)}{T} dT \simeq \frac{D_0RT}{b(E+RT)} \exp\left(\frac{-E}{RT}\right) \quad (10)$$

$$D_0\Theta_c = \frac{D_0}{c}\int_{T_0}^{T} \frac{\exp\left(\frac{-E}{RT}\right)}{T^2} dT \approx \frac{D_0R}{cE} \exp\left(\frac{-E}{RT}\right) \quad (11)$$

The linearization of the above equations allows to calculate the activation energy of the diffusion process E and the coefficient D_0:

$$\ln \frac{D_0\Theta_a}{T^2} = \frac{-E}{RT} + \ln \frac{D_0R}{a(E+2RT)} \quad (12)$$

$$\ln \frac{D_0\Theta_b}{T} = \frac{-E}{RT} + \ln \frac{D_0R}{b(E+RT)} \quad (13)$$

$$\ln D_0\Theta_c = \frac{-E}{RT} + \ln \frac{D_0R}{cE} \,. \quad (14)$$

Finally it should be noted that in the general case, the activation energy values E calculated by the two methods suggested in this paper for solving the diffusion equation Eq. (4) will be identical, but the values of the coefficient D_0 will slightly differ.

References

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