

THE CORRELATION BETWEEN ISOTHERMAL AND NON-ISOTHERMAL KINETICS IN THERMOGRAVIMETRY

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It is shown that the total differential of the function of the amount of conversion versus temperature and time ($\alpha = f(T, t)$) is equal to zero non-isothermal kinetics at constant heating rate. Hence, the mathematical expression used in the literature for the rate of the non-isothermal transformation, $\frac{d\alpha}{dt} = \left(\frac{\partial\alpha}{\partial t}\right)_T + \left(\frac{\partial\alpha}{\partial T}\right)_t \cdot \frac{dT}{dt}$, is not valid.

The determination of the most important kinetic characteristic of thermal decomposition, the activation energy, is usually carried out by a classical method, by running a series of experiments under isothermal conditions. The determination of the activation energy directly from one thermogravimetric curve relates to the widespread introduction of thermogravimetric methods in experimental practice. Accordingly, the questions of the suitability of such a determination of the activation energy and of the identity of the latter with the activation energy from the isothermal investigation have been discussed in the recent literature.

The communication of MacCallum and Tanner [1] is devoted to this problem; the authors attempted to consider the relationship between isothermal and non-isothermal kinetics. The activation energy from the non-isothermal thermogravimetric data is usually determined from the following relation:

$$d\alpha/dt = \phi(\alpha) Z \exp(-E/RT) \quad (1)$$

where Z is the pre-exponential factor in the Arrhenius equation;

α is the amount of conversion;

$\phi(\alpha)$ is a function of the amount of conversion (usually $(1 - \alpha)^n$, n is the formal reaction order).

MacCallum and Tanner consider the use of equation (1) as incorrect under non-isothermal conditions. In their opinion equation (1) is applicable for isothermal conditions only and must accordingly be written in the following form:

$$(d\alpha/dt)_T = \phi(\alpha) Z \exp(-E/RT) \quad (2)$$

If one follows the authors of the above communication and consider that $\alpha = f(T, t)$, the total differential of this function will be written:

$$d\alpha = (\partial\alpha/\partial t)_T dt + (\partial\alpha/\partial T)_t dT$$

or:

$$(dx/dt)_{f(T,t)} = (\partial\alpha/\partial t)_T + (\partial\alpha/\partial T)_t \cdot q \quad (3)$$

where $q = dT/dt$ is the heating rate (it is usually constant under experimental conditions). Substituting Eq. (2) into Eq. (3) the authors have:

$$(dx/dt)_{f(T,t)} = \phi(\alpha) Z \exp(-E/RT) + (\partial\alpha/\partial T)_t \cdot q \quad (4)$$

MacCallum and Tanner believe Eq. (4) to be applicable only to the description of non-isothermal kinetics. They conclude that the activation energy and the formal reaction order must be determined only from the results of the isothermal conduction of the decomposition or transformation processes. If agreement with the results of the determination of the kinetic characteristics (E and n) under isothermal conditions is observed in the case of the given non-isothermal experiment, the authors explain this by the second term on the right side of the Eq. (4) i.e. $\left(\frac{\partial\alpha}{\partial T}\right)_t \cdot q$ (being negligible in the given experiment).

We do not agree with the mathematical substantiation of the foregoing, though we do not deny the importance of the investigations under isothermal conditions for the correct determination of the activation energy and the formal reaction order.

The heating rate is always maintained constant in the non-isothermal process, i.e. $\frac{dT}{dt} = q = \text{const}$. This means that there is a functional relationship between T and t , i.e. a certain fixed temperature corresponds to a certain point of time, and conversely. The total differential for the equation $\alpha = f(T, t)$ is equal to zero, i.e.:

$$d\alpha = \left(\frac{\partial\alpha}{\partial t}\right)_T dt + \left(\frac{\partial\alpha}{\partial T}\right)_t dT = 0$$

Let us write the relation between T and t as an implicit function: $\phi(\alpha, T, t) = 0$.

Then, in accordance with the known relation in differentiating implicit functions [2], we have:

$$(\partial\alpha/\partial T)_t \cdot (\partial T/\partial t)_\alpha \cdot (\partial t/\partial\alpha)_T = -1$$

One can assume, without a significant error, that $(\partial T/\partial t)_\alpha = q$. We have in this case:

$$(\partial\alpha/\partial T)_t = -\frac{1}{q}(\partial\alpha/\partial t)_T \quad (5)$$

Substituting Eq. (5) into Eq. (3) we obtain:

$$(dx/dt)_{f(T,t)} = (\partial\alpha/\partial t)_T + (\partial\alpha/\partial T)_t \cdot q = 0$$

Thus, the interpretation of Eq. (4) for description of non-isothermal kinetics is incorrect. There is nothing to do but to assume that Eq. (1):

$$dx/dt = \phi(x) Z \exp(-E/RT)$$

or:

$$d\alpha/dT = \phi(\alpha) \frac{Z}{q} \exp(-E/RT)$$

is applicable for determination of the activation energy and the formal reaction order under non-isothermal conditions.

If disagreements are observed in the characteristics determined under isothermal and non-isothermal conditions, we are agreed that the principal reason is that the process of the transformation for one and the same substance can proceed with different formal reaction orders depending on the experimental conditions, and this results in different values of the effective activation energy [3]. The larger the formal order of the reaction, the larger the effective value of the activation energy.

References

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