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PROPER DETERMINATION OF ORDER OF REACTIONS BY THERMAL ANALYSIS

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The relationship $1-\alpha_m = 1.062\, n^{1/1-n}$, well-known in non-isothermal kinetics and applied for determination of the kinetic exponent n, is not universal. A more accurate modification of the given equation is proposed in the form of a more complex function $1-\alpha_m = \varphi(n, X_m)$, where $X_m = E/RT_m$ is the dimensionless Arrhenius' criterion.

The following kinetic equation is usually used to describe one-step topochemical transformations in the moving interphase surface model:

$$\frac{d\alpha}{dt} = K(T)(1-\alpha)^n = A\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{1a}$$

or

$$\frac{d\alpha}{dt} = \frac{A}{q}\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{1b}$$

where α is the degree of transformation, $K(T)$ is the rate constant, q is the linear heating rate, and n is the order of reaction or the kinetic exponent characteristic of the geometry of movement of the interphase surface (for a contracting or expanding cylinder $n = 1/2$; for a sphere $n = 3/2$; in real experimental situations n may have intermediate or extreme values). However, the initial kinetic equation (1) in a generalized form is also applicable to the description of the process of diffusional mass transport in the studied substance and that of mass exchange through stationary phase boundaries [1, 2]. In these cases the following kinetic equations, identical in form with Eq. (1), were obtained via the study of dehydroxylation processes of porous substances:

$$\frac{d\alpha}{dt} = \frac{B}{q}\exp\left(-\frac{W}{RT}\right)(1-\alpha)^{n'} \quad \text{if} \quad Q = W \tag{2}$$

$$\frac{d\alpha}{dt} = \frac{B}{q}\exp\left(-\frac{Q}{RT}\right)(1-\alpha)^{n'} \quad \text{if} \quad Q > W \tag{3}$$

where O is the heat of desorption of moisture from the outer surface of the substance, W is the activation energy for diffusion of water inside the porous substance, and B is a pre-exponential factor which depends on the mass-exchange coefficient, the geometrical shape and the dimensions of the investigated substance. The kinetic exponent n' depends on the geometry of the sample: for a disk $n' = 3$, and for a sphere $n' = 5/3$. It should be emphasized that the physical senses of the kinetic constants in Eqs (1), (2) and (3) are different, though these equations are formally identical.

Consequently, the kinetic exponent n must be known for a proper understanding of the mechanisms of thermal transformations, and in order to determine the energy characteristics E, Q and W, as well as the pre-exponential factor in the general form:

$$A = \frac{(1-\alpha_m)^{1-n}}{n} \frac{Eq}{RT_m^2} \exp\left(\frac{E}{RT_m}\right) \tag{4}$$

The most convenient way to determine kinetic characteristics is from differential thermoanalytical curves (DSC, DTA), EGA coupled to gas chromatographic detectors, etc. We put down the system of the following two equations:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A - \frac{E}{RT} + n \ln(1-\alpha)$$

$$\ln\left(\frac{d\alpha}{dt_m}\right) = \ln A - \frac{E}{RT_m} + n \ln(1-\alpha_m)$$

Subtracting the second equation from the first and turning to corresponding amplitudes in the thermoanalytical curve, we obtain:

$$\frac{\frac{h}{h_m}}{\ln\left(\frac{1-\alpha}{1-\alpha_m}\right)} = \left(\frac{E}{RT_m}\right) \frac{T-T_m}{T \ln\left(\frac{1-\alpha}{1-\alpha_m}\right)} + n$$

If the corresponding graphical dependence is constructed, it is easy to find a means of independent determination of the value of n, in parallel with determination of the dimensionless ratio $\frac{E}{RT_m}$. The given method for the determination of E and n is in general a modification of the well-known Freeman–Carroll method [3]. Nevertheless, its application to the determination of n from integral kinetic curves is difficult.

Another analytical method is described in the literature for the determination of the kinetic exponent n based on the following relationship [4]:

$$1 - \alpha_m = n^{1/1-n} \tag{5}$$

where α_m is the degree of transformation at the point of maximum rate of transformation. This expression is stated more accurately in [5]:

$$1 - \alpha_m = 1.062\, n^{1/1-n} \tag{6}$$

The above equations give appreciably different results when $1-\alpha_m > 0.5$. For instance, for $1-\alpha_m = 0.5$ we have $n = 2$ from Eq. (5) and $n = 1.7$ from Eq. (6).

Let us analyze the general form of Eq. (6):

$$1-\alpha_m = \sigma n^{1/1-n} \tag{7}$$

If σ^{1-n} is designated by y, the

$$(1-\alpha_m)^{1-n} = yn \tag{8}$$

We rewrite the initial kinetic equation (1) in integral form, using Balarin's solution of the Arrhenius integral [6] as the most general of the proposed earlier solutions [7, 8]. As a result, the following can be written for the peak of the DTG curve:

$$\frac{[1-(1-\alpha)^{1-n}]n}{(1-\alpha)^{1-n}(1-n)} = \left(1+\frac{4}{X_m}\right)^{-0.5} \tag{9}$$

where $X_m = \frac{E}{RT_m}$ is the dimensionless Arrhenius' criterion. Substituting Eq. (9) we obtain:

$$\frac{(1-yn)}{y(1-n)} = \left(1+\frac{4}{X_m}\right)^{-0.5} = Z \tag{10}$$

from which $y = [n+(1-n)Z]^{-1}$ and

$$\sigma = [n+(1-n)Z]^{-1/1-n} \tag{11}$$

It is seen from Eq. (11) that in the case $n = \text{const}$, σ depends on $X_m = \frac{E}{RT_m}$

Using the following known formula

$$E = \frac{nRT_m^2\left(\frac{d\alpha}{dT}\right)_m}{1-\alpha_m}$$

and substituting $\frac{E}{RT_m}$ from it into Eq. (11), an extended form of Eq. (7) is obtained:

$$1-\alpha_m = \left\{\frac{n}{n+(1-n)\left[1+\frac{4}{n\delta}\right]^{-0.5}}\right\}^{1/1-n} \tag{12}$$

where

$$\delta = \frac{T_m\left(\frac{d\alpha}{dT}\right)_m}{1-\alpha_m}.$$

There is another way of calculating $n\delta$ using the section of the differential peak at its half-height. In this case $\left(\frac{d\alpha}{dt}\right)_1 = \left(\frac{d\alpha}{dt}\right)_2$ [9]. After mathematical transformations

Table 1 Comparative calculation of kinetic exponent *n* using Equations (6) and (12)

n_{mod}	$\bar{A}_{\mathrm{mod}} = \frac{A(n-1)}{q}$	$1-\alpha_m$	$\left(\frac{d\alpha}{dT}\right)_m$	T_m, K	δ	*n* from Eq. (12)	Error, %	*n* from Eq. (6)	Error, %
1.5	1	25.2	0.5618	0.003684	55263	1.54	2.7	2.4	60
1.5	$5 \cdot 10^6$	117.6	0.4857	0.009000	709.0	13.1277	1.51	0.7	6.7
3.0	1	33.6	0.7142	0.001408	822.5	1.6212	3.08	2.7	120

of the equation $A\exp\left(-\frac{E}{RT_1}\right)(1-\alpha_1)^n = A\exp\left(-\frac{E}{RT_2}\right)(1-\alpha_2)^n$ the following result is obtained:

$$E = \frac{nRT_1T_2\ln\left(\frac{1-\alpha_1}{1-\alpha_2}\right)}{T_2-T_1}$$

or

$$X_m = \frac{E}{RT_m} = n\frac{T_1T_2\ln\left(\frac{1-\alpha_1}{1-\alpha_2}\right)}{T_m(T_2-T_1)},$$

and

$$\delta = \frac{T_1T_2\ln\left(\frac{1-\alpha_1}{1-\alpha_2}\right)}{T_m(T_2-T_1)}$$

Thus, values of $1-\alpha_m$ and δ in Eq. (12) are easily determined from exponential thermal curves and the only unknown quantity is the kinetic exponent n. Since Eq. (12) is obtained using the approximate formula (9), its validity should be examined using a computer. Giving a computer parameters n_{mod}, E_{mod} and $\overline{A_{\mathrm{mod}}} = \frac{A(n-1)}{q}$, DTG and TG curves are calculated from Eq. (1) and its integral. Hence, the quantities $1-\alpha_m$, $\left(\frac{d\alpha}{dT}\right)_m$, T_m and δ are obtained. n is determined by substituting $1-\alpha_m$ and δ into Eq. (12) and it is compared to its modelling value. It is seen that the replacement of Eq. (6) by Eq. (12) decreases the value of error in the determination of n to a considerable degree; functionally, it reflects the dependence of the inflection points to TG curves on the dimensionless Arrhenius' criterion $\frac{E}{RT_m}$.

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