

## MATHEMATICAL ANALYSIS OF THERMOKINETIC CURVES

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For every actual thermokinetic curve described by the equation

$$\frac{dx}{dT} = (1 - \alpha)^n \frac{A}{q} \exp\left(-\frac{E}{RT}\right)$$

the constancy of the ratio  $\left(\frac{E}{n}\right)$  is observed, independently of the accuracy of the determination of the effective order of reaction  $n$ , i.e.  $\frac{E_{\text{true}}}{n_{\text{true}}} = \frac{E_x}{n_x}$ , where  $n_{\text{true}}$  and  $E_{\text{true}}$  are the true values, while  $n_x$  and  $E_x$  are experimentally-determined values. Accurate knowledge of the value  $\tilde{E} = \left(\frac{E}{n}\right)$  allows estimation of the value  $E_y$  for another approximate value  $n_y$  by means of the formula  $E_y = n_y \tilde{E}$ .

In the practice of kinetic studies of reactions of the type  $A_s \rightarrow B_s + C_g$  under non-isothermal conditions, the activation energy  $E$  and the effective order of the reaction  $n$  are determined [1, 2] from DTA, TG, scanning calorimetry data and gas release curves measured in gas-chromatograph systems [3]. No accurate methods for determining the effective order of reaction have been described in the literature. The methods used [4, 5] all yield approximate values for  $n$ . It has been demonstrated [6, 7] that in the general case, the effective activation energy of the reaction and the effective order of reaction are interrelated, i.e. the higher the value of  $n$ , the higher (under otherwise equal conditions) the value of  $E$ , and vice versa. This relationship raises the necessity of analyzing to what extent an inaccuracy in the determination of the order of reaction from a given thermokinetic curve is reflected in the value of the activation energy determined.

Let us consider some thermogravimetric curve (TG and DTG) measured, for example, with a Paulik – Paulik – Erdely derivatograph. From the kinetic equation

$$\frac{dx}{dt} = (1 - \alpha)^n A \exp\left(-\frac{E}{RT}\right) \quad (1)$$

the order of reaction  $n$  is estimated from the known relationship [4]

$$n \approx (1 - \alpha_s)^{1-n} \quad (2)$$

where  $\alpha_s$  is the conversion at the point where the reaction has reached maximum development, at the corresponding temperature  $T_s$ . The rate constant of the reaction can be described [4, 6] by the relationship

$$k = \frac{(1 - \alpha_s)^{1-n}}{n} \cdot \frac{Eq}{RT_s^2} \exp\left(\frac{E}{RT_s}\right) \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where  $q$  is the linear heating rate. At the point  $T_s$  Eq. (3) assumes the simpler form

$$k_s = \frac{(1 - \alpha_s)^{1-n}}{n} \cdot \frac{Eq}{RT_s^2}. \quad (4)$$

Let us assume that the true value of the order of reaction,  $n_{\text{true}}$ , and the experimentally-determined value,  $n_x$ , are known. The values  $(1 - \alpha_s)$  and  $T_s$  obviously remain unchanged in both cases. Hence

$$\frac{(1 - \alpha_s)^{1-n_{\text{true}}}}{n_{\text{true}}} \cdot \frac{E_{\text{true}} \cdot q}{RT_s^2} \cdot (1 - \alpha_s)^{n_{\text{true}}} = \frac{(1 - \alpha_s)^{1-n_x}}{n_x} \cdot \frac{E_x \cdot q}{RT_s^2} (1 - \alpha_s)^{n_x}$$

or, after performing the required simplifications

$$\tilde{E} = \frac{E_{\text{true}}}{n_{\text{true}}} = \frac{E_x}{n_x}. \quad (5)$$

For another approximate value  $n_y$ ,

$$E_y = n_y \tilde{E}.$$

The relationship (5) can also be obtained by starting from other premises. At the temperature  $T_s$  where the reaction reaches highest development

$$\left(\frac{E}{n}\right) = \frac{RT_s^2}{1 - \alpha_s} - \left(\frac{d\alpha}{dt}\right)_s = \left(\frac{E_x}{n_x}\right). \quad (6)$$

For two rates of reactions [3]

$$\left(\frac{d\alpha}{dt}\right)_1 = \left(\frac{d\alpha}{dt}\right)_2$$

the following relationship can be written:

$$\left(\frac{E}{n}\right) = \frac{RT_1 T_2 \ln \frac{1 - \alpha_1}{1 - \alpha_2}}{T_2 - T_1} = \left(\frac{E_x}{n_x}\right). \quad (7)$$

The value of  $\left(\frac{E}{n}\right)$  can be determined fairly accurately (as compared to the esti-

mation of the order of reaction  $n$ ) by using our solution of Eq. (1):

$$\frac{1 - (1 - \alpha)^{1-n}}{1 - n} = (T/T_s)^2 \left( \frac{E}{E + 2RT} \right) \exp \left[ \frac{(T - T_s)E}{RT_s T} \right]. \quad (8)$$

By substituting the value  $n_x$  into this equation, we obtain

$$\frac{1}{n_x} \ln \left\{ \frac{1 - (1 - \alpha)^{1-n_x}}{(1 - n_x)T^2} \right\} = \left( \frac{E}{n} \right) \frac{T - T_s}{RT_s T} + \frac{1}{n_x} \ln \frac{E}{T_s^2(E + 2RT)}. \quad (9)$$

For the case  $n \rightarrow 1$ , after resolving the indefiniteness  $0/0$ , we obtain

$$\ln \left[ \frac{-\ln(1 - \alpha)}{T^2} \right] = E \frac{T - T_s}{RT_s T} + \ln \frac{E}{T_s^2(E + 2RT)}.$$

If the plot  $\frac{1}{n_x} \ln \left\{ \frac{1 - (1 - \alpha)^{1-n_x}}{(1 - n_x)T^2} \right\}$  versus  $\frac{T - T_s}{RT_s T}$  yields a straight line, whose slope allows determination of the value of  $\left( \frac{E}{n} \right)$ .

Thus, given any approximate value  $n_x$ , the ratio  $\left( \frac{E}{n} \right)$  can be determined with satisfactory accuracy for the given actual kinetic curve. Obviously, it will be expedient for a comparative kinetic analysis of a number of chemical reactions of the same type to utilize a characteristic activation energy value  $\bar{E}_i$  equal to the ratio  $\left( \frac{E}{n} \right)_i$ .

Let us analyze the case when  $n \rightarrow 0$ . Then, Eq. (8) will assume the form

$$\ln \frac{\alpha}{T^2} = \frac{E_0(T - T_s)}{RT_s T} + \ln \frac{E_0}{T_s^2(E_0 + 2RT)} \quad (10a)$$

or

$$\ln \frac{\alpha}{T^2} = -\frac{E_0}{RT} + \text{const.} \quad (10b)$$

which, by differentiation, yields the equation

$$\frac{d \ln \alpha}{dT} = \frac{E_0}{RT^2} - \frac{2}{T} = \frac{E_0 - 2RT}{RT^2}. \quad (11)$$

According to Gorbachev et al. [6], Nikolaev et al. [7] and Stepin et al. [8], the value of the activation energy  $E_0$  is close to the corresponding enthalpy change  $\Delta H$  of the endothermic reaction.

## References

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ZUSAMMENFASSUNG — Für jede kinetische Kurve, welche mit der Gleichung

$$\frac{dx}{dT} = (1 - \alpha)^n \frac{A}{q} \exp\left(-\frac{E}{RT}\right)$$

zu beschreiben ist, wurde die Konstanz des Verhältnisses  $\frac{E}{n}$  beobachtet. Dies bestätigte sich unabhängig von der Genauigkeit der Bestimmung der tatsächlichen Reaktionsordnung  $n$ , d. h.  $\frac{E_{\text{wahr}}}{n_{\text{wahr}}} = \frac{E_x}{n_x}$ , wo  $n_{\text{wahr}}$  und  $E_{\text{wahr}}$  sind die realen Werte, während  $n_x$  und  $E_x$  experimentell bestimmte Werte sind. Die genaue Kenntnis des Wertes  $\tilde{E} = \frac{E}{n}$  gestattet die Schätzung des Wertes  $E_y$  für einen weiteren annähernden Wert von  $n_y$  mittels der Formel  $n_y = n_y \tilde{E}$ .

RÉSUMÉ — Pour les courbes thermocinétiques auxquelles on peut effectivement appliquer l'équation

$$\frac{dx}{dT} = (1 - \alpha)^n \frac{A}{q} \exp\left(-\frac{E}{RT}\right)$$

on a observé une valeur constante pour le rapport  $E/n$  et cela, indépendamment de l'exactitude de la détermination de l'ordre de réaction  $n$  effectif; ceci veut dire que  $\frac{E_{\text{vrai}}}{n_{\text{vrai}}} = \frac{E_x}{n_x}$ , où  $n_{\text{vrai}}$  et  $E_{\text{vrai}}$  sont les valeurs vraies tandis que  $n_x$  et  $E_x$  sont les valeurs déterminées par voie d'expérience. La connaissance exacte de la valeur  $\tilde{E} = E/n$  permet d'estimer la valeur  $E_y$  pour une autre valeur approximative de  $n_y$  par la formule  $n_y = n_y \tilde{E}$ .

Резюме — Для каждой конкретной термокинетической кривой, описываемой уравнением

$$\frac{dx}{dT} = (1 - \alpha)^n \frac{A}{q} \exp\left(-\frac{E}{RT}\right)$$

соблюдается постоянство отношения  $(E/n)$  независимо от точности определения эффективного порядка  $n$ , т. е.  $\frac{E_{\text{ист}}}{n_{\text{ист}}} = \frac{E_x}{n_x}$ , где  $n_{\text{ист}}$  и  $E_{\text{ист}}$  истинные значения, а  $n_x$  и  $E_x$  экспериментально полученные величины. Точное знание величины  $\tilde{E} = (E/n)$  дает возможность оценить величину  $E_y$  для другого приближенного значения  $n_y$  по формуле  $E_y = n_y \tilde{E}$ .