Thermochimica Acta, 92 (1985) 85-88
Elsevier Science Publishers B.V., Amsterdam

KINETIC PARAMETERS FROM INFLECTION POINTS OF THERMOANALYTICAL CURVES

Heinz Anderson
E.M.-Arndt-University Greifswald, Department of Chemistry,
Greifswald, GDR

ABSTRACT

With increasing accuracy of the thermoanalytical techniques methods of kinetical evaluation can be realized, which did not need the whole information of the measured curves. It will be shown a quantitative connection between the order of reaction and the following values at the inflection point: Turnover of reaction, rate of reaction and acceleration or retardation of reaction respectively. In case of hyperbolic heating programme these values are entire independent of frequency factor and activation energy.

In the last twenty years kinetical considerations kept their place in thermal analysis (TA). According to the type of process or reaction different mathematical descriptions have been prefered. Naturally this proceeding is senseless if the mathematical model does not agree sufficiently with the real reaction. The ascertainment of the classical kinetic parameters activation energy E, reaction order n, rate constant k and factor of frequency k_0 have been realized by evaluation of the thermoanalytical curves using differential and integral methods respectively (1-3). There exist also procedures, in connection with the position of peak maximum(4). In this paper the inflection points of that TA-curves are the basis, which hold the reaction rate as a function of time or temperature. Investigations of model curves according to eq.7 yielded a form index as the ratio of the slopes of the tangents at the first and second inflection point.

$$S_x = \frac{(d^2x/dt^2)_1}{(d^2x/dt^2)_2} \quad \text{and for DTA-curves} \quad S_T = \frac{(d\Delta T/dt)_1}{(d\Delta T/dt)_2} \qquad (1)$$

If the temperature is programmed by equation (2), then for the form

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Proceedings of ICTA 85, Bratislava

index result relations, which contain the square root of the reaction order (5).

$$dT/dt = Q_b T^b \qquad (2)$$

With b = 0, linear heating $\quad S_{xo} = p_o\, n^{0,5} + q_o \qquad (3)$

b = 1, exponential $\quad S_{x1} = p_1\, n^{0,5} + q_1 \qquad (4)$

b = 2, hyperbolic $\quad S_{x2} = p_2\, n^{0,5} + q_1 \qquad (5)$

Results of eq.(3) agree approximately with the relation of Koch (6). Other relations (7,1) deviate considerably to eq.3.
An important knowledge from the investigation at many exact model curves is the fact, that p_o, q_o resp. p_1 and q_1 show a weak dependence to the logarithm of frequency factor. Power series with three terms describe this coherence, for example:

$$p = d + e \cdot \log k_o + f \cdot \lg^2 k_o \qquad (6)$$

Exclusive for hyperbolic heating programme (b = 2; $p_2 = -1{,}181$; $q_2 = 0{,}664$) the dependence to lg k_o disappear.
On the premises of a normal statement about the reaction rate of simple chemical reactions, from the consideration of the third derivations to the time yielded an expression for the form index eq.7.

$$dx/dt = k_o \exp(-E/RT)\,(c_o - x)^n \qquad (7)$$

$$\Big[(n/c_o - x) \cdot dx/dt\Big]_{1,2} = EQ_2/R \cdot (3 \mp \alpha)/\beta \qquad (8)$$

$$S_{xb} = \frac{(c_o - x_1)\ (3 - \alpha_1)\ (\beta - 3 + \alpha_1)}{(c_o - x_2)\ (3 + \alpha_2)\ (\beta - 3 - \alpha_2)} \cdot (T_2/T_1)^{2(2-b)} \qquad (9)$$

$$\text{with } \alpha_{1,2} = \left[9 - 4(2 - 1/n)(1 - (2-b)RT_{1,2}/E)\right]^{1/2} \qquad (9a)$$

$$\beta = 2(2 - 1/n)$$

For b=2 according to eq.10 S_{x2} is consisted of three factors. Because of the only dependence of n for F_1 and F_2 the ratio of the remaining concentrations $(c_o - x)$ is even a function of n alone.

$$S_{x2} = \frac{(c_o - x_1)\ (3 - \alpha)\ (\beta - 3 + \alpha)}{(c_o - x_2)\ (3 + \alpha)\ (\beta - 3 - \alpha)} = \frac{(c_o - x_1)}{(c_o - x_2)} \cdot F_1 \cdot F_2 \qquad (10)$$

The new method of kinetical evaluation yields from following steps.

1. Calculation of the reaction order with help of eq.5 by putting in the slope of tangents at both inflection points.
2. After this we use eq.8 for the first inflection point with experimental values of x_1 and $\left(\frac{dx}{dt}\right)_1$. With this we receive the activation energy.
3. Finally with the basic formular 7 the determination of the frequency factor k_0 is possible.

Repeating this procedure at the second inflection point should give the same values E and k_0. Therefore this kind of evaluation accepts the character of a test of consistency between experimental values (c_0-x), $\dot{x}$ and $\ddot{x}$ at the inflection points and the calculated parameters n, E, k_0.

The main advantage of this method always then appears, if we search not for any values of reaction order but only for integer or selected broken values. In such cases the claims to the experimental accuracy according to $\ddot{x}$ are not to high. The determinations of x_1 and $\dot{x}_1$ are less difficult.

There is no doubt about it that the described procedure of evaluation could be transfered to thermoanalytical curves under exponential and linear heating programmes respectively. Then we need additionally those temperatures of the curve, where the inflection points have been observed. In good approximation α may the same for both inflection points, for example taking the temperature of peak maximum as a mean value for eq.9a.

Nevertheless a sufficient evaluation by this method is only then possible, if the experimental thermoanalytical technique stands on a high level. Therefore the proposed procedure turns out as a relativ sensible detector for experimental errors and disturbations or mistakes in the mathematical model of the reaction under investigation.

An other consequence of eq.10 for hyperbolic heating programmes leads to new parameters for the characterization of the inflection points of TA-curves. The instantaneous ratio of the remaining concentrations of a reaction under thermoanalytical conditions depends on the reaction order alone (eq.11).

$$\frac{c_0-x_1}{c_0-x_2} = \frac{S_{x2}}{F_1 \cdot F_2} = \varphi(n) \qquad (11)$$

By application of eq.8 for both inflection points of one curve we receive the ratio of the reaction rates at this points as an only function of reaction order.

$$\frac{c_o - x_2}{c_o - x_1} \cdot \frac{(dx/dt)_1}{(dx/dt)_2} = \frac{3 - \alpha}{3 + \alpha} = F_1 \qquad (12)$$

$$\frac{(dx/dt)_1}{(dx/dt)_2} = \frac{c_o - x_1}{c_o - x_2} \circ F_1 = \frac{S_{x2}}{F_2} = \psi(n) \qquad (13)$$

The three conditions of eq.10,11 and 13 give several possibilities of evaluation of thermoanalytical curves. The different behaviour of the parameter S_{x2}, φ and ψ allow a critical calculation of kinetic parameters.

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