QUANTITATIVE PARAMETERS BY THERMOANALYTICAL METHODS

H. Anderson

DEPARTMENT OF CHEMISTRY, E. M.-ARNDT UNIVERSITY OF GREIFSWALD, G.D.R.

The conditions and premises of the kinetic evaluation of thermoanalytical curves on the basis of chemical kinetics are demonstrated, and the limits of their availability are pointed out. For reactions with an unclear structural and chemical course, some appropriate definitions of terms are proposed.

The possibilities of the use of the inflection points of the reaction rate versus time curve are presented. New methods of determination of kinetic parameters are described, including the ratio of the degrees of reaction x, the ratio of the reaction rates $\dot{x}$ and the ratio of the tangent slopes $\ddot{x}$ at these points.

A century after the first application of a thermoanalytical technique by Le Chatelier, some problems of thermal analysis remain. One point of controversy relates to the quantitative evaluation of nonisothermal experiments. At present, it seems doubtful whether the accuracy of isothermal investigations will ever be attained, and Benoit *et al.* [1] conclude that before a quantitative non-isothermal investigation can be evaluated an isothermal

measurement has to be performed, which confirms the constancy of reaction order in this temperature range. Here, TG results will be valued much more highly than those of DTA, although the one method cannot be substituted by the other.

Kinetic findings from TG and DTA

As concerns the methods used for kinetic evaluation, we distinguish differential and integral methods on the one hand, and difference and single point methods on the other. Increasingly, computers are connected with the thermoanalytical instrument or employed off-line to decide on the evaluation equation. Some years ago we compared 9 different methods for kinetic parameter calculation on the basis of computerized TG/DTA model curves [2].

This attempt showed that several methods are mathematical approximations with a tendency to gross errors. Others methods are mathematically exact, but supersensitive to small deviations from the theoretical model curves, and hence to any experimental uncertainty. Incidentally, methods which take into account only a single point are much more subject to mistakes than those which consider the total information content of the curve. Mathematical error-equalizing by means of least squares will lead to satisfactory success only when the complete curve is included. Because of the lower expense, the evaluation method should in every case be more than one hundred times more precise than the measurement [3]. Today we possess methods of kinetic evaluation for all situations. The choice of method should correspond to the experimental level employed. The main problem, however, is still the acceptance of a uniform one-step mechanism which is assumed to control the rate of the process or reaction considered. In most TA experiments with solid-state materials, this assumption does not correspond to the real situation. At this point we need independent investigations supplementary to TA, which enable us to decide on the rate control in any phase of the reaction.

Parameters defined by the kinetics of chemical reactions are meaningless if the chemical background has not been clarified or if more than one process step — consecutive or simultaneous — makes a substantial contribution to the recorded TA curve. Before computerizing the experimental data at all, we should check the fulfilment of certain questions, irrespectively of whether we have worked isothermally or non-isothermally:

1. What do we know about the reproducibility of the total experimental performance and the measuring accuracy?
2. What intermediates and final products were detected? – Chemical analysis!
3. What changes of phases and structure were observed?
   – Physical analysis!
4. What physical event or chemical reaction should be the pace-maker?
5. What mechanism could be proposed for the pace-maker? Which adequate mathematical description is justified?

Besides scientifically based model equations, formal mathematical descriptions are used as an expression of the empirical applied research work. In these cases the terms of reaction kinetics should be avoided. For this reason, we propose the use of the following definitions of quantitative terms.

The process under investigation is structurally and chemically

clarified	*partially or totally unclear*
Reaction rate dx/dt	Process rate, e. g. dm/dt
Activation energy E in E/RT	Characteristic temperature A in A/T
Frequency factor k_0	Preexponential factor Z
Order of reaction n	Process exponent ν

In this way the confusion at present prevailing in the literature and in some disputes will disappear.

Special information deduced from the inflection points of the TA curve

Any TG curve contains some characteristic positions with distinguished values of the reaction rate. The derivative curve (DTG) shows a maximum (rm) with the greatest reaction rate and two points where the slope reaches an extremum, i.e. the first and second inflection points. On the other hand, the parameters of the positions of the inflection points are calculated on the basis of model curves obtained by integration of the differential equation corresponding to a linear or non-linear heating rate [4]:

$$\frac{dT}{dt} = Q_b \cdot T^b \qquad \text{e.g. } b = 0 \text{ linear} \qquad (1)$$
$$b = 1 \text{ exponential}$$
$$b = 2 \text{ hyperbolic}$$

The slopes of the tangents at the inflection points lead to the shape index for the reaction rate curve S_x, for example for DTG, and to S_T for the DTA curve.

$$S_x = \frac{(d^2 x/dt^2)_1}{(d^2 x/dt^2)_2}; \qquad\qquad S_T = \frac{(d\Delta T/dt)_1}{(d\Delta T/dt)_2} \qquad (2)$$

In the case of S_x, we found [5] a relation which contains the square root of the reaction order (see Kissinger [6], Heek [7], Koch [8]:

$$S_{xb} = p_b \cdot n^{1/2} + q_b \qquad (3)$$

As the exponent b varies from 0 to 2, the coefficients p and q will change. For constant b, with the exception of hyperbolic heating, the coefficients depend weakly on the logarithm of the frequency factor. On the premises of Arrhenius statement about the reaction rates of simple chemical reactions, a consideration of the third derivatives with respect to time will yield an expression of the shape index S_{xb}, according to Eq. 6:

$$\frac{dx}{dt} = k_0 \exp(-E/RT)(c_0 - x)^n \qquad (4)$$

$$[n/(c_0 - x) \cdot \frac{dx}{dt}]_{1,2} = \frac{EQ_b}{R}(3 \mp \alpha)/\beta \qquad (5)$$

$$S_{xb} = \frac{(c_0 - x_1)(3 - \alpha_1)(\beta - 3 + \alpha_1)}{(c_0 - x_2)(3 + \alpha_2)(\beta - 3 - \alpha_2)} \cdot \left(\frac{T_2}{T_1}\right)^{2(2-b)} \qquad (6)$$

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

If $b = 2$, i.e. for hyperbolic heating, we get a shortened formula (Eq. 7), in which α is only a function of the reaction order:

$$S_{x_2} = \frac{(c_0 - x_1)(3 - \alpha)(\beta - 3 + \alpha)}{(c_0 - x_2)(3 + \alpha)(\beta - 3 - \alpha)} = \frac{c_0 - x_1}{c_0 - x_2} \cdot F_1 \cdot F_2 \qquad (7)$$

According to this relation, the shape index is given by n and by the concentrations at the inflection points, independently of the activation parameters. The new method of kinetic evaluation involves the following steps. First, we calculate the reaction order n with the help of Eq. (3) by putting in the slopes of the tangents at both inflection points. Secondly, we apply

Formula (5) to the first inflection point and introduce x_1 and $(dx/dt)_1$ to get the activation energy E. When we do the same at the second inflection point, the result in E must agree with that above. In this way we test the consistency of experiment and theoretical model. In a third step, we determine the frequency factor with the help of Eq. 4.

The essential advantage becomes manifest whenever we search not for any values of reaction order, but only for integral or selected fractional values. In such cases the claims on the experimental accuracy corresponding to $\ddot{x} = d^2x/dt^2$ are not too high. It is well known that determination of x and $\dot{x}$ is less difficult.

Nevertheless, a satisfactory kinetic evaluation by this method is practicable only if the experimental technique is on a high level. Therefore, the proposed procedure turns out to be a relatively sensitive indicator of experimental uncertainties or of a bad choice of the equation of the reaction model which misrepresents the real process. In most of these cases, this suggests complex reactions [9]. A similar proceeding is allowed to evaluate TA curves under linear or exponential heating or for any values of b. For this we additionally need the temperatures T_1 and T_2 of the inflection points and an estimated E value in Eq. 6. In order to improve the accuracy, the evaluation should be repeated with the approximately determined E value from the first course. Finally, we attain the same quality of results as for the hyperbolic heating programme.

Further conclusions from S_{x_2}

From the modelled thermoanalytical curves, we derived the shape index for hyperbolic heating in the form of Eqs 3 and 7:

$$S_{x_2} = -1.182\, n^{1/2} + 0.664 \tag{3a}$$

S_{x_2}, F_1 and F_2 are exclusively dependent on the reaction order. After a simple transposition of Eq. 7, an important proposition arises. Now a summary of the three rations at the inflection points, i.e. of the unreacted parts $(c_0 - x)$, of the reaction rates $\dot{x}$ and the reaction accelerations or retardations $\ddot{x}$, may be given:

$$\frac{c_0 - x_1}{c_0 - x_2} = \varphi\,(n) \tag{8a–c}$$
$$\dot{x}_1/\dot{x}_2 = \varphi\,(n)\cdot F_1 = \Psi\,(n)$$
$$\ddot{x}_1/\ddot{x}_2 = \varphi\,(n)\cdot F_1\cdot F_2 = \Psi\,(n)\cdot F_2 = S_{x_2}$$

Table 1 Values of φ, Ψ, S_{x_2} as function of reaction order

n	F_1	$-F_2$	$-S_x = -\dfrac{\dot{x}_1}{\ddot{x}_2}$	$\dfrac{S_x}{F_2} = \dfrac{\dot{x}_1}{\dot{x}_2}$	$\dfrac{S_x}{F_1 F_2} = \dfrac{c_0 - x_1}{c_0 - x_2}$
0.5	0	0	0.171	∞	∞
0.6	0.0400668	$8.535935 \cdot 10^{-2}$	0.250798	2.93815	73.3312
2.3	0.0627463	0.138998	0.300	2.15830	34.3973
0.8	0.1010386	0.240408	0.39232	1.63188	16.1511
1.0	0.145898	0.381965	0.517	1.35352	9.2772
1.33	0.2	0.600	0.700	1.16666	5.8333
1.5	0.220802	0.703465	0.782424	1.11224	5.0372
2.0	0.267949	1.000	1.000	1.000	3.7320
2.5	0.300827	1.283195	1.20332	0.93775	3.1172
3.0	0.325247	1.558256	1.382	0.88688	2.7268
5	0.381966	2.618035	1.976796	0.75506	1.9767
10	0.434363	5.175201	3.070649	0.59335	1.3661
∞	0.500	∞	∞	0,5	1,0
				$\Psi_{(n)}$	$\varphi_{(n)}$
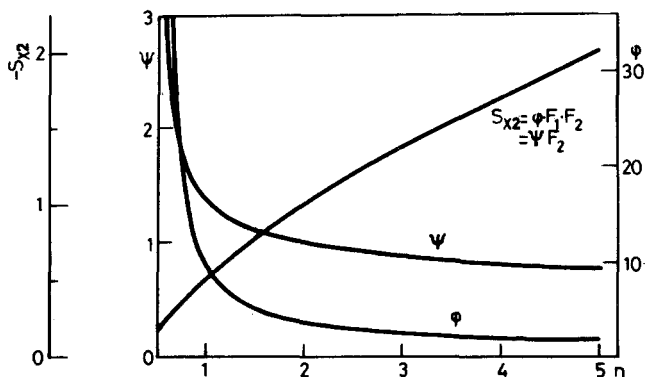
Fig. 1   Shape index S_{x_2} and coefficients φ and Ψ as functions of reaction order n

Table 1 shows discrete values of φ, Ψ and S_{x_2} as functions of the reaction order above $n = 0.5$. The S_{x_2} values for $n = 2/3$, 4/3, 2 and 5 are noteworthy, as are the Ψ values for $n = 4/3$ and 2. The φ value of about 2.0 for $n = 5$ is equal to that of S_{x_2} because $F_1 \cdot F_2 = -1$. Figure 1 depicts the dependences of the functions φ, Ψ and $-S_{x_2}$ on the reaction order. While the first and the second decrease with increasing n, the negative S_{x_2} value

rises continuously. The Ψ curve reveals that with increasing reaction order n the ratio of the reaction rates at the inflection points, $\dot{x}_1/\dot{x}_2$, decreases. Above $n = 2$, the reaction rate at the second inflection point is absolutely larger than that at the first.

Another interesting observation is the fact that for $n = 2$ not only the rates of reaction at both inflection points are equal, but also their derivatives with respect to time, i.e. the acceleration at point 1 and the retardation at point 2. In Fig. 1 we see that the parameter Ψ is very insensitive to changes in n in the region above $n = 2$. In contrast to this tendency, both Ψ and φ are much more sensitive in the lower region, especially for $n < 1$. Therefore, we shall find the optimal application of the three parameters together in that range in which most practical cases occur. This opens a way to a new method of estimating the activation energy. After the determination of the reaction order with the help of Eq. 3, e.g. with a value 2, we formulate

$$\Psi = 1 = \exp\left[-E/R(1/T_1 - 1/T_2)\right] \cdot \varphi^2$$

(9)

$$E = 21.899 \frac{T_1 \cdot T_2}{T_2 - T_1} \text{ J} \cdot \text{mole}^{-1}$$

For this we only need the temperatures of both inflection points. This procedure may be generalized for any reaction order. Since the φ value contains the integrated TA curve from the start to the respective inflection points, this evaluation method is not to be put on a par with those which include only one item of information about a selected point. In principle, all these considerations are transferable to linear and exponential heating programmes if one is ready to accept a slight loss of accuracy, which can be compensated for by weak corrections, however. Figure 2 shows a generalized thermo-analytical curve $\dot{x}$ vs. t or T, e.g. a DTG curve. Since not any reaction order is concerned and only certain values of n are to be taken into account, e.g. an integer or selected vulgar fractions, it is allowed to use some advantages to secure a good quality of the evaluated reaction parameters. The arrows in Fig. 2 at the first and the second inflection points demonstrate how both points are shifted, if one of them is fixed inaccurately. For deviations from the correct inflection points, the three characteristic functions show different behaviour in so far as the reaction order can be supposed to be constant.
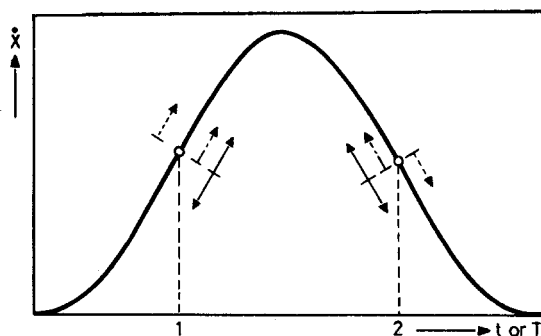
Fig. 2   Influence of errors from the first on the second inflection point

1. $\varphi(n)$ remains constant only when both points move to the right or to the left. An increase of x_1 can be compensated for only by an increase of x_2.

2. $\Psi(n)$ remains constant only when both points move towards the peak or outwards.

3. S_x remains constant only when, with diminution of the slope of the first inflection tangent the slope of the second is also reduced. This can be effected, however, by shifting in both directions, starting from one inflection point, i.e. when the shape index S_x is correct, the pair of inflection points is not necessarily the right one, because other pairs of tangents could form the same ratio S_x.

However, if the functions φ, Ψ and S_x calculated from a TA curve correspond to the same value of the reaction order, then experiment and evaluation are excellent. On the other hand, all calculations acquire more certainty when the above three functions are applied jointly. Consequently, the results of the respective evaluation method can be improved.

References

1 H. Anderson, W. Besch and D. Haberland, J. Thermal Anal.; 12 (1977) 59.

2 P. M. D. Benoit, R. G. Ferrillo and A. H. Granzow, J. Thermal Anal., 30 (1985) 869.

3 S. V. Vyazovkin and A. J. Lesnikovich, J. Thermal Anal., 31 (1986) 319.

4 H. Anderson, D. Haberland and E. Witte, J. Thermal Anal., 17 (1979) 409.

5 H. Anderson, E. Witte and D. Haberland, J. Thermal Anal., 21 (1981) 327.

6 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.

7 H. Jüntgen and K. H. Heek. Ber. Bunsenges. Physik. Chem., 72 (1968) 1223.

8 E. Koch and B. Stylkerieg, Thermochim. Acta, 17 (1976) 1.

9 M. Balarin, Thermochim. Acta, 33 (1979) 341.

Zusammenfassung – Bedingungen und Voraussetzungen der kinetischen Auswertung thermoanalytischer Meßkurven auf der Basis der chemischen Kinetik werden dargestellt, gleichzeitig wird auf die Grenzen ihrer Gültigkeit hingewiesen. Für Reaktionen mit unklarem chemischem oder strukturellem Ablauf werden geeignete neue Bezeichnungen definiert.

Die Möglichkeit zur Verwendung der Wendepunkte 'der Kurve Reaktionsgeschwindigkeit gegen Zeit vorgestellt. Neue Methoden werden beschrieben, die zur Bestimmung kinetischer Parameter das Verhältnis der Umsätze x_1/x_2, das Verhältnis der Reaktionsgeschwindigkeiten $\dot{x}_1/\dot{x}_2$, und das Verhältnis der Tangentensteigungen $\ddot{x}_1/\ddot{x}_2$ an den Wendepunkten verwenden.

РЕЗЮМЕ — Показаны условия и предпосылки кинетической оценки термоаналитических кривых на основании данных химической кинетики. Отмечены также пределы их пригодности. Для реакций с неясным структурным и химическим ходом были предложены некоторые подходящие определения терминов. Показана возможность использования точек инфлексии на кривой в координатах скорость реакции — время. Описаны новые методы определения кинетических параметров, включая отношение степеней реакции (x), отношение скоростей реакции $(\dot{x})$ и отношение тангенсов наклона $(\ddot{x})$ в этих точках.