Journal of Thermal Analysis, Vol. 19 (1980) 289—296

DIRECT LEAST SQUARES FIT OF CHEMICAL REACTION CURVES AND ITS RELATION TO THE KINETIC COMPENSATION EFFECT

N. EISENREICH

Fraunhofer-Institut für Treib- und Explosivstoffe Institutsstraße D 7507 Pfinztal-Berghausen, BRD

(Received September 14, 1979)

The evaluation of kinetic parameters from chemical reaction curves implies data-fitting procedures. Direct search methods are studied to minimize the Chi Square Function with respect to the activation energy and pre-exponential factor. The geometrical shape of the Chi Square Function can be related to the kinetic compensation effect as discussed in the literature. The minimization with respect to the pre-exponential factor can be solved analytically if the Chi Square Function includes integrated forms of the reaction mechanisms.

The investigation of chemical reactions under programmed temperature variations allows the evaluation of the reaction parameters (see e.g. [1] and references cited therein). Their calculation depends on the solution of the least squares fit problem. Commonly used methods involve exact or approximated linear relations between theoretical and experimental data. The possible linear regression analysis is the corresponding analytical solution of the fit problem. The facilities of computers, which are now used to an increasing extent [1—7], allow the numerical minimization of the Chi Square Function.

In this paper the geometrical shape of the Chi Square Function is studied with respect to the activation energy and pre-exponential factor. In addition some direct search methods are tested.

Kinetic equations

In general, solid-state reactions can be described in the following form, if substitution is made to account for linear heating [1, 8, 9]:

$$\frac{dc}{dT} = -\frac{k(T)}{B} f(c) \tag{1}$$

c = reactant not yet converted
$f(c)$ = mathematical form of reaction mechanism
B = heating rate
$k(T)$ = usually Arrhenius rate constant

$$k(T) = Ze^{-E/(RT)}$$

E = activation energy
Z = pre-exponential factor.

The integrated form of (1) is given by (2) [1, 8–10]:

$$g(c) = -\frac{Z}{B} S(T, E)$$

$$g(c) = \int \frac{\mathrm{d}c}{f(c)} \tag{2}$$

$$S(T, E) = \int e^{-E/(RT)} \mathrm{d}T$$

$S(T, E)$ can be obtained by numerical integration or by an asymptotic expansion (see e.g. [1, 10, 11]).

By inverting (2), one can obtain an expression for c:

$$c = F\left(\frac{Z}{B} S(T, E)\right). \tag{3}$$

Experimental reaction curves (e.g. TG curves) are directly related to (3). The differential curves are proportional to (1) if c is substituted by (3). Necessary corrections due to the experimental set-up have to be carried out in a separate procedure [1, 5, 12].

Least squares fit

A theoretical curve $h(x, a, b, \ldots)$ is fitted to N data points y_i, x_i by the minimization of the so-called Chi Square Function Q with respect to the fitting parameters $a, b \ldots$

$$Q(a, b, \ldots) = \sum_{i=1}^{N} (y_i - h(x_i, a, b, \ldots))^2 W_i \tag{4}$$

The weighting factors W_i are set equal to 1 in the further discussion. In the case of reaction curves, y_i and x_i correspond to the digitized values c_i and T_i of an experimental curve – a TG curve, for example – and $h(x, a, b, \ldots)$ corresponds to (3). For differential curves, y_i has to be substituted by the digitized and normalized measured values. $h(x, a, b, \ldots)$ is then given by (1), with c substituted by (3), however.

The minimum of $Q(a, b, \ldots)$ can be found analytically only if $h(x, a, b, \ldots)$ is a linear function of a, b etc. As (1) and (3) are not linear with respect to the relevant fitting parameters E and Z, the problem has to be solved numerically.

A simplification can be obtained if (2) is used for the formation of Q:

$$Q(E, Z) = \sum_{i=1}^{N} \left(g(c_i) + \frac{Z}{B} S(T_i, E)\right)^2 \tag{5}$$

$h(T_i, E, Z)$ is linear with respect to Z in (5). Hence the relative minimum of $Q(E, Z)$ can be found after differentiation in an analytical procedure:

$$\frac{Z}{B} = -\frac{\sum_{i=1}^{N} S(T_i, E)g(c_i)}{\sum_{i=1}^{N} S^2(T_i, E)} \quad (6)$$

Thus, the number of fitting parameters to be calculated numerically is reduced by one.

Besides E and Z, the least squares fit can be extended to other parameters involved in $g(c)$.

Geometrical shape of the Chi Square Function

The minimization of (4) was carried out by applying different direct search methods for given reaction mechanisms. Test functions of the type (3) and (1), and experimental TG and DTA curves were studied.

The simplest approach to find the minimum of (4) is to form a two-dimensional grid with E and Z as coordinates, and to compare the values of $Q(E, Z)$. In addition, the Chi Square Function can be mapped in order to study its geometrical shape.

Applied to test functions, the minimum was found at the exact values (E_{min}, Z_{min}) with Q equal to 0. Figure 1 represents a typical example of a mapped Chi Square Function. $Q(E, Z)$ consists of a narrow elongated valley. The projection of the valley bottom on the E – log Z plane is a straight line. The parameters of this line are listed in Table 1. The slow variation of Q along this valley bottom is shown

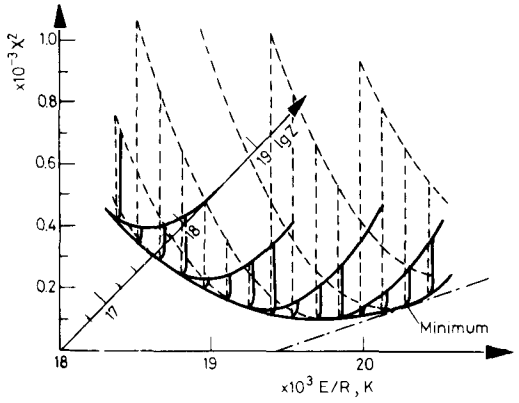

Fig. 1. Geometrical representation of a Chi Square Function of a test function a reaction curve of order 1 (E/R = 20000, log Z = 17, $h(T, Z, E) = c(T) = \exp(-ZS(E, T)/B)$)

in Fig. 2. The increase in direction of higher values of the reaction parameters is quite small. A steep rise, in contrast, is observed if one parameter is kept constant. In this case $Q(E, Z)$ arrives at plateaus on each side of the valley. The qualitative behavior of $Q(E, Z)$ is independent of the reaction mechanism and is similar for differential curves. An example of a Chi Square Function of this type of curve is depicted in Fig. 3.

The consequences of experimental curves are also evident in Fig. 3 because an experimental DTA curve (DuPont 990 Thermal Analyzer) was studied. $Q(E_{min}, Z_{min})$ is no longer 0. The increase of $Q(E, Z)$ along the relative minimum is essen-

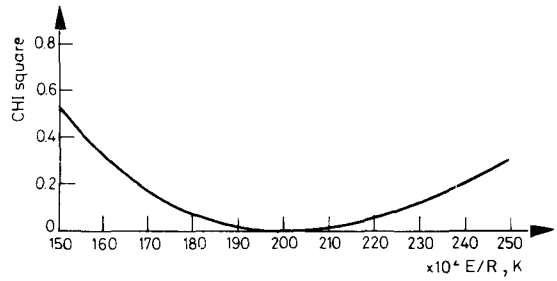

Fig. 2. A cut through the Chi Square Function in the direction of the valley bottom (for test function see Fig. 1)

tially slower than for test functions. The reaction investigated is the decomposition of nitrocellulose in double-base propellants. The obtained values of the minimum are 45.2 kcal/mole and 18.7 for E and log Z, respectively. These values agree well with those published in the literature [13 – 15]. The parameters of the straight line of the projection of the valley bottom on the E – log Z plane are listed in Table 1. Further results involving this method are published elsewhere [10, 16].

Table 1

Parameters of the relative minima

	Calculated according to Nikolaev et al.		Relative minimum of Chi Square Function	
	a	*b*	*a*	*b*
Test function (see Fig. 1)	$1.003\ 10^{-3}$	−3.052	$1.029\ 10^{-3}$	−3.589
Test function use of (6)	$1.003\ 10^{-3}$	−3.052	$0.996\ 10^{-3}$	−2.921
Exp. DTA curve (Fig. 3)	$0.895\ 10^{-3}$	−1.496	$0.9075\ 10^{-3}$	−1.816
Exp. TG curve (*)	$5.727\ 10^{-4}$	−3.184	$6.065\ 10^{-4}$	−3.884
Exp. TG curve (**)	$5.727\ 10^{-4}$	−3.184	$5.788\ 10^{-4}$	−3.302

(*) Oxidation of activated charcoal [16], $E_{min} = 45.2$ kcal/mole, log $Z_{min} = 9.78$
(**) The same reaction fitted by use of (6)

A fast and rapid converging direct search method was introduced by Powell [17]. Applying it to the same test functions and experimental curves, the fit parameters agreed well with those obtained above. The accuracy of agreement naturally depends on the width of the grid mesh of the method described first. However, the computing time was reduced by several orders of magnitude. If, especially, more parameters have to be evaluated, this method should be preferred. A problem with respect to initial values arises from the plateaus of the Chi Square Function. In the case of values E and Z on these plateaus, the corresponding reaction intervals are

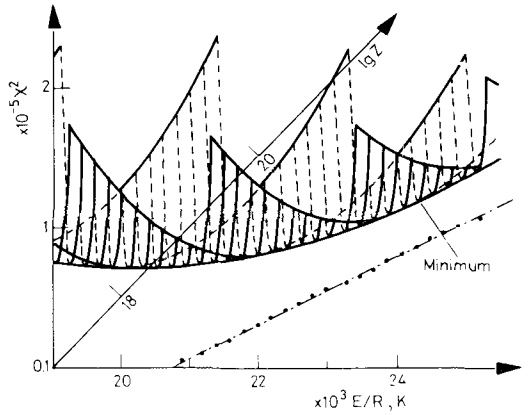

Fig. 3. Geometrical representation of a Chi Square Function of an experimental DTA curve (decomposition of nitrocellulose in a double base propellant as referred to in the text $h(T, Z, E) = Z/B \exp(-E/(RT)) \exp(-ZS(E, T)/B)$)

completely outside the reaction interval of the curve to be fitted. Then, $Q(E, Z)$ is given by $N(1 - c_i)^2$ or Nc_i^2 for reaction curves, and Nq_i^2 for differential curves (q_i experimental values), and does not vary with altered parameters. Thus, both initial values have to be selected carefully to have an initial reaction interval which overlaps the reaction interval of the curve to be fitted. Taking into account the special geometrical shape of the Chi Square Function, the valley bottom can be found in a first step. Then, further iteration can take place along the straight line of the valley bottom, if its direction is obtained in a second step. In the case of reaction curves, (6) can be used. For arbitrarily, but reasonably chosen parameters E, the corresponding parameter Z is calculated, resulting in an initial reaction interval still overlapping the curve to be fitted.

Applying (6) for the least squares fit, approximately the same reaction parameters were obtained. A plot of log Z versus E of (6) resulted in straight lines with high correlation coefficients ($r > 0.999$). Small differences of the parameters of the straight line (see Table 1) can be explained by the different weighting of data points if $g(c_i)$ is used instead of c_i to form the Chi Square Function. Equation (6) need not necessarily coincide with the valley bottom of the least squares fit, as it is only the relative minimum with respect to Z.

As an experimental example, the oxidation of activated charcoal, recorded in a TG experiment, was studied. The reaction parameters are 45.2 kcal/mol and 9.78 for E and $\log Z$. They agree well with those obtained by the application of the method described first, which are 46.8 kcal/mol and 10.27, respectively [16].

Kinetic compensation effect

The kinetic compensation effect was recently reinvestigated [18–22]. The results obtained from the shape of the Chi Square Function reveal a pure mathematical or numerical influence of the Arrhenius rate constant. However, they do not indicate any physical nature of the effect.

The relative minimum of the Chi Square Function can be represented by a linear equation, just as that of the kinetic compensation effect:

$$\log Z = b + aE/R. \tag{7}$$

Also, the calculation of the relative minimum with respect to Z according to (6) leads to the same relation of the fitting parameters.

Especially the Chi Square Function of the experimental curves increases very slowly, if the fitting parameters are varied according to the valley bottom of the Chi Square Function. This means that a wide range of theoretical reaction curves fit the curve under investigation within the experimental error. However, their parameters E and Z have to satisfy (7). All these curves have similar reaction intervals. Curves with higher values of E are steeper and those with lower values are flatter. Curves with one parameter of the minimum and the other altered are shifted parallel to the reference curve. Then, the Chi Square Function increases rapidly. According to the approach of Nikolaev *et al.* [18, 19] the parameters a and b are:

$$b = \log EB/(RT_p^2) \qquad a = \log e\, 1/T_p \tag{8}$$

T_p = peak temperature of differential curves or point of inflexion of reaction curves

The parameters a and b obtained from (8) by setting E equal to E_{min} are listed together with those of the least squares fit in Table 1. The parameters approximately agree. The value of b from (8) corresponds to the reaction rate at the peak temperature. The parameters of the least squares fit are related in the same way via temperature T_m:

$$T_m = \log e\, 1/a \qquad b = \log (Z_{min}\, e^{-E_{min}/(RT_m)}) \tag{9}$$

T_m seems to be a mean temperature of the reaction interval and b is the logarithm of the corresponding reaction rate. The formation of the mean values is not evident, but depends on the weighting of the data points. T_m is lower than T_p if it is obtained from a fit according to (4), and is higher if (6) is used.

Frequently, E and Z are calculated from $k(T)$ using an Arrhenius plot, which implies a linear regression analysis. The rate constants k_i are obtained either from isothermal measurement or from non-isothermal experiments [2–6].

The relative minima with respect to E and $\ln Z$ are equations of the type (7):

$$\ln Z = (\sum_{i=1}^{N} (1/T_i \ln k_i) + \sum_{i=1}^{N} 1/T_i^2 \, E/R)/\sum_{i=1}^{N} 1/T_i \tag{10}$$

$$\ln Z = (\sum_{i=1}^{N} \ln k_i + \sum_{i=1}^{N} 1/T_i \, E/R)/N. \tag{11}$$

Sometimes isothermal experiments and often non-isothermal experiments are carried out within a temperature interval which is small compared to the actual temperature (e.g. mean temperature of the reaction interval). In this case the straight lines (10) and (11) approximately coincide and, in addition, approximately coincide with the projection of the valley bottom of the Chi Square Function. Small experimental errors in the measurement of k_i and T_i can be the reason for a considerable shift of the point of intersection of (10) and (11) which defines E_{min} and $\ln Z_{min}$.

A similar situation, but more complex, is also encountered for the direct fit of reaction curves and differential curves, as discussed above. In this case the integrals of the Arrhenius rate constant are involved, and the relative minima are only approximately straight lines.

References

1. E. KOCH, Non-Isothermal Reaction Analysis, Academic Press, London 1977.
2. L. BATTEZZATI, A. LUCCI and G. RIONTINO, Thermochim. Acta, 23 (1978) 213.
3. K. BÖHME, S. ROY, K. HEIDE and W. HÖLAND, Thermochim. Acta, 23 (1978) 17.
4. W. HÖLAND and K. HEIDE, Thermochim. Acta, 23 (1978) 183.
5. P. HOLBA, M. NEVRIVA and J. SESTÁK, Thermochim. Acta, 23 (1978) 223.
6. J. M. CRIADO, J. MORALES and V. RIVES, J. Thermal Anal., 14 (1978) 221.
7. A. I. BENIN, I. S. IZRAELIT, A. A. KOSSOI and YU. E. MALKOV, Fiz. Gor. i Vzryva, 9 (1973) 54.
8. J. ŠESTAK and G. BERGGREN, Thermochim. Acta, 3 (1973) 1.
9. V. ŠATAVA and F. ŠKVARA, J. Am. Ceram. Soc., 52 (1969) 591.
10. N. EISENREICH, Dissertation, Techn. Univ. Munich, 1978.
11. C. D. DOYLE, J. Appl. Polymer Sci., 5 (1961) 285.
12. H. J. BORCHARDT and F. DANIELS, J. Am. Chem. Soc., 79 (1957) 41.
13. R. W. PHILLIPS, C. A. ORLICH and R. STEINBERGER, J. Phys. Chem., 59 (1955) 1034.
14. N. EISENREICH and A. PFEIL, Proc. 1st. Europ. Symp. Thermal Analysis, Salford, Heyden and Son, 1976, p. 452.
15. N. EISENREICH and A. PFEIL, Thermochim. Acta, 27 (1978) 339.
16. N. EISENREICH and A. PFEIL, Thermochim. Acta, 29 (1979) 305.
17. M. J. D. POWELL, Computer J., 7 (1964) 155.
18. A. V. NIKOLAEV, V. A. LOGVINENKO, V. M. GORBACHEV and L. J. MYACHINA, Proc. 4th ICTA (Budapest 1974) Vol. 1, p. 47, 1975.
19. A. V. NIKOLAEV and V. A. LOGVINENKO, J. Thermal Anal., 9 (1976) 363.
20. P. D. GARN, Proc. 4th. ICTA (Budapest 1974) Vol. 1, p. 47, 1975.
21. J. ZSAKÓ, J. Thermal Anal., 9 (1976) 101.
22. P. D. GARN, J. Thermal Anal., 10 (1976) 99.

RÉSUMÉ — L'évaluation des paramètres cinétiques obtenus à partir des courbes des réactions chimiques exige de procédures d'ajustement de données. On a étudié des méthodes de recherche directe pour minimaliser la fonction de chi carré par rapport à l'énergie d'activation et au facteur pré-exponentiel. La forme géometrique de la fonction de chi carré peut être reliée à l'effet de compensation cinétique comme il est discuté dans la littérature. La minimalisation par rapport au facteur pré-exponentiel est résolue par des méthodes analytiques, pourvu que la fonction de chi carré comprenne des formes intégrées des mécanismes de réaction.

ZUSAMMENFASSUNG — Die Berechnung kinetischer Parameter aus Messkurven vom Verlauf chemischer Reaktionen erfolgt aufgrund von Anpassungsverfahren. In dieser Arbeit werden Methoden untersucht, bei denen die Fit-Parameter, insbesondere Aktivierungsenergie und Vorfaktor, direkt variiert werden. Das Minimum der Chi-Quadrat-Funktion kann im Hinblick auf den Vorfaktor analytisch gefunden werden, wenn zu ihrer Bildung die integrierte Form des Reaktionsmechanismus verwendet wird. Die geometrische Form der Chi-Quadrat-Funktion läßt sich zum kinetischen Kompensationseffekt in Beziehung setzen.

Резюме — Выделение кинетических параметров из кривых химической реакции означает методы подгонки данных. Изучены прямые поисковые методы, чтобы свести до минимума Чи Квадратную Функцию по отношению к энергии активации и предэкспоненциального фактора. Геометрический вид этой функции может быть связан с кинетическим компенсационным эффектом, как это обсуждено в литературе. Что касается предэкспоненциального фактора, доводка его до минимального значения может быть решена аналитически, если Чи Квадратная функция включает интегральные формы механизмов реакции.