Thermochimica Acta, 46 (1981) 229—237
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

DETERMINATION OF KINETIC PARAMETERS FROM TG CURVES BY NON-LINEAR OPTIMIZATION

S. BOY and K. BÖHME

VEB Mansfeld Kombinat "W. Pieck", Forschungsinstitut für NE-Metalle, Freiberg (D.D.R.)

(Received 23 September 1980)

ABSTRACT

The results obtained so far by kinetic analysis of non-isothermal experiments indicate that the kinetic parameters found by the conventional methods, in general, do not describe the experimental curve in an optimum manner. This is due to the fact that the initial differential equation is transformed into the logarithmic and, consequently, linear form and that the initial and final weights of the conversion curve cannot be determined exactly, which may falsify the slope of the curve.

Investigations have shown that the determination of the kinetic parameters by non-linear optimization (simplex method) results in a better fit of the theoretical conversion curve to the experimental one. But this procedure gives optimum results only when the initial and final weights of the reaction can be determined exactly. If this is impossible, exact parameters can be obtained only by the use of the non-standardized TG curve.

Examples are cited to prove that it is possible to evaluate overlapping reactions by the formation of intervals. However, the evaluation of conversion curves merely by the use of mathematical methods can easily result in an erroneous interpretation of the reaction course investigated. Therefore, it is necessary to check the mathematical results as to their physical and chemical meaning.

INTRODUCTION

At present, thermogravimetric curves obtained under non-isothermal conditions are widely used to study the kinetics of solid-state reactions. However, until now not all of the problems arising in the determination of the kinetic parameters from experimental values have been solved. On the one hand, only a limited number of kinetic model equations are available for describing various time laws [1] and, thus, it is not possible to describe all potential reaction courses. However, for the determination of the parameters, mathematical simplifications are made, such as the linearization of the initial differential equation and the standardization of the conversion curve [2,3] which, in general, affect the findings. As a result, in practice, the kinetic parameters found often do not describe the experimental curves in an optimum manner.

With this work we attempt to achieve a better fit of the theoretical conversion curve to the experimental one by determining the kinetic parameters by non-linear optimization (NLO). The residual dispersion is used as the optimization criterion. By the use of the non-standardized TG curve it should also be possible to determine the paramters exactly for partial intervals of the conversion curve, thus also enabling us to evaluate overlapping reactions by this procedure.

2. SOURCES OF ERROR IN THE DETERMINATION OF THE PARAMETERS

2.1. Inaccurate determination of the parameters by the use of linear regression

For the determination of kinetic parameters under non-isothermal conditions several methods have been described in the literature, all based on the fundamental kinetic equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\mathrm{f}(\alpha) \tag{1}$$

using the Arrhenius equation

$$k = k_0\,\mathrm{e}^{-E/RT} \tag{2}$$

E and $\ln k_0$ are to be determined. From eqn. (1) these parameters cannot be determined by linear regression, so we must transform it into a linear form, i.e. in this case into the logarithmic form. This is true of both the differential methods [3—5], giving by linearization the straight-line equations

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \ln k_0 + \ln \mathrm{f}(\alpha) - \frac{E}{RT} \tag{3a}$$

$$y = \ln\frac{\mathrm{d}\alpha}{\mathrm{d}t} - \ln \mathrm{f}(\alpha) = \ln k_0 - \frac{E}{RT} \tag{3b}$$

and the integral method [2,6] with

$$y = \ln \mathrm{g}(\alpha) - 2\ln T = \ln k_0 + \ln\frac{R}{E} - \frac{E}{RT}$$

$$\mathrm{g}(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{\mathrm{f}(\alpha)} \tag{4}$$

From eqns. (3a) and (4) the parameters E and $\ln k_0$ can be obtained by linear regression. This procedure is called quasi-linear regression.

The kinetic parameters so determined are expectance—true estimates for eqns. (3a) and (4), i.e. they are optimum solutions with regard to the residual dispersion. However, this is not true of eqn. (1). Thus, we obtain

$$\sum_{i=1}^{n} (\hat{y}_i - y_{i_{\mathrm{exp.}}})^2 \rightarrow \mathrm{min.}$$

with $\hat{y}$ being calculated from eqns. (3a) and (4) by the use of the estimated coefficients E and k_0

$$\hat{y} = \ln \hat{k}_0 - \frac{\hat{E}}{RT}$$

$$\hat{y} = \ln \hat{k}_0 - \frac{\hat{E}}{RT} + \ln \frac{R}{\hat{E}}$$

$y_{\text{exp.}}$ being calculated from measured values

$$y_{\text{exp.}} = \ln \frac{d\alpha}{dt} - \ln f(\alpha)$$

$$y_{\text{exp.}} = \ln g(\alpha) - 2 \ln T$$

The parameters so obtained by eqn. (1) need not be the optimum, i.e. in general, there does not hold the condition

$$\sum_{i=1}^{n} (\hat{\alpha}_i - \alpha_{i_{\text{exp.}}})^2 \rightarrow \text{min.}$$

This work is intended to indicate possibilities of improving the determination of the kinetic parameters with the view of obtaining a minimum residual dispersion between α and $\alpha_{\text{exp.}}$, i.e. the TG or DTG curve measured should be described by the parameters as closely as possible. This procedure is illustrated by the use of the integral method and, after having been subjected to some modifications, can be transferred to the differential method.

2.2. Inaccurate determination of initial and final weights of the conversion curve

If non-overlapping reactions are proceeding, the TG step of which is characterized by the fact that the weight is constant before the reaction has begun and after it has been completed, the usual standardization by

$$\alpha = \frac{G_0 - G_T}{G_0 - G_E}$$

can be performed without falsifying the results. In all the other cases this standardization gives results more or less erroneous.

If $\alpha(T) = 0$ does not hold from $T = 0$ to the moment, TA, of the beginning of the evaluation, a falsification of the α-curve by a factor θ is obtained. Thus

$$1 - \beta = \theta(1 - \alpha)$$

where

$$\beta = \frac{G_1 - G_T}{G_1 - G_E} \quad (G_1 < G_0)$$

In this case, with all integral methods an error in the determination of the kinetic parameters results from the use of the exponential integral. On the assumption that $\alpha(T) = 0$ at $0 \leqslant T < TA$ and, thus, $\int_0^{TA} e^{-E/RT} dT = 0$, for the evaluation we can set

$$\int_0^T e^{-E/RT}\, dT = \frac{RT^2}{E}\, e^{-E/RT}$$

This is no larger true when $G_0 \neq G(TA)$, because for this case we obtain $\alpha >$ o and $\int_0^{TA} e^{-E/RT}\,dT \neq 0$. The solution of the exponential integral gives

$$\int_{TA}^{T} e^{-E/RT}\,dT = \frac{RT^2}{E}\,e^{-E/RT} - \frac{RTA^2}{E}\,e^{-E/RTA}$$

and can no longer be evaluated by the linear procedure. Neglecting the integral $\int_0^{TA} e^{-E/RT}\,dT \neq 0$ by setting $TA = 0$ results in an increase of the E-values.

An inaccurate determination of the final weight results in a falsification of the $(1-\alpha)$-curve and, consequently, in a change of the slope. Thus, from both the integral and the differential methods too high E-values are obtained.

3. POSSIBILITIES OF IMPROVING THE DETERMINATION OF THE PARAMETERS

3.1. *Evaluation of standardized conversion curves*

3.1.1. *E-correction for the initial curve*

Based upon the results obtained by the use of the programme previously described [6], the E-value is gradually changed. Studies have shown that the parameters in the linear eqn. (4) are always too small. Tests are performed with E gradually increasing by 1 kJ mole^{-1} to see if the residual dispersion

$$S^2 = \frac{1}{n-1} \sum_{i=1}^{n} (\hat{\alpha}_i - \alpha_{i_{\mathrm{exp.}}})^2 \qquad (5)$$

reaches the minimum. k_0 and $\ln k_0$, respectively, are linearly corrected in dependence upon E. Thus, it becomes

$$\ln k_0 = \frac{1}{n} \sum_{i=1}^{n} y_i - (E + j \cdot 1\ \mathrm{kJ\ mole}^{-1})\,\frac{1}{n} \sum_{i=1}^{n} \frac{1}{T_i}$$

where $j \geqslant 0$ is the number of corrections. The programme stops once the residual dispersion has reached the minimum.

3.1.2. *Non-linear optimization*

A further step to describe the TG curve more accurately is the determination of the parameters from eqn. (1) by non-linear optimization based upon the simplex method [7]. With this method a simplex is formed from three starting points that must not be connected linearly. Of them the point is determined which most badly describes the initial curve. This point is tilted about the two others and so a new simplex is formed. The direction of displacement of the simplex centre oscillates about the gradient direction. If by this procedure an improvement of the residual dispersion cannot be obtained any longer, we must shorten the distances between the points of the last simplex. This causes all the three points given to approach the optimum value that is given by eqn. (5).

It follows that the correction of the E-values as described in Sect. 3.1.1 is a special case of the non-linear optimization. In this case the initial points are linearly connected, i.e. they form a straight line and not a simplex. This gives only the possibility of optimizing along the straight line and therefore, in general, the optimum cannot be reached.

3.2. Evaluation of non-standardized conversion curves

The evaluation of non-standardized conversion curves is based on the integrated form of the kinetic fundamental equation (without limitation of the generality $n = 1$)

$$1 - \alpha = e^{-k\,I(T)} \tag{6}$$

The following equation is valid

$$\alpha = \frac{TG_0 - TG(t)}{TG_0 - TG_E}$$

Thus, we obtain

$$\frac{TG(t) - TG_E}{TG_0 - TG_E} = e^{-k\,I(T)} \tag{7}$$

where

$$I(T) = \frac{RT^2}{E}\, e^{-E/RT} \tag{8}$$

and

$$TG(t) = (TG_0 - TG_E)\, e^{-k\,I(T)} + TG_E \tag{9}$$

In a similar way to the method of non-linear optimization described in Sect. 3.1.2, from given E and ln k_0 values the optimum values are determined, with the conversion (TG_0—TG_E) and the final weight TG_E being obtained by linear regression from eqn. (9). By this means, in addition to S^2 we obtain a further criterion of the accuracy of the parameters determined. $TG_0 = 1$ and $TG_E = 0$ must be valid for a completely detected non-overlapped weight step. For a reaction with the weight step being overlapped in the initial stage there becomes $TG_0 < 1$, and when overlapped in the final stage $TG_E > 0$.

As the optimization criterion, again the residual dispersion, in this case between the experimental and theoretical TG curves, is used. The number of iterations required amounts to 50.

4. EXAMPLES

Some selected examples are given to illustrate the possibilities of improving the parameter determination mentioned in Sect. 3.

The thermoanalytical experiments were carried out by the use of Mettler

TA1 with data transfer system. The following parameters were applied: middle-range furnace 25—1000° C; microcrucible holder Pt/Pt—Rh, microcrucible Al_2O_3; heating rate 10° C min^{-1}; TG range 100 mg; sample ground in the mortar and homogenized, <40 μm; air atmosphere (5 l h^{-1}).

The data transfer was performed by means of perforated tape. The calculations were carried out by a small computer with a memory capacity of 16 K (KRS 4200, Fa. Robotron). The software is given by FORTRAN.

4.1. The influence of the procedure

For the dehydration of calcium oxalate with conversions from 0.5 to 99% the kinetic parameters have been calculated by the integral method [6], by the method of E-corrections (cf. Sect. 3.1.1) and by the method of non-linear optimization with α-values (cf. Sect. 3.1.2). The results given in Table 1 and Fig. 1 show that the parameters obtained by non-linear evaluation best describe the experimental curve.

For each of the evaluation methods described, the most probable time law for the process of dehydration was selected by the use of 10 model equations in such a way that the residual dispersion between the experimental and theoretical curves was minimized. The same result was obtained by comparing the evaluation methods on the basis of the kinetic analysis of the thermal decomposition of raw meal (dehydration of montmorillonite). Here even the bare E-correction method as a special case of non-linear optimization allows a precise enough description of the experimental curve.

4.2. The influence of standardization

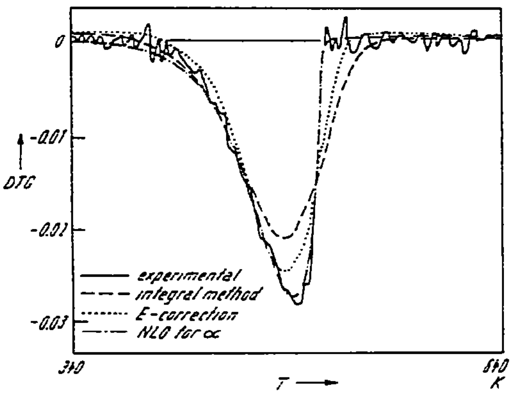
For the following examples the kinetic parameters have been determined on the basis of the non-standardized TG curve (cf. Sect. 3.2). If, as in the case of calcium oxalate, the conversion curve is not overlapped and there is no weight drift, the non-linear optimization of standardized and non-standardized values must give the same kinetic parameters within the limits of error (cf. Table 2).

If these conditions are not fulfilled, which takes place in many cases in practice (e.g. dehydroxylation of kaolin), we obtain erroneous results with all evaluation methods. Amongst them the non-linear optimization of non-standardized conversion curves gives the best fit (Fig. 2, Table 3), because

TABLE 1

Activation energies for calcium oxalate obtained by various evaluation methods

Method	n	E (kJ $mole^{-1}$)	ΔE (kJ $mole^{-1}$)	ln k_0	S^2 ($\times 10^{-3}$)
Integral method	1	62.3	4.1	14.1	0.74
E-correction	1	77.3	3.5	18.0	0.48
NLO for α	0.5	61.9	1.9	13.8	0.12



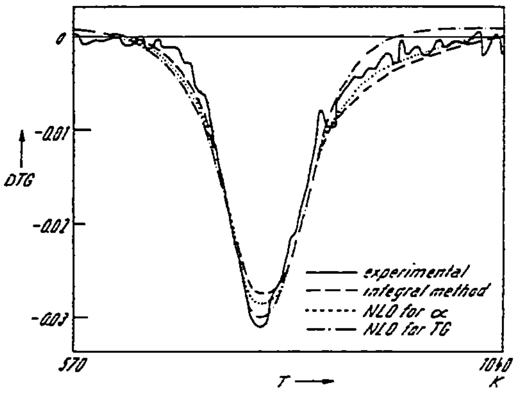


Fig. 1. Experimental and theoretical DTG curves of the separation of water from calcium oxalate. (Conversion 0.5—99%.)

Fig. 2. Experimental and theoretical DTG curves of the dehydroxylation of kaolin (Conversion 0.5—99%.)

only a part of the conversion curve is erroneous due to overlapping. On the other hand, under the same conditions the whole α-curve is falsified, as described in Sect. 2.2.

If the extent of overlapping can be estimated, the use of non-standardized TG curves allows the kinetic parameters to be determined in a non-overlapped interval. It is evident from Fig. 3 and Table 4 that the kinetic parameters so calculated do describe the experimental curve within the non-overlapped range in an optimum manner. The diagrammatic representation of the dif-

TABLE 2

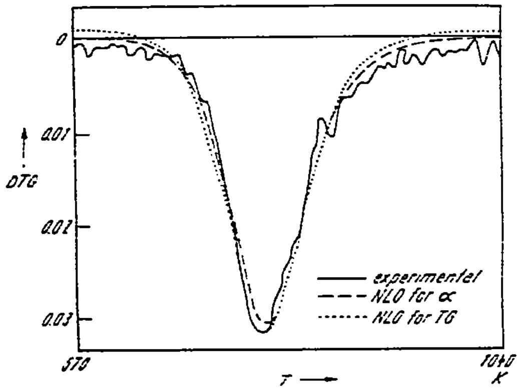
Activation energies for calcium oxalate obtained by the use of standardized and non-standardized conversion curves

Method	n	E (kJ mole^{-1})	ΔE (kJ mole^{-1})	ln k_0	S^2 (× 10^{-3})
NLO for α	0.5	61.9	1.9	13.8	0.12
NLO for TG	0.5	62.9	2.1	14.1	0.10

TABLE 3

Activation energies for the dehydroxylation of kaolin (conversion 0.5—99%)

Method	n	E (kJ mole^{-1})	ΔE (kJ mole^{-1})	ln k_0	S^2 (× 10^{-3})
Integral method	2	144.2	7.5	20.2	0.16
E-correction	2	149.2	6.1	21.0	0.14
NLO for α	2	148.6	5.9	20.9	0.14
NLO for TG	2	162.1	3.2	22.6	0.10



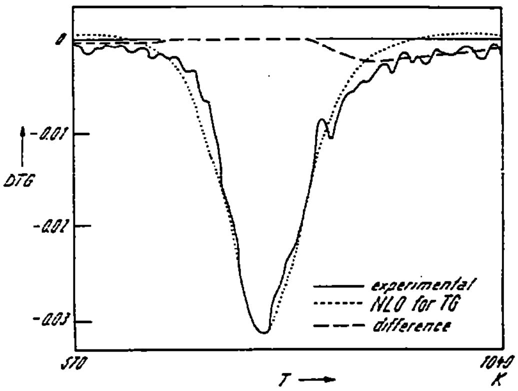


Fig. 3. Experimental and theoretical DTG curves in the evaluation of non-overlapped regions. (708.6—855.5 K corresponds to 3.7—81.2% conversion.)

Fig. 4. Representation of the difference between the experimental and theoretical curve ($n = 2$; 3.7—81.2%) of the dehydroxylation of kaolin.

TABLE 4

Activation energies for the dehydroxylation of kaolin obtained by evaluation of non-overlapped ranges ($n = 2$)

Method	Range (%)	E (kJ mole^{-1})	ΔE (kJ mole^{-1})	ln k_0	S^2
NLO for α	3.7—81.2	160.0	5.8	22.7	0.3×10^{-4}
	30.7—63.7	161.1	5.8	22.9	0.6×10^{-4}
NLO for TG	3.7—81.2	183.9	3.6	26.6	0.1×10^{-4}
	30.7—63.7	180.8	3.5	26.2	0.6×10^{-5}

ference between the calculated conversion curve and the experimental one (Fig. 4) shows that the erroneous TG values lie outside the selected interval (3.7—81.2%) and, thus, do not affect the kinetic parameters.

From the physical and chemical points of view the overlapping of various reaction courses proved by the use of mathematical models can be interpreted as the dehydration steps of kaolinite and illite.

5. DISCUSSION OF THE RESULTS

The investigations carried out to improve the determination of the parameters for the kinetic analysis of solid-state reactions under non-isothermal conditions show that the non-linear evaluation allows a better description of the experimental curve than linear regression.

The problem of determining kinetic parameters from standardized conversion curves can be solved only when the initial and final weights can be determined exactly. This condition excludes all reactions that are overlapped in any way. These reactions are capable of being evaluated only if the non-standardized TG values are utilized to determine the kinetic parameters. In this way, a parameter determination can be performed in non-overlapped intervals, which is the condition of the separation of additively overlapping weight steps. This fact is of great importance because in practice simultaneously proceeding reactions accompanied with weight losses can often be observed. A quantitative evaluation of the thermoanalytical experiments is based upon the exact determination of the partial weight losses of overlapping TG steps.

However, it has to be taken into consideration that such a procedure of using intervals, as has been applied, for example, to kaolin, is successful only when information on the physical and physicochemical nature of the substances has been obtained. An entirely mathematical evaluation of conversion curves may result in false interpretations.

REFERENCES

1 J. Sestak, V. Satava and W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
2 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
3 F.S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
4 K. Heide, Wiss. Z. Friedrich-Schiller-Univ., Jena, 20 (1971) 39.
5 S. Boy and K. Böhme, Thermochim. Acta, 27 (1978) 390.
6 S. Boy and K. Böhme, Thermochim. Acta, 20 (1977) 195.
7 K. Hartmann, E. Lezki and W. Schäfer, Statistische Versuchsplanung und -auswertung in der Stoffwirtschaft, VEB Dt. Verlag für Grundstoffindustrie, Leipzig, 1974.