

REMARKS ON THE DETERMINATION OF KINETIC CONSTANTS FROM THERMOGRAVIMETRIC DATA

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(Received December 5, 1981; in revised form March 1, 1982)

The methods for determining kinetic constants may have significant effects on the estimation results. The two-variable linear correlation method leads to values of the kinetic constants for which the difference between the calculated and measured values is comparable to or greater than the measurement precision. The non-linear method for calculating kinetic constants by searching for the minimum of the error function

$$S1 = \sum_{i=1}^N (m_{it} - m_i)^2/N, \text{ where } m_i \text{ and } m_{it} \text{ are the measured and calculated values,}$$

respectively, and N is the number of experimental data, gives very precise results. A simple calculating technique is necessary for the fitting of the minimum point and the confidence region limit at the significance level. An appropriate calculation was made for metal oxidation according to the parabolic law.

The estimation of kinetic constants from thermogravimetric data is a specific case of the wide problem of the estimation of mathematical model parameters from experimental data. When the number of observations is greater than the number of parameters estimated, the task consists in choosing the parameter values best describing the phenomenon investigated. The sum of the square differences of the measurement results and the values predicted for the given model parameters is usually assumed as an accordance value.

Those values are the best whose sum is the least. The estimation is therefore frequently identified with the least squares method. The problem formulated above is an example of determining the constraint minimum, where the sum of square differences is the minimized objective function, and the mathematical model equation is the constraint generator for the individual experimental data. For a given constraint system:

$$F_j(\sigma, Y_j) = 0 \quad j = 1, 2, \dots, \quad (1)$$

it is necessary to find the parameter values of the model $\sigma^T = (\sigma_1, \sigma_2, \dots, \sigma_p)^T$ giving the minimum value of the objective function

$$f = \sum_{j=1}^N \sum_{i=1}^W \left(\frac{Y_{ij} - \bar{Y}_i}{\mu_{ij}} \right)^2 \quad (2)$$

where N is the number of experimental data, w is the number of values measured, p is the number of estimated values for the vector σ , $[Y_{1j}, Y_{2j}, \dots, Y_{wj}]^T$ is the j -th experimental data vector and $[\bar{Y}_1, \bar{Y}_2, \dots, \bar{Y}_w]^T$ the values estimated for the given parameter vector σ . μ_{ij} is the precision of the measurement determined by the value of the standard deviation. The task is simplified when additional assumptions are introduced regarding the kind of values measured. As the independent values, the values in the given measurement are taken, and the dependent value is the response of the object investigated. It has been assumed that only the dependent values are charged with the measuring error. The calculating estimation procedure is the simplest in the case of the linear constraints (1), and thus it is intended to obtain either a linear mathematical model of the phenomenon investigated or to present in the longer form the relations between the functions of the values measured. To obtain a linear relationship, for example logarithms of the initial equation of the mathematical model are taken, yielding the relation

$$Y = AX + B \quad (3)$$

where Y and X are the known functions of the values measured, and A and B are the known functions of the model parameters. The values charged with error are arbitrarily selected from variables X and Y .

Such a procedure is treated as the most acceptable although there is an opinion that it may garble the estimation results. Usually this kind of reckoned error is taken as insignificant.

This allows determination of the minimum (2) under non-linear conditions, leading to the values of parameters estimated, describing the set of experimental data more precisely [1].

The task of this paper is to present the effect of the method of determining the kinetic constants on the estimation result. Although the calculations involved the estimation of kinetic constants from thermogravimetric measurement results obtained under conditions of linear temperature increase, the results presented here have a broader meaning. Similar problems also occur in the case of using isothermal thermogravimetric data, as well as in each case of estimating the mathematical model parameters from experimental data. A wrong calculation procedure may lead to unacceptable parameter values. Errors, even significant ones, occur when the experimental data do not fulfil the assumptions of the selected estimation procedure.

The linear correlation as a method of the estimation of kinetic constants

The majority of methods used for estimating the kinetic constants are based on the linear correlation of two variables. The advantage of these methods lies in the fact that the equations combining the estimated parameter values and the experimental data are the simplest [2]. The methods for estimation of the precision of the results obtained are also known.

Among many methods for determining the constants from measurements under

conditions of linear temperature increase, the most popular are the differential method, the integral Coats-Redfern method [3], and the logarithmic integral McCallum-Tanner method [4]. For metal oxidation according to the parabolic law

$$\frac{dm}{dt} = \frac{k_0 \exp(-E/RT)}{2} \frac{1}{m} \quad (4)$$

where m = mass, t = time and T = temperature, E = activation energy, R = gaseous constant and k_0 = pre-exponential constant different linear equations are obtained, depending on the method applied. For the differential method, we have

$$\ln \left(\frac{dm}{dt} \right) = \ln \frac{k_0}{2} - \frac{E}{R} \frac{1}{T}. \quad (5)$$

The integral Coats-Redfern method is based on the relation

$$2 \ln (m/T) = \ln \frac{k_0 R}{\beta E} - \frac{E}{R} \frac{1}{T} \quad (6)$$

where β is the heating rate.

The logarithmic integral McCallum-Tanner method leads to the equation

$$2 \ln m = \left(\ln \frac{k_0 E}{\beta R} - 0.02965 E^{0.4351} \right) - (1034 + 0.119331 E) \frac{1}{T} \quad (7)$$

where the activation energy E is expressed in J/mol.

The integral method equations have been obtained by integrating Eq. (4) for the initial conditions $m = 0$, $T = T_0$ for $t = 0$. The temperature integral $\int_0^T \exp(-E/R\xi) d\xi$ has been approximated by means of the asymptotic approximation expression [5] limited to the first two terms in the case of the Coats-Redfern method, and by means of the logarithmic approximation expression of McCallum-Tanner (more precise than the similar Doyle approximation expression [6]) in the case of the McCallum-Tanner method. It has also been assumed that for $T = T_0$ the temperature integral value is small enough to be neglected. Additionally, in the case of the Coats-Redfern method it has been assumed that $2RT/E$ is smaller than one.

The Eqs (5) to (7) are linear ones of the form $Y = AX + B$. The known estimation procedures based on the least squares allows for determining the constants A and B , and thus the activation energy E and the pre-exponential constant can be obtained. These calculations may also take into account the statistical weight of the dependent variable determined by the value of the standard deviation $s(Y)$. Since the variables Y and X are functions of the values measured, there is no limitation to the use of an equation reverse to Eq. (3)

$$X = \frac{1}{A} Y - \frac{B}{A} \quad (8)$$

as the basis for the estimation of the kinetic constants A and B . In the case of a linear equation of two variables, six different forms of the linear dependence exist between the variables [7]. Each of them may be a basis for estimation of the kinetic constants. The best pair of kinetic constants may be selected either on the basis of the statistical estimation parameters, such as the correlation coefficient and the standard deviation in the estimated parameters, or by comparing the values calculated for a given pair of kinetic constants with the measured values [8].

$$S1 = \sum_{i=1}^N (m_{it} - m_i)^2 / N \quad (9)$$

where m_i , m_{it} mean the values measured and calculated, respectively, for the kinetic constant values.

Calculation of the kinetic constant values according to the principles presented has been done both for the "experimental data" calculated with an assumed activation energy $E = 86640$ J/mol and pre-exponential constant $k_0 = 44670$ mg²/min cm² for the heating rate $\beta = 9.68$ degree/min, and for the real experimental results. The results obtained have been presented separately [7–9]. In general, the following comments seem to be fitting:

1) The two-variable linear correlation method leads to values of the kinetic constants for which the difference between the calculated and measured values of the mass change is comparable to or greater than the measurement precision.

2) Taking into account the dependent variable statistical weight in the estimation calculations leads to the estimated constants being more similar to the correct values. The assumption of the lower standard deviation values has an insignificant effect on the estimation result.

3) The values of the standard deviations of the parameters estimated depend on the assumed values of the standard deviations in the individual measurements. Assuming the lower values of the standard deviations of the measurement results may lead to too optimistic an opinion of the estimation precision.

The basis for verification may be the values of standard deviations of kinetic parameters estimated by means of a method which does not take into account the statistical weight of the measurements.

4) The activation energy values calculated by the various methods differed by up to 10% from the assumed values. In the case of determination of the value of the pre-exponential constant k_0 , a significant error was noted. For the logarithmic method this error was of the order of 400%. In the case of the Coats-Redfern method the estimated values of k_0 were lower than the assumed ones by 50%. In general, the various methods led to different values of the parameters estimated. The estimations of the kinetic constants in the range of individual variants of the same methods differed less significantly than the average values determined for different methods.

5) The correlation coefficient was not a good basis for estimating the quality of the results obtained.

In all cases its value was high, exceeding 0.9. Even with the high correlation coefficient value, the values of parameters estimated may differ significantly from the actual ones. The opinion obtained as to the estimation quality by comparing the values of the error function $S1$ for different pairs of the kinetic constants allowed in principle selection of the best values, but this dependence was not explicit and slight deviations were possible.

Function error minimum

The results presented indicate that estimation of the kinetic constants by means of methods based on the linear correlation of two variables may be a source of error comparable with the measuring error. The only way to reduce this error is the application of the error function $S1$ (9), not only as a criterion for the quality estimation of the kinetic constants estimated, but directly as a basis for determining the kinetic constants. The literature on this problem includes a set of various methods for determining the constraint minimum for non-linear limiting constraints [1]. The task consists in the selection of the most effective method. The additional, specific element for the problem of elaborating the experimental data is the opinion as to the precision of determination of the kinetic constant values.

Sometimes, due to the form of the given kinetic function, it is not purposeful to apply more general procedures for determining the constraint minimum, but rather other, more effective ones.

In the case of the determination of metal oxidation constants according to the parabolic law for non-isothermal data, the two-stage procedure is more effective. In the first stage the analytical form of the equation determining the pre-exponential constant value of the minimizing error function $S1$ at the activation energy assumed is determined. The second stage consists in determining the absolute minimum of the error function, checking out the changes in error function values for the minima given above, together with the change in activation energy.

Also, it is necessary to transform the kinetic function in such a way as to obtain a convenient form of equation determining the minimum assumptions for the cross-section. For example, in the case of determining the oxidation kinetic constants from isothermal measurements, the relation $m_0 = c\sqrt{k}$, (where m_0 = initial mass, c = constant and k = oxidation kinetic constant under isothermal conditions) is presented, and subsequently the error function minimum is determined at a given constant value c . During the second stage the effect of change in the c value on the determined minimum value is examined. In both cases, the task of determining the minimum depending on two parameters consists in determining the single-parameter function minimum, depending on the activation energy in the first case or "constant" c in the second one.

A disadvantage of using the error function $S1$ as a basis for estimating the kinetic constants is the characteristic shape of the $S1$ surface. In the case of non-isothermal measurements in the $(S1, k_0, E)$ space, the surface $S1$ similar rather to a narrow channel than a round hollow is determined by Eq. (9), and its lowest point determines the kinetic constant values minimizing the $S1$ error. Thus, there exist many pairs of

kinetic constant values for which the $S1$ error values differ relatively insignificantly from each other. It is therefore necessary to be careful in completing the calculations even for small differences between the subsequent values of $S1$ errors.

The precision of the kinetic constants may be estimated by the limit of the kinetic constant confidence region which could be expected with a given probability $1 - \alpha$ to include the actual values of the parameters estimated.

The basis for such an estimation could be the standard deviations of both parameters estimated. To determine them, it is necessary either to know the equations forming the parameters minimizing the error function $S1$ with the experimental data, or to know the values of the partial derivatives of both parameters in relation to all values measured at the minimum point. On the one hand it is usually difficult to determine the analytical form of the equation sought, while on the other hand the calculation of the derivative values is always possible, but the appropriate procedures are complicated.

Another method for the estimation of the precision in the determination of the parameters seems to be more effective. As the sample of experimental data is representative of the whole population of the experimental data, the given surface of the error function in space $(S1, k_0, E)$ is representative of the whole family of surfaces determined by various samples from the experimental result population.

For the given kinetic constant values k_0 and E the probability of obtaining the given value of the error $S1$ is determined by the probability of an experimental data sample occurrence.

Assuming that the distribution of function $S1$ values is similar to the chi square distribution for the actual values of the kinetic constants, and for the normal distribution of the kinetic constants different from the real one, an attempt can be made to determine the limit of the estimated parameter confidence region.

For the minimum point $S1$ there is a probability $(1 - \alpha)$ that the error function $S1$ value for the actual values of the kinetic constants will be lower than or equal to

$$G1 = \chi^2(\alpha, h) \cdot s^2(m)/N \quad (10)$$

where $\chi^2(\alpha, h)$ is determined from the chi square distribution for h degrees of freedom at the significance level α , and $s(m)$ is the standard deviation of the experimental result.

For other points $S1$ there is a probability $(1 - \alpha)$ that the error function $S1$ value for values of the kinetic constants k_0 and E different from the real ones will be higher than

$$G2 = S1(k_0, E) - t(\alpha, h)s[S1(k_0, E)] \quad (11)$$

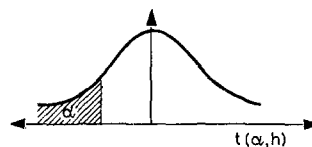


Fig. 1

where $t(\alpha, h)$ is determined from Student's distribution for h degrees of freedom at the significance level α , and $s[S1(k_0, E)]$ is the standard deviation of the error function.

In both cases the number of degrees of freedom is equal to the number of experimental data N . The confidence region limit is determined by

$$G1 = G2. \quad (12)$$

There is a probability $(1 - \alpha)$ that the actual values of the kinetic constants will be situated inside this region.

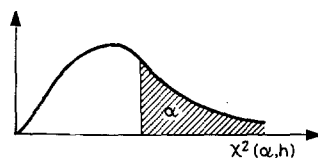


Fig. 2

The standard deviation $s[S1(k_0, E)]$ may be calculated from the law of error propagation

$$s^2[S1(k_0, E)] = \sum_{i=1}^N \left(\frac{\partial S1}{\partial m_i} \right)^2 s^2(m) = \frac{4}{N} s^2(m) S1(k_0, E), \quad (13)$$

Taking into account the above, the following relation is obtained from Eq. (12)

$$\sqrt{S1(k_0, E)_{\text{lim.}}} = \frac{s(m)}{\sqrt{N}} [t(\alpha, N) + \sqrt{t^2(\alpha, N) + \chi^2(\alpha, N)}] \quad (14)$$

determining the error value on the confidence region limit.

In the knowledge of the $S1(k_0, E)_{\text{lim.}}$, it is possible to determine the course of the confidence region limit on the k_0, E plane at the significance level α assumed. The location of the limit depends not only on the assumed significance level, but also on the measurement precision. The confidence region is greater when the standard deviation $s(m)$ is greater and the measurement precision is lower. Also it is smaller when a greater value of error α is assumed.

Due to the shape of the $S1(k_0, E)$ surface, determination of the confidence region limits is relatively precise. At a fixed value of one of the constants, e.g. the activation energy, the $S1$ value change together with the constant k_0 change is relatively high.

In the case of difficulties in obtaining the analytical dependence between $S1(k_0, E)_{\text{lim.}}$ and k_0, E relatively good results may be obtained by determining the $S1$ error value for several values of the constant k_0 at fixed E , the intermediate points being interpolated by means of the square function. For the calculation of the limit error $S1(k_0, E)_{\text{lim}}$ value, it is unnecessary to know either the values of minimum

error $S1$ or the values of parameters minimizing the $S1$ error; hence, in doing this we can combine the procedure of minimum determination with the procedure of estimating the kinetic constant confidence region limits. By determining the locations of these points for several values of the activation energy, both the minimum location and the confidence region limit can easily be determined. Such a procedure can be easily programmed, using a simple computer, independently of the form of the kinetic equation describing the hypothetical course of the reaction examined.

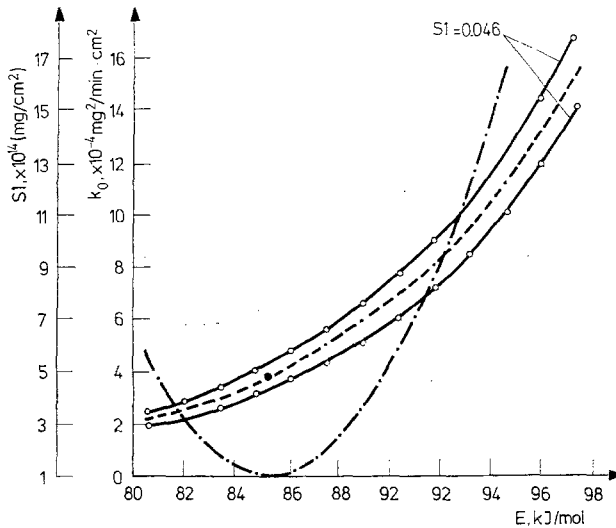


Fig. 3

The program for determining the best values of the kinetic constants, minimizing the error function $S1$ as well as the calculations of the course of the confidence region limit, has been elaborated for the computer operated at the Institute of Non-Ferrous Metals. Calculations of the kinetic constant values according to the principles have been done for the "experimental" data already calculated, which have been used in testing the methods based on the linear correlation of two variables.

Figure 3 shows the course of the confidence region limits (continuous line) with marking of the $S1$ function minimum point (marked by a cross).

The significance level assumed was $\alpha = 0.01$. Additionally, the $S1$ function minimum values change (broken line with points) in subsequent cross-section of the $S1$ surface by $E = \text{const.}$ planes (broken line) have been shown in Fig. 3. The results obtained allow the following comments:

1. The method for calculating the kinetic constants by searching for the minimum of the $S1$ function gives very precise results with a simultaneously simple calculating technique. Although the calculations have been done for 13 sections for the activation energies in the range 80–98 kJ/mol, the activation value determined differs only by 1.5% from the assumed value, while the exponential constant value dif-

fers by 15% from the assumed one. The estimation error determined by the SI function value is less by at least two orders than the value determined by methods based on the linear correlation of two variables.

2. The course of the confidence region limit indicates the variety of the confidence region shapes, depending on the form of the mathematical model equation.

3. The microcomputer operation time in searching for the error function minimum was much shorter than in the case of applying the methods based on the linear correlation of two variables, and the calculation results obtained gave a better possibility of a correct measurement quality estimation.

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ZUSAMMENFASSUNG — Die Methode zur Bestimmung von kinetischen Konstanten kann einem wesentlichen Einfluß auf den Estimationsergebnis ausüben. Die linearen Korrelationsmethode von zwei Variablen führt zur konstanten kinetischen Werten, für die die Differenz zwischen den berechneten und gemessenen Werten vergleichbar oder größer als der Messfehler ist. Sehr genaue Resultate ergibt die nicht-lineare Methode zur Bestimmung der kinetischen Konstanten durch Ermittlung des Minimums der Fehlerfunktion

$$SI = \sqrt{\frac{1}{N} \sum_{i=1}^N (m_i - m_{it})^2 / N}$$

worin m_i bzw. m_{it} die gemessenen bzw. berechneten Werte und N

die Zahl der experimentellen Daten bedeuten. Eine einfache Berechnungstechnik ist zur Festlegung des Minimumpunktes und der Grenzen des Vertrauensbereichs erforderlich. Eine genaue Berechnung wurde nach dem parabolischen Gesetz für die Metalloxydation ausgeführt.

Резюме — Значительное влияние на оценку результатов оказывает метод определения кинетических констант. Двухпеременный линейно-корреляционный метод приводит к значениям кинетической константы, для которой различие между вычисленным и измеренным значением является сравнимым или большим, чем точность измерения. Нелинейный метод вычисления кинетических констант поиском минимума функции ошибки

$$SI = \sqrt{\frac{1}{N} \sum_{i=1}^N (m_i - m_{it})^2 / N}$$

где m_i и m_{it} означает, соответственно, измеренное и вычисленное

значение, N -число экспериментальных данных, дает очень точные результаты. Простой метод вычисления необходим для подгонки точки минимума и доверительного интервала при значительном уровне. Соответствующее вычисление было проведено для реакции окисления металла, исходя из параболического закона.