ELSEVIER

Thermochimica Acta 285 (1996) 309–323

thermochimica acta

# Integral method to analyze the kinetics of heterogeneous reactions under non-isothermal conditions

## A variant on the Ozawa–Flynn–Wall method

C. Popescu

*LACECA Research Center, Str. Siret nr. 95, RO-78308, Bucharest, Romania*

Received 7 March 1995; accepted 12 February 1996

## Abstract

The paper describes an integral method of investigating the kinetics and mechanism of reactions based on the use of the degree of conversion measured at the same temperatures on curves recorded for a reaction carried out at various heating rates. The main advantage of this method is that it is not based on any assumption concerning the temperature integral, giving, thus, a higher degree of precision to the results. Since it is an integral method, the results are expected to be less affected by experimental errors. The method also allows the computation of the pre-exponential factor, $A$, and of the activation energy, $E$, if the Arrhenius-type relationship is assumed for the rate constant. The approach may be considered as a variant on the Ozawa–Flynn–Wall method.

Theoretical considerations are verified on two sets of generated data from the literature, as well as on the experimental data acquired for the calcium oxalate dehydration reaction.

*Keywords:* Kinetics; Heterogeneous reactions; Non-isothermal; Ozawa–Flynn–Wall method

## 1. Introduction

One of the main targets of most papers dealing with non-isothermal experiments is the determination of the kinetic parameters, i.e. the values of the activation energy $E$ and of the pre-exponential factor $A$, and the analytical form of the function of conversion $f(\alpha)$. Although many methods and much ingenuity has been applied, it seems that the problem is still unsolved. One of the reasons for this is that in most cases the function of conversion may be determined only after the values of the activation energy $E$ and the pre-exponential factor $A$ are calculated [1]. In this way, the analytical form of the function of conversion seems to depend on $E$ and $A$.

0040-6031/96/$15.00 © 1996 – Elsevier Science B.V. All rights reserved

*PII:* S0040-6031(96)02916-4

The methods used for computing the kinetic parameters are usually classified as differential and integral methods [2]. Both types of methods may be classified further as being based on data acquired for one or more heating rates. It is considered that methods based on experiments carried out under various heating rates give more reliable results than those based on data from a single experiment. It is also considered that the integral methods are less subjected to experimental errors (noise of the device, etc.) as they evaluate the whole experimental data set and are based on the primary experimentally acquired data, $\alpha$ and $T$. As a consequence, it may be considered that an integral method based on data recorded for various heating rates could give results which are more reliable and less affected by errors. This is, probably, one of the reasons why the Ozawa–Flynn–Wall method [3] is so popular for calculating the values of the kinetic parameters.

Based on a similar approach, the present paper proposes an integral method to determine the proper form of $f(\alpha)$ by using data obtained from experiments carried out under various heating rates without any preliminary computation or assumption of the values of $E$ or $A$. In this way, the function of conversion may be obtained as a primary result from the experimentally recorded data.

## 2. Theory

As in many other papers, one assumes that the reaction rate for the heterogeneous processes under non-isothermal conditions depends only on the degree of conversion $\alpha$ and temperature $T$, and that these two variables are independent ones, i.e. [4]

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

where $t$ is time. By the usual change of the variable time into temperature, Eq. (1) becomes

$$\mathrm{d}\alpha/\mathrm{d}T = 1/\beta f(\alpha)k(T) \tag{2}$$

where $\beta = \mathrm{d}T/\mathrm{d}t$ is the heating rate. In most experiments the heating rate is kept constant, and only this type of experiment will be taken into consideration in this paper.

The integral form of Eq. (2) is, then

$$\int_{\alpha_m}^{\alpha_n} \frac{\mathrm{d}x}{f(x)} = \frac{1}{\beta}\int_{T_m}^{T_n} k(y)\mathrm{d}y \tag{3}$$

where $\alpha_m$, $\alpha_n$ are two different degrees of conversion and $T_m$, $T_n$ are their corresponding temperatures. By using the notations

$$F(\alpha)_{mn} = \int_{\alpha_m}^{\alpha_n} \frac{\mathrm{d}x}{f(x)} \tag{4}$$

and

$$I(T)_{mn} = \int_{T_m}^{T_n} k(y)\mathrm{d}y \tag{5}$$

for the integral of conversion and of temperature, respectively, Eq. (3) may be written in a short form as

$$F_{mn} = 1/\beta I_{mn} \tag{6}$$

Eq. (6) is actually the basis of the method for finding the most probable kinetic mechanism of the studied reaction.

One has to assume, firstly, that over certain ranges of $\alpha$ and $\beta$ values, the kinetics of the reaction do not change, i.e. the analytical forms of $f(\alpha)$ and $k(T)$, and consequently of $F_{mn}$ and $I_{mn}$, do not change when either $\alpha$ or $\beta$ changes. This assumption is actually included in the general assumption made by Eq. (1) because, if the kinetic mechanism is changing with the change in heating rate, or the extent of the reaction, the expression of the rate of reaction would not have the analytical form of Eq. (1) [5].

Let us consider, now, several experiments using various heating rates. For the sake of simplicity, we shall consider experiments using five heating rates only, $\beta_1, \beta_2, \cdots \beta_5$. A typical plot in $(\alpha, T)$ co-ordinates of the five sets of experimental data is given in Fig. 1.

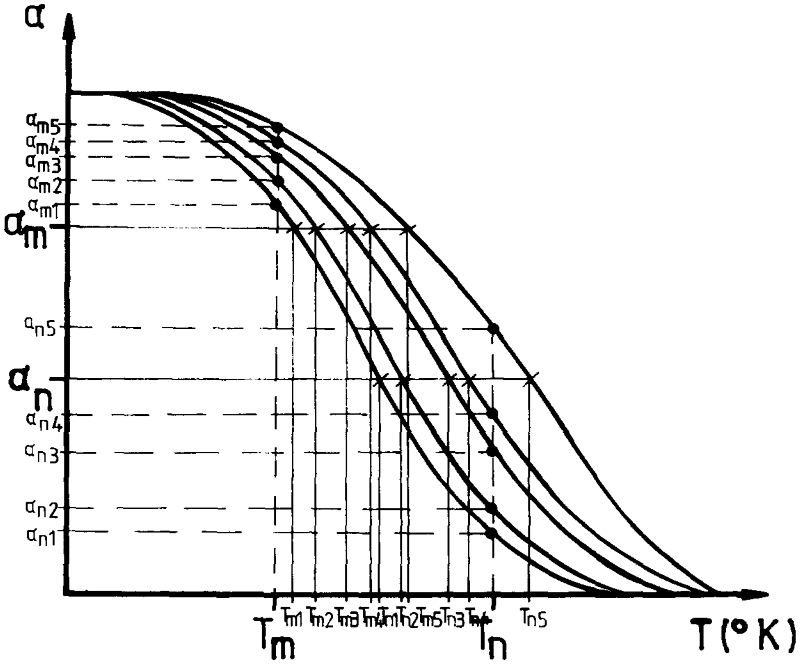

Fig. 1. TG curves corresponding to a reaction studied using five different heating rates.

Two straight lines $T = T_m$ and $T = T_n$, drawn on the plots from Fig. 1, will determine, on each curve, a pair of values of $\alpha$, i.e. $(\alpha_{m1}, \alpha_{n1}), \cdots, (\alpha_{m5}, \alpha_{n5})$, as shown in Fig. 1.

With the help of these pairs and using various conversion functions, such as those given in Table 1, the values of $F_{mn1}, F_{mn2}, \cdots F_{mn5}$ can be computed according to Eq. (4), and for each conversion function, $f(\alpha)$, five values are obtained. As the temperatures $T_m$ and $T_n$ are the same for all the experiments, according to Eq. (5) it follows that $I_{\mathrm{mn}}$ is constant, and, from Eq. (6), a plot of the values of $F_{mn}$ versus $1/\beta$ has to lead to a straight line with an intercept of zero if the analytical form of $f(\alpha)$ is properly chosen. The procedure may be repeated for other pairs of temperatures and, consequently, other straight lines will be obtained for the correct form of $f(\alpha)$. Finally a family of straight lines, as shown in Fig. 2, will indicate the best kinetic model for the acquired experimental data. In practice, the best correlation coefficient can be used to choose the proper kinetic function.

Table 1
Analytical forms of various conversion functions, $f(\alpha)$, and their integral form

| Mechanism (code) | Differential form $f(\alpha)$ | Integral form $F(\alpha)$ |
|---|---|---|
| Avrami–Erofeev ($m = 2, 3, 4$) (Code: AE2, AE3, AE4) | $(1-\alpha)[-\ln(1-\alpha)]^{1/m}$ | $m[-\ln(1-\alpha)]^{1/m}$ |
| Diffusion mechanism: (D1) | $\alpha^{-1}$ | $1/2 \cdot \alpha^2$ |
| (D2) | $[-\ln(1-\alpha)]^{-1}$ | $(1-\alpha) \cdot \ln(1-\alpha) + \alpha$ |
| (D3) | $[1-(1-\alpha)^{1/3}]^{-1} \cdot (1-\alpha)^{2/3}$ | $3/2 \cdot [1-(1-\alpha)^{1/3}]^2$ |
| Ginstling–Brounshtein (D4) | $[(1-\alpha)^{-1/3} - 1]^{-1}$ | $3/2 \cdot [1 - 2\alpha/3 - (1-\alpha)^{2/3}]$ |
| Reaction order (R) $n = 1$ | $1-\alpha$ | $-\ln(1-\alpha)$ |
| $n \neq 1$ | $(1-\alpha)^n$ | $[1-(1-\alpha)^{1-n}]/(1-n)$ |

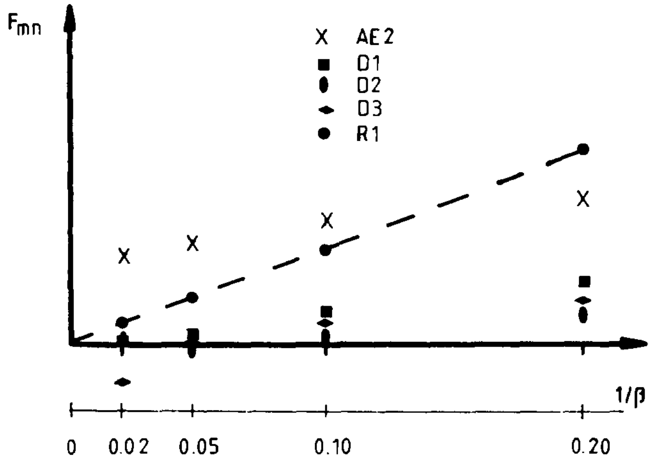

Fig. 2. Plots of $F_{mn}$ versus $1/\beta$ for various temperature intervals, as taken from Fig. 1.

It has to be stressed that the condition for testing the model is that the intercept of the straight line is zero, i.e. the straight line should pass through the origin of the axes. It is recommended that the point (0, 0) is taken together with $(F_{mn}, 1/\beta)$ points when the correlation coefficients are computed in order to increase the number of pairs through which the straight line has to pass and thus to decrease the standard deviation.

It has to be said that an advantage of the method is that no approximations of the temperature integral have to be assumed in order to determine the kinetic model. A single assumption adopted is that the function $k(T)$ depends on temperature and not on $\beta$ or $\alpha$, without any further assumption on the analytical form of $k(T)$.

### 2.1. *The influence of the heating rate on the kinetics of the reaction*

Let us suppose, now, that the kinetic mechanism and, consequently, the kinetic parameters change when $\beta$ is higher than a certain value, $\beta_S$. Thus, the values of $F_{mn}$ and $I_{mn}$ will change for heating rates higher than $\beta_S$. Therefore, the points $(F_{mn}, 1/\beta)$ will lie on a certain straight line when $\beta < \beta_S$ and on another one when $\beta > \beta_S$. The final plot of $F_{mn}$ versus $1/\beta$ will produce lines as shown on Fig. 3.

The modification of the slope from a certain value of the heating rate will, therefore, indicate that the kinetic mechanism has changed.

### 2.2. *The influence of the conversion degree on the kinetics of the reaction*

The two parallel lines $T_m$ and $T_n$ produce five conversion degree pairs $(\alpha_{m1}, \alpha_{n1}), \cdots (\alpha_{m5}, \alpha_{n5})$, as already mentioned. Obviously the range $(\alpha_{m1}, \alpha_{n1})$ is the largest and $(\alpha_{m5}, \alpha_{n5})$ the narrowest. By first plotting the straight line which passes through

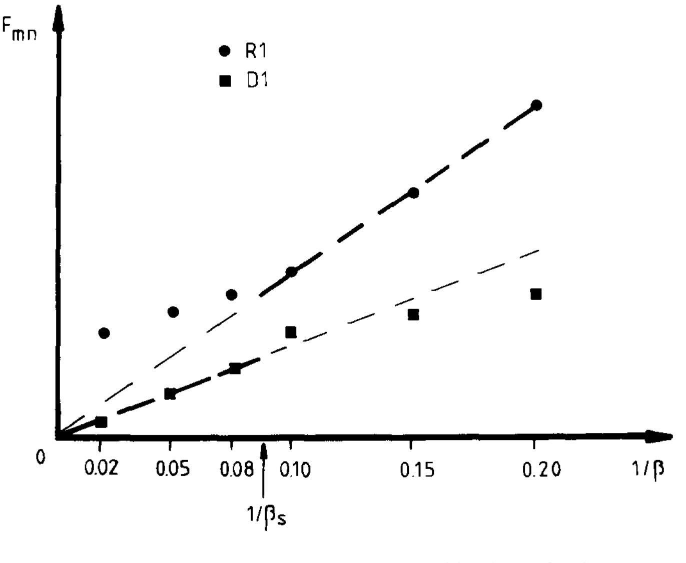

Fig. 3. Influence of the heating rate on the kinetic mechanism.

$F_{mn5}$, $F_{mn4}$ and $F_{mn3}$, and verifying if the other two values, $F_{mn2}$ and $F_{mn1}$ respectively, also lie on it, it is easy to notice whether or not the kinetics change with the value of the conversion degree.

### 2.3. Calculation of the kinetic parameters

In order to calculate the values of the activation energy $E$ and the pre-exponential factor $A$, one has to assume, firstly that $k(T)$ obeys an Arrhenius-type relationship

$$k(T) = A\exp(-E/RT) \tag{7}$$

The pre-exponential factor $A$ is considered to be independent of temperature. Taking into consideration Eq. (7), Eq. (3) becomes

$$\int_{\alpha_m}^{\alpha_n} \frac{\mathrm{d}x}{f(x)} = \frac{A}{\beta}\int_{T_m}^{T_n} \exp\left(-\frac{E}{R\,y}\right)\mathrm{d}y \tag{8}$$

By using the notation

$$H_{mn} = \int_{T_m}^{T_n} \exp\left(-\frac{E}{R\,y}\right)\mathrm{d}y \tag{9}$$

and those given by Eq. (4), one may write, in a short form

$$F_{mn} = A/\beta\, H_{mn} \tag{10}$$

An evaluation of the integral $H_{mn}$ has now to be considered in order to be able to compute the value of the activation energy $E$.

In this respect, the simplest approach is to use the first mean value theorem for definite integrals and thus to write

$$H_{mn} = (T_n - T_m)\exp(-E/RT_\xi) \tag{11}$$

where $T_\xi$ belongs to the range $T_m$, $T_n$. Eq. (10) then becomes

$$F_{mn} = A/\beta(T_n - T_m)\exp(-E/RT_\xi) \tag{12}$$

or, after taking the logarithms and rearranging the terms

$$\ln\frac{\beta}{T_n - T_m} = \ln\frac{A}{F_{mn}} - \frac{E}{R\,T_\xi} \tag{13}$$

In order to calculate the kinetic parameters $A$ and $E$ by Eq. (13), let us consider two straight lines, $\alpha = \alpha_m$ and $\alpha = \alpha_n$ drawn on the plots from Fig. 1. The two lines will determine, on each curve, a pair of values of $T$, i.e. $(T_{m1}, T_{n1})$, $(T_{m2}, T_{n2})$, $\cdots$, $(T_{m5}, T_{n5})$, as shown on Fig. 1. The plot of $\ln[\beta/(T_n - T_m)]$ versus $1/T_\xi$ leads to a straight line whose slope, equal $-E/R$, allowing calculation of the value of the activation energy $E$. As the form of the conversion function is already known, the value of $F_{mn}$ may easily be calculated and, from the value of the intercept of the above plot, $\ln A/F_{mn}$, the pre-exponential factor $A$ can also be calculated.

The procedure may be repeated for other pairs of conversion degrees and, consequently, other straight lines whose slopes equal $-E/R$ are obtained. In each case, the pre-exponential factor $A$ is calculated from the value of the intercept.

It may be observed that the values of both the activation energy $E$ and the pre-exponential factor $A$ are affected by the choice of the temperature $T_\xi$ within the range $[T_m, T_n]$. A simple evaluation is to consider that $T_\xi$ is just the average value

$$T_\xi = (T_m + T_n)/2 \tag{14}$$

A better approach would be to calculate the interval within which the value of $E$ lies.

### 2.4. Remarks on "why a variant on the Ozawa–Flynn–Wall method?"

It may be noticed that the proposed method is similar to the Ozawa–Flynn–Wall [3]. The major difference between them lies in the fact that the present method uses definite integrals, i.e. conversion degree and temperature intervals with both limits well defined, whilst the Ozawa–Flynn–Wall method takes into consideration intervals whose first limit is assumed to be zero. This assumption allows the use of Doyle's approximation for computing the temperature integral [6]. However, this assumption requires two conditions to be fulfilled:

(i) In all the cases the value of the temperature integral from zero to the onset temperature $T_0$, i.e. the highest temperature for which the conversion degree is still zero, may be neglected, or else its value must also be considered and the Doyle approximation does not apply. Mathematically, this condition is written as

$$\int_0^{T_0} \exp\left(-\frac{E}{Ry}\right) \mathrm{d}y = 0 \tag{15}$$

The fulfilling of this condition is questionable as the value of the integral in Eq. (15) is never zero, but one may accept that up to a certain temperature the value of the integral is small enough to be neglected.

(ii) For all the experiments with the same reaction carried out at various heating rates, the value of the onset temperature is the same, independent of the heating rate, or, in other words, all the experimental curves from Fig. 1 have to emerge from the same point. If this condition is fulfilled, the onset temperature would be an experimental invariant which could characterize the chemical reaction in a better way than the kinetic parameters do. This condition is even more questionable than the first one, as is shown by the following example Let us consider the case for which the onset temperature changes when the heating rate is changed, i.e. one records $T_{01}$ for $\beta_1$ and $T_{02}$ for $\beta_2$, respectively, and $T_{02} > T_{01}$. According to condition (i) the value of the temperature integral may be neglected for a temperature up to $T_{01}$. This means that the integral from $T_{01}$ to $T_{02}$ cannot be neglected and Doyle's approximation is, thus, invalid. However, this situation is closer to reality than condition (ii) which has to be fulfilled in order to apply Doyle's approximation.

The method proposed here avoids the necessity of these two conditions by taking into consideration the definite limits of the integrals and performing the calculation accordingly.

It has to be stressed that condition (ii) is not required when the integral method is used for the analysis of experimental data obtained from only one heating rate.

## 3. Experimental

The method described above has been applied to the study of two sets of data published in the literature [7], and to a set of experimental data acquired for the dehydration reaction of calcium oxalate monohydrate.

### 3.1. Literature data set

The data from the literature are generated for [7]

1. $f(\alpha) = 1 - \alpha$, $E = 83.680\,\mathrm{kJ\,mol^{-1}}$; $A = 1.0 \times 10^{12}\,\mathrm{min^{-1}}$

and heating rates of 1, 2, 5, 10, 20, 50 and 100 K min$^{-1}$, respectively.

2. $f(\alpha) = (1-\alpha)[-\ln(1-\alpha)]^{1/2}$ $E = 125.520\,\mathrm{kJ\,mol^{-1}}$; $A = 6.667 \times 10^{8}\,\mathrm{min^{-1}}$

and heating rates of 1, 2, 4, 6, and 8 K min$^{-1}$ respectively.
Some temperatures $T_m$ and $T_n$, and the corresponding conversion degrees for each of them are given in Tables 2a and 2b respectively, for the two data sets.

With the help of the functions from Table 1 and by using the least squares method, Tables 3a and 3b were obtained, wherein the correlation coefficients for each plot of

Table 2a
Conversion degrees corresponding to various temperatures as taken from Ref. [7] for the first data set

| Temp/K | $\beta = 1$ K min$^{-1}$ | $\beta = 2$ K min$^{-1}$ | $\beta = 5$ K min$^{-1}$ | $\beta = 10$ K min$^{-1}$ | $\beta = 20$ K min$^{-1}$ | $\beta = 50$ K min$^{-1}$ | $\beta = 100$ K min$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 336.245 | 0.65093 | 0.41006 | 0.19220 | 0.10000 | – | – | – |
| 344.346 | 0.89114 | 0.67195 | 0.36213 | 0.20000 | 0.10747 | – | – |
| 352.535 | – | 0.90000 | 0.60187 | 0.37090 | 0.20660 | 0.08100 | – |
| 362.363 | – | – | 0.87502 | 0.65092 | 0.41000 | 0.19219 | 0.1000 |
| 367.602 | – | – | – | 0.80000 | 0.55325 | 0.27785 | 0.1558 |

Table 2b
Conversion degrees corresponding to various temperatures as taken from Ref. [7] for the second data set

| Temperature/K | $\beta = 1$ K min$^{-1}$ | $\beta = 2$ K min$^{-1}$ | $\beta = 4$ K min$^{-1}$ | $\beta = 6$ K min$^{-1}$ | $\beta = 8$ K min$^{-1}$ |
|---|---|---|---|---|---|
| 647.87588 | 0.81286 | 0.34628 | 0.10000 | – | – |
| 651.90380 | 0.90000 | 0.43900 | 0.14120 | – | – |
| 666.16084 | – | 0.81286 | 0.34628 | 0.17641 | 0.10000 |
| 670.41116 | – | 0.90000 | 0.43900 | 0.22897 | 0.14119 |
| 676.47904 | – | – | 0.59056 | 0.32946 | 0.20000 |

Table 3a
Correlation coefficients corresponding to various kinetic mechanisms for the plot $F_{mn}$ vs $1/\beta$ using the first data set

| Model code | $T_m = 336.245$<br>$T_n = 344.346$ | $T_m = 344.346$<br>$T_n = 352.535$ | $T_m = 352.535$<br>$T_n = 362.363$ | $T_m = 362.363$<br>$T_n = 367.602$ |
|---|---|---|---|---|
| AE2 | 0.9509 | 0.9480 | 0.9419 | 0.9457 |
| AE3 | 0.8776 | 0.8699 | 0.8575 | 0.8621 |
| AE4 | 0.8157 | 0.8053 | 0.7876 | 0.7915 |
| D1 | 0.9646 | 0.9658 | 0.9757 | 0.9881 |
| D2 | 0.9944 | 0.9964 | 0.9963 | 0.9968 |
| D3 | 0.8832 | 0.8915 | 0.8476 | 0.8291 |
| D4 | 0.9967 | 0.9971 | 0.9963 | 0.9948 |
| R($n = 1$) | **0.9999** | **0.9999** | **0.9999** | **0.9999** |

Table 3b
Correlation coefficients corresponding to various kinetic mechanisms for the plot $F_{mn}$ vs $1/\beta$ using the second data set

| Model code | $T_m = 647.87588$<br>$T_n = 651.90380$ | $T_m = 666.16084$<br>$T_n = 670.41116$ | $T_m = 670.41116$<br>$T_n = 676.47904$ | $T_m = 666.16084$<br>$T_n = 676.47904$ |
|---|---|---|---|---|
| AE2 | **0.9983** | **0.9977** | **0.9980** | **0.9999** |
| AE3 | 0.9704 | 0.9702 | 0.9946 | 0.9878 |
| AE4 | 0.9270 | 0.9240 | 0.9841 | 0.9704 |
| D1 | 0.9825 | 0.9730 | 0.8966 | 0.8918 |
| D2 | 0.9618 | 0.9521 | 0.8720 | 0.8695 |
| D3 | 0.9238 | 0.8206 | 0.8478 | 0.8474 |
| D4 | 0.9474 | 0.9387 | 0.8634 | 0.8617 |
| R($n = 0.5$) | 0.9974 | 0.9946 | 0.9716 | 0.9468 |
| R($n = 0$) | 0.9541 | 0.9920 | 0.9914 | 0.9947 |

$F_{mn}$ versus $1/\beta$ are given. The correlation coefficients are calculated for the straight lines which pass through the five computed points ($F_{mn}$, $1/\beta$) and the origin of the axes, i.e. point (0, 0), because as mentioned, the intercept of the plot has to be zero.

One may notice that the best correlation coefficients are obtained for the reaction order model R with $n = 1$, in the case of data set (1), and AE2, respectively, in the case of data set (2). The same result was obtained for all cases which, for the sake of simplicity, are not listed in this paper.

Some conversion degrees, $\alpha_m$ and $\alpha_n$, and the corresponding pairs of temperatures determined on each curve, are given in Tables 4a and 4b.

According to Eq. (13), the plot of $\ln[\beta/(T_n - T_m)]$ versus $1/RT_\xi$ leads to a straight line whose slope is the value of the activation energy $E$. Values of the activation energy thus computed, as well as the corresponding correlation coefficients, are given in Tables 5a and 5b. The values of the pre-exponential factor $A$ calculated from the values of the

Table 4a
Temperatures (K) corresponding to various values of conversion degrees, as taken from Ref. [7] for the first data set

| $\alpha$ | $\beta = 1$ K min$^{-1}$ | $\beta = 2$ K min$^{-1}$ | $\beta = 5$ K min$^{-1}$ | $\beta = 10$ K min$^{-1}$ | $\beta = 20$ K min$^{-1}$ | $\beta = 50$ K min$^{-1}$ | $\beta = 100$ K min$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0.1 | 313.549 | 320.062 | 329.085 | 336.245 | 343.715 | 354.097 | 362.363 |
| 0.4 | 328.774 | 335.921 | 345.845 | 353.738 | 361.988 | 373.482 | 382.657 |
| 0.8 | 340.773 | 348.441 | 359.105 | 367.602 | 376.497 | 388.913 | 398.844 |
| 0.9 | 344.694 | 352.535 | 363.447 | 372.146 | 381.257 | 393.984 | 404.170 |

Table 4b
Temperatures (K) corresponding to various values of conversion degrees, as taken from Ref. [7] for the second data set

| $\alpha$ | $\beta = 1$ K min$^{-1}$ | $\beta = 2$ K min$^{-1}$ | $\beta = 4$ K min$^{-1}$ | $\beta = 6$ K min$^{-1}$ | $\beta = 8$ K min$^{-1}$ |
|---|---|---|---|---|---|
| 0.1 | 614.06505 | 630.53379 | 647.87588 | 658.45268 | 666.16084 |
| 0.4 | 632.88629 | 650.35488 | 668.77657 | 680.02523 | 688.22942 |
| 0.8 | 647.28140 | 665.53364 | 684.80303 | 696.58003 | 705.17467 |
| 0.9 | 651.90380 | 670.41116 | 689.95679 | 701.90611 | 710.62817 |

Table 5a
Values of the kinetic parameters computed by Eq. (13) for the data from Table 4a

| $\alpha_n \cdots \alpha_m$ | $E$/kJ mol$^{-1}$ | $A \times 10^{12}$/min$^{-1}$ | Correlation coeff. |
|---|---|---|---|
| 0.4···0.1 | 83.597 | 1.0690 | 0.9999 |
| 0.8···0.1 | 83.498 | 1.2039 | 0.9999 |
| 0.9···0.1 | 83.455 | 1.2605 | 0.9999 |
| 0.8···0.4 | 83.617 | 1.0356 | 0.9999 |
| 0.9···0.4 | 83.597 | 1.0612 | 0.9999 |

Table 5b
Values of the kinetic parameters computed by Eq. (13) for the data from Table 4b

| $\alpha_n \cdots \alpha_m$ | $E$/kJ mol$^{-1}$ | $A \times 10^{8}$/min$^{-1}$ | Correlation coeff. |
|---|---|---|---|
| 0.4···0.1 | 125.42 | 6.7551 | 0.9999 |
| 0.8···0.1 | 125.37 | 6.9537 | 0.9999 |
| 0.9···0.1 | 125.34 | 7.0366 | 0.9999 |
| 0.8···0.4 | 125.43 | 6.7047 | 0.9999 |
| 0.9···0.4 | 125.42 | 6.7425 | 0.9999 |

intercept of the above plot, by taking into consideration that

$$F_{mn} = \ln\frac{1-\alpha_m}{1-\alpha_n}$$

for data set (1), and

$$F_{mn} = [-\ln(1-\alpha_n)]^{1/2} - [-\ln(1-\alpha_m)]^{1/2}$$

for data set (2) respectively, are also given.

The values of the activation energy and the pre-exponential factor, calculated according to the Ozawa–Flynn–Wall method [3], as well as the corresponding correlation coefficients, are listed in Tables 6a and 6b.

Summing up all the results obtained for the value of the activation energy $E$ and the pre-exponential factor $A$, one may write:

(i) For data set (1)

Proposed method:
$E = 83.425 \pm 0.3996488$ kJ mol$^{-1}$; $A = (1.0859 \pm 0.095278) \times 10^{12}$ min$^{-1}$;
$r = -0.99999 \pm 1.61 \times 10^{-5}$.
Ozawa–Flynn–Wall method:
$E = 84.910 \pm 0.2414789$ kJ mol$^{-1}$; $A = (0.10301 \pm 0.019806) \times 10^{12}$ min$^{-1}$;
$r = -0.99999 \pm 1.874 \times 10^{-5}$.

(ii) For data set (2)

Proposed method:
$E = 125.41 \pm 0.0279824$ kJ mol$^{-1}$; $A = (6.7827 \pm 0.10223) \times 10^{8}$ min$^{-1}$;
$r = -1$. Ozawa–Flynn–Wall method:
$E = 129.36 \pm 0.1804751$ kJ mol$^{-1}$; $A = (0.12863 \pm 0.017351) \times 10^{8}$ min$^{-1}$;
$r = -0.999999 \pm 2.6532 \times 10^{-8}$.

where $r$ is the correlation coefficient.

Table 6a
Values of the kinetic parameters for the data from Table 4a computed by the Ozawa–Flynn–Wall method

| $\alpha$ | $E$/kJ mol$^{-1}$ | $A \times 10^{12}$/min$^{-1}$ | Correlation coeff. |
|---|---|---|---|
| 0.1 | 84.701 | 0.6486000 | 0.9999 |
| 0.4 | 84.962 | 0.0302760 | 0.9999 |
| 0.8 | 84.374 | 0.0024884 | 0.9999 |
| 0.9 | 85.236 | 0.0016345 | 0.9999 |

Table 6b
Values of the kinetic parameters for the data from Table 4b computed by the Ozawa–Flynn–Wall method

| $\alpha$ | $E$/kJ mol$^{-1}$ | $A \times 10^{8}$/min$^{-1}$ | Correlation coeff. |
|---|---|---|---|
| 0.1 | 129.03 | 0.14902 | 0.9999 |
| 0.4 | 129.33 | 0.11346 | 0.9999 |
| 0.8 | 129.55 | 0.13502 | 0.9999 |
| 0.9 | 129.63 | 0.16645 | 0.9999 |

Comparing the results given above with the values of activation energy and pre-exponential factor used for generating the data, one can see that the proposed method offers results which are closer to those used for simulation than the results obtained by the Ozawa–Flynn–Wall method.

In conclusion, the use of the proposed method to analyze the generated data given in Ref. [7] leads to values of the kinetic parameters which are in excellent agreement with those used for simulation. In spite of the rough approximation used for computing the value of $T_\xi$ (the use of Eq. (14)), the results seem to be better than those obtained by the Ozawa–Flynn–Wall method.

### *3.2. The dehydration reaction of calcium oxalate monohydrate*

Three heating rates, 1.25, 2.5 and 5 K min$^{-1}$, were programmed on a Netzsch TG 209 thermogravimetric device, and the reaction was studied under air atmosphere, with an air draft of about 10 cm$^3$ min$^{-1}$. The recorded curves are given in Fig. 4.

The temperatures $T_m$ and $T_n$, and the measured conversion degrees for each of them, are given in Table 7.

Using the conversion functions listed in Table 1 and various pairs of temperatures from Table 7, one obtains, by least squares, the results listed in Table 8. The correlation coefficients are computed for the straight lines which pass through the four $(F_{mn}, 1/\beta)$ points and through the origin (0, 0). In the case of the reaction order model, R, only the value of the reaction order $n$ which allows the best correlation coefficient to be obtained is given.

One can see from Table 8 that the best correlation coefficient is obtained for the bi-dimensional diffusion model, D2. One may thus assume that the kinetic function which fits the experimental data best is

$$f(\alpha) = [-\ln(1-\alpha)]^{-1} \tag{16}$$

By taking various conversion degrees and measuring the temperatures which correspond to these on the three experimental curves, Table 9 is obtained.

By using the data from Table 9, according to Eq. (13), the plot of $\ln[\beta/(T_n - T_m)]$ versus $/RT_\xi$, with $T_\xi = (T_m + T_n)/2$ leads to straight lines whose slope equal the value of the activation energy $E$. The computed values of the activation energy, as well as the correlation coefficients, are given in Table 10. From the intercept, according to Eq. (13), the value of the pre-exponential factor, as $\ln A$, is also calculated and listed in Table 10 for the conversion function given by Eq. (16).

One may note that the values for both the activation energy $E$ and the pre-exponential factor $A$ are not very dispersed, i.e. $E = 174.25 \pm 6.7613$ kJ mol$^{-1}$; $\ln A = 43.6844 \pm 2.1717$ s$^{-1}$; $r = 0.9974 \pm 0.0032$.

The same experimental data have been used to compute the kinetic parameters using the software included in the Netzsch TG 209 equipment. The values obtained for the kinetic parameters are: $E = 179.63 \pm 33.821$ kJ mol$^{-1}$; $\ln A = 42.8889 \pm 9.7476$ s$^{-1}$; $r = 0.9000 \pm 0.2055$; with the kinetic model D2.

One can notice that the results are in good agreement with those obtained by the proposed method, and also that they are more dispersed than those given above.

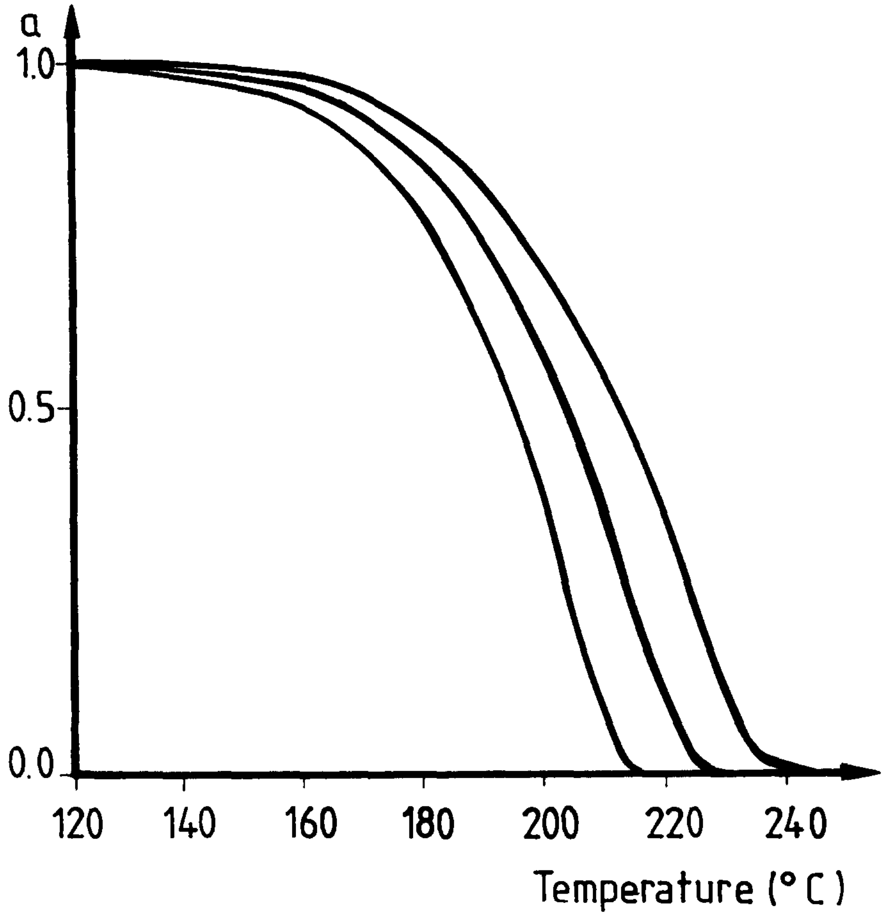

Fig. 4. TG curves recorded for the dehydration reaction of $CaC_2O_4 \cdot H_2O$.

Table 7
Conversion degrees measured for given temperatures on the curves from Fig. 4

| Temperature/K | $\beta_1 = 125\,\mathrm{K\,min^{-1}}$ | $\beta_2 = 2.5\,\mathrm{K\,min^{-1}}$ | $\beta_3 = 5\,\mathrm{K\,min^{-1}}$ |
|---|---|---|---|
| 431 | 0.40 | 0.20 | 0.20 |
| 435 | 0.50 | 0.32 | 0.28 |
| 439 | 0.60 | 0.40 | 0.35 |
| 441 | 0.70 | 0.50 | 0.38 |
| 444 | 0.80 | 0.567 | 0.45 |
| 447 | 0.90 | 0.667 | 0.52 |

Table 8
Correlation coefficients obtained for the kinetic functions from Table 1 by using the conversion degrees from Table 7

| Model code | $T_m = 435$<br>$T_n = 447$ | $T_m = 431$<br>$T_n = 444$ | $T_m = 431$<br>$T_n = 447$ | $T_m = 435$<br>$T_n = 444$ | $T_m = 439$<br>$T_n = 447$ |
|---|---|---|---|---|---|
| AE2 | 0.9814 | 0.9739 | 0.9889 | 0.9655 | 0.9897 |
| AE3 | 0.9577 | 0.9400 | 0.9694 | 0.9353 | 0.9725 |
| AE4 | 0.9407 | 0.9095 | 0.9527 | 0.9154 | 0.9597 |
| D1 | 0.9919 | 0.9930 | 0.9896 | 0.9962 | 0.9871 |
| D2 | **0.9988** | **0.9995** | **0.9994** | **0.9986** | **0.9996** |
| D3 | 0.9791 | 0.9892 | 0.9822 | 0.9853 | 0.9807 |
| D4 | 0.9942 | 0.9975 | 0.9959 | 0.9953 | 0.9957 |
| R($n = 1.00$) | 0.9966 | 0.9945 | 0.9985 | 0.9986 | 0.9971 |
| R($n = 0.90$) | 0.9982 | 0.9903 | 0.9977 | 0.9976 | 0.9993 |
| R($n = 4/3$) | 0.9830 | 0.9985 | 0.9894 | 0.9950 | 0.9820 |

Table 9
Temperatures (K) measured for various conversion degrees on the curves from Fig. 4

| Conversion degree | $\beta_1 = 1.25\,\mathrm{K\,min^{-1}}$ | $\beta_2 = 2.5\,\mathrm{K\,min^{-1}}$ | $\beta_3 = 5\,\mathrm{K\,min^{-1}}$ |
|---|---|---|---|
| 0.20 | 424.5 | 431.0 | 431.0 |
| 0.40 | 431.0 | 439.0 | 442.0 |
| 0.80 | 444.0 | 450.5 | 457.0 |
| 0.90 | 447.0 | 454.0 | 461.0 |

Table 10
The values of the kinetic parameters for the dehydration reaction of calcium oxalate computed by Eq. (13) and the data from Table 9

| $\alpha_n \cdots \alpha_m$ | $E/\mathrm{kJ\,mol^{-1}}$ | $A \times 10^{19}/\mathrm{s^{-1}}$ | Correlation coeff. |
|---|---|---|---|
| 0.8···0.2 | 178.92 | 9.89190 | 0.9990 |
| 0.9···0.2 | 171.17 | 1.20350 | 0.9982 |
| 0.8···0.4 | 170.42 | 0.85541 | 0.9987 |
| 0.9···0.4 | 160.41 | 0.56524 | 0.9998 |

## 4. Conclusions

An integral method to determine the reaction mechanism model and to compute the kinetic parameters is proposed. The method is based on the data acquired for a reaction investigated under various heating rates and may be considered as a variant of the Ozawa–Flynn–Wall method. The assumptions and approximations on which the proposed method is based are the following:

(i) Assumption 1 (A1): the rate of the chemical reaction depends on two independent variables: $\alpha$, the degree of conversion, and $T$, the temperature.

(ii) Assumption 2 (A2): the analytical forms of the $\alpha$-dependence and the $T$-dependence do not change when $\alpha$ ranges from $\alpha_a$ to $\alpha_b$ (generally from 0.1 to 0.9) and the heating rate, $\beta$, ranges from 0 to $\beta_S$.

(iii) Assumption 3 (A3): the temperature dependence obeys the Arrhenius relationship.

(iv) Approximation 1(App. 1): the temperature $T_\xi$, used for calculating the temperature integral, is the average of the considered temperature interval.

The analysis of the kinetic mechanism is based on assumptions A1 and A2, whilst the calculation of the kinetic parameters may be performed only if A1, A2, A3 and App. 1 are used together.

It appears, thus, that the kinetic mechanism can be determined with a higher degree of precision than the values of the two kinetic parameters and it is suggested, therefore, that the kinetic mechanism would offer a better description of the heterogeneous reaction than the values of the two kinetic parameters. It is also suggested that it might be better to give intervals of values, rather than exact values, for the activation energy $E$ and the pre-exponential factor $A$.

The proposed method has been tested on data given in the literature for a simulated reaction [7] and on those obtained for the dehydration reaction of calcium oxalate. In the case of the data from the literature the calculated results are in excellent agreement with those used for simulation. In the case of the calcium oxalate dehydration reaction, the results are in good agreement with those obtained using the Netzsch TG 209 software (in fact the Ozawa–Flynn–Wall method [3]).

## Acknowledgments

The author wishes to acknowledge a scholarship received from Deutscher Akademischer Austauschdienst, the generosity of the International Wool Secretariat - AEEA Düsseldorf and the hospitality of the Deutsches Wollforschungsinstitut Aachen, where the present work was completed.

## References

[1] T.P. Prasad, S.B. Kanungo and H.S. Ray, Thermochim. Acta, 203 (1992) 503.
[2] J. Sestak, J. Therm. Anal., 16 (1979) 503.
[3] T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
J.H. Flynn and L.H. Wall, J. Res. Bur. Stand., 70A (1966) 487.
[4] J. Sestak, V. Satava and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
[5] P. Garn, Thermochim. Acta, 160 (1990) 135.
[6] C.D. Doyle, J. Appl. Polym. Sci., 6 (1962) 639.
[7] A.A. Zuru, R. Whitehead and D.L. Griffiths, Thermochim. Acta, 164 (1990) 285.