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A computer program for the kinetic parameters evaluation under CRTA conditions

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Abstract

An algorithm and a computer program for the evaluation of kinetic parameters under constant reaction rate conditions were elaborated. The computing procedure allows the observation of reaction mechanism changes as well as the evaluation of activation parameters. The algorithm was tested using some simulated decomposition curves as well as the constant rate decomposition curves of calcium oxalate. The program is written in Visual BASIC 3.0 and 4.0 and can run under MS Windows 3.1x or Windows 95©. © 1998 Elsevier Science B.V.

1. Introduction

The constant rate thermal analysis method (CRTA) was proposed by Rouquerol [1] and Paulik et al. [2]. In this paper, the theoretical grounds of the CRTA as suggested by Fătu and Segal [3], will be used.

Lately, the CRTA method was extended for diffusion models [4]. It was shown that the temperature of the half-conversion depends on the activation energy and that the shape of (conversion, T) plots depends on the reaction mechanism. A graphical method which allows to find the form of the conversion function was also proposed by Fătu and Segal [3]. However, a more reliable method of the kinetic parameters evaluation is proposed here. This method requires at least two decomposition curves, recorded at two different constant decomposition rates.

2. Theoretical considerations

In order to describe solid–gas decomposition reactions, either for the deceleration or for acceleration, the following form of the reaction rate can be used:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Ae^{-E/RT}\alpha^m(1-\alpha)^n \tag{1}$$

where the symbols have the usual meanings in kinetics. It has to be emphasized that m is the accelerating exponent and n the decelerating exponent (also known as the reaction order). If m=n=1, Eq. (1) reduces to the differential form of the Prout–Tompkins equation [5]; for m=0 and n=2/3, the contracting-sphere equation is obtained. The decompositions which exhibit an acceleration period can be described by Eq. (1) with n=0 and m>0. The decompositions which do not exhibit an acceleration period can be described by Eq. (1) with m=0 and n>0.

If the isokinetic conditions are fulfilled, the reaction rate is kept at a constant value ($\mathrm{d}\alpha/\mathrm{d}t$=$C$); thus,

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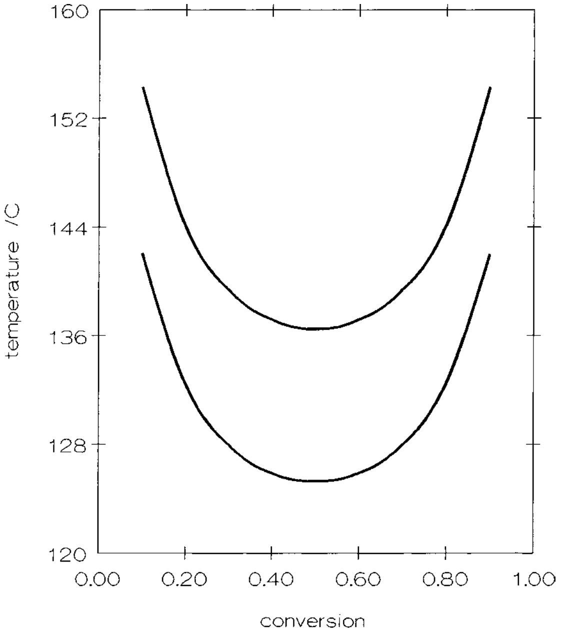

Fig. 1. Simulated solid–gas decomposition under the CRTA conditions: the decomposition rates (a) $C_1=1.66\times10^{-5}\ \mathrm{s}^{-1}$, (b) $C_2=3.33\times10^{-5}\ \mathrm{s}^{-1}$, and with the activation parameters $A=6.23\times10^{-6}\ \mathrm{s}^{-1}$, $E=83.00$ kJ/mol, $n=1$ and $m=1$.

Eq. (1) can be written as:

$$T=\frac{E/R}{\ln\left((A/C)\,\alpha^m(1-\alpha)^n\right)} \tag{2}$$

In order to evaluate the activation energy, independently of the conversion function form, we need at least two decomposition curves, recorded at two constant decomposition rates C_1 and C_2. When $m>0$ and $n>0$, the (α,T) plots exhibit a minimum [3]. For example, in Fig. 1 two decomposition curves are presented, and conversion function of the Prout–Tompkins type calculated.

In isoconversion conditions, the activation energy can be calculated from the formula:

$$E=\frac{RT_1T_2}{T_2-T_1}\ln\frac{C_2}{C_1} \tag{3}$$

where T_1 and T_2 are the temperature values for the same conversion degree α, recorded at the decomposition rates C_1 and C_2, respectively. For the (T,α) curve, we can obtain the following equations which allows the evaluation of n and m, using the minimum condition $(\mathrm{d}T/\mathrm{d}\alpha)=0$ at the conversion $\alpha_{\min}$:

$$n=\frac{E}{R}\frac{\mathrm{d}T/\mathrm{d}\alpha}{T^2}\frac{\alpha(1-\alpha)(1-\alpha_{\min})}{\alpha(1-\alpha_{\min})-\alpha_{\min}} \tag{4}$$

$$m=\frac{n\alpha_{\min}}{1-\alpha_{\min}} \tag{5}$$

The evaluation of the preexponential factor becomes obvious from the Eq. (1):

$$A=\frac{C\exp\left(E/RT\right)}{\alpha^m(1-\alpha)^n} \tag{6}$$

Concerning Eqs. (4) and (5), one has to note that n and m cannot be computed for the points $\alpha=0$, $\alpha=\mathrm{a}_{\min}$ and $\alpha=1$. These difficulties are easily overcome: n can be evaluated for the range $0<\alpha<1$ with $\alpha\neq\alpha_{\min}$ (in the calculation, we simply skip the $\alpha=\alpha_{\min}$ point). The conditions that $\alpha=0$ and $\alpha=1$ will not interfere with the calculations, taking into account that the isoconversion condition can hardly be reached either for $\alpha=0$ or $\alpha=1$.

3. The algorithm and the computer program

We can evaluate the activation parameters from two data sets $(T_i,\ \alpha_i)$ and $(T_i',\ \alpha_i)$ obtained with the decomposition rates C and C', respectively, based on the above-mentioned equations (for a better description, see Ref. [3]). In order to avoid the difficulty of obtaining T_i and T_i' for the same α_i, a polynomial interpolation schema will be used. This will produce the $(T,\ \alpha)$ curves independently of the measured values of α and will smooth the data values. The smoothing procedure permits the elimination of the random errors.

The algorithm consists in:

1. The input data $(T_i,\ \alpha_i)$ and $(T_i',\ \alpha_i)$ for the decomposition rates C and C' are smoothed by an interpolation polynomial of a degree between 2 and 7. In the usual cases, a polynomial of degree 4 is good enough to describe the data. The polynomial coefficients a_i and a_i' for each of the recorded curves are computed using the pseudo-inverse matrix method [6].
2. Once the interpolation polynomials are known, the j values of temperatures T_{1j}, T_{2j} for the two curves can be computed, the temperatures of which cor-

respond to the same values of conversion degree α_j. The number of α_j values is selected by the user; a suitable value lies in the 20–100 range (in this version, the program accepts $10<j<999$). Therefore, we can compute j values of the activation energy using Eq. (3); it is obvious that activation energy can be computed only for the common α_j values corresponding to the two curves. If the E_j values do not vary (in the limit of the experimental errors), it can be concluded that the decomposition process is unique.

3. In order to evaluate the n and m exponents of the conversion function, four cases can be considered:

(a) If the temperature does not vary in the considered domain, the process is independent of n ad m, and therefore $n=m=0$. This case is unusual and somehow superfluous. That is the reason why it is not considered.

(b) If the (α, T) curve has a positive slope, then $m=0$ and n is computed using the formula:

$$n = \frac{E}{2RT_{1/2}^2}\left(\frac{\mathrm{d}T}{\mathrm{d}\alpha}\right)_{1/2} \tag{7}$$

where 1/2 refers to the half-conversion point.

(c) If the (α, T) curve has a negative slope, then $n=0$ and m is computed using the formula:

$$m = -\frac{E}{2RT_{1/2}^2}\left(\frac{\mathrm{d}T}{\mathrm{d}\alpha}\right)_{1/2} \tag{8}$$

(d) If the (α, T) curve exhibits a minimum, then $n\neq 0$ and $m\neq 0$ and their values can be computed from Eqs. (4) and (5). If their values do not change with the degree of conversion, this is a proof that the decomposition process is described by a unique conversion function.

In order to calculate the derivatives $\mathrm{d}T/\mathrm{d}\alpha$, the interpolation polynomial is used.

4. Results and discussion

The computer program allows the user to edit an input file. This file must contain the decomposition rates in mg/min, the temperature and the mass values in the range where the decomposition rate is constant. In order to compute the conversion degree and the decomposition rate as s^{-1} two other values are requested, namely: the mass values for $\alpha=0$ and for $\alpha=1$. The user can input the data as: the decomposition rates in s^{-1} and the conversion values for each temperature.

The user can select the degree of the interpolation polynomial (between 2 and 7) and the number of computation intervals (between 10 and 999). As already stated, for $\alpha=1/2$, n cannot be computed, thus in the program we skip all the α values in the $1/2-\varepsilon<\alpha<1/2+\varepsilon$ range, we will, hereafter, call ε as “the exclusion domain”. In this version of the program, the exclusion domain, ε, is fixed at 0.02.

There is also a graphic routine which permits the user to observe the interpolated values of the temperature as well as the experimental values or the differences between them.

The program allows the user to save the results or print the graphics.

5. Program testing

For the simulated curves presented in the Fig. 1, which correspond to a Prout–Tompkins decomposition, the input data file is:

```
testing a Prout-Tompkins decomposition


9
0           1
0.001
0.1         142.06
0.2         132.58
0.3         128.00
0.4         125.94
0.5         125.39
0.6         125.94
0.7         128.00
0.8         132.58
0.9         142.06
9
0           1
0.002
0.1         154.32
0.2         144.12
0.3         139.47
0.4         137.22
```

Table 1
Results obtained with ICAR for the curves presented in Fig. 1. The calculated parameters for these curves are n=1, m=1, A=6.23×10^6, E=83.600 kJ/mol and C_1=1.66×10^{-5} s^{-1}, C_2=3.33×10^{-5} s^{-1}

Degree of polynomial	Number of intervals	α_{min}	T_{min}/C	$10^4 dT/d\alpha_{min}$	n	m	10^{-6}A/ s^{-1}	E/(kJ/mol)
	10	0.463	125.49	7.2	1.06	0.91	6.47	83.777
4	100	0.496	125.42	7.2	0.98	0.96	6.23	83.774
	500	0.499	125.42	7.2	0.97	0.97	6.22	83.784
	10	0.463	125.45	0.28	1.07	0.93	6.80	83.855
6	100	0.496	125.38	0.28	1.00	0.99	6.76	83.931
	500	0.499	125.38	0.28	1.00	0.99	6.76	83.932

```
0.5        136.54
0.6        137.22
0.7        137.47
0.8        144.12
0.9        154.32
```

The first line contains the title of the experiment and the second the number of points N_1 for the first decomposition rate. The third line contains the TG values (mass, conversion or any other value directly proportional to the mass) for α=0 and α=1. The fourth line contains the decomposition rate in mg/min (or TG unit/min). N_1 lines follow with the values of α and T. For the second decomposition rate, there is an identical format but without an additional title.

The numbers of points for the two decomposition rates do not have to be the same, neither the values of the conversion degree, nor the values of the temperature.

An example of computing with this program (called ICAR) for the presented data is shown in Table 1.

We note a very good consistency between the calculated and the simulated values. One can observe that the results are better described if the number of intervals is higher. We emphasise that a higher value of the degree of polynomial does not always give the best solution. In fact, smoothing the data means a lower polynomial degree. One has to check the difference between the recorded values of the temperature and the interpolated ones; this difference must be kept at a minimum. However, owing to the smoothing by an interpolation polynomial, the value $\sum(T_{exp}-T_{calc})$ for all α is practically nil. Hence, the activation parameters are correct only if there are no systematic errors. These errors may arise if the experimental setup is inadequate (too high decomposition rate, too high sample mass,...). In these unfortunate and avoidable cases the results are inaccurate, therefore an analysis of the experimental data before carrying out calculations is a good experimental practice (it is worthwhile to note that, if the errors are the same for each curve, the value of the activation energy is not strongly affected).

Let us now analyze the results which we obtained using this program in the treatment of the experimental data obtained for the dehydration of the calcium oxalate at two constant decomposition rates C_1=0.05 mg/min and C_2=0.1 mg/min. The degree of the polynomial used for interpolation was 4 (no significant difference between the parameters was obtained with the polynomial degree ranging from 2 to 6). The obtained parameters are[1]:

Activation energy: 138.700±8.700 kJ/mol
Preexponential factor (1.378±0.36)10^{13} l/s
Parameter m=0
Parameter n=0.34±0.2

The first observation we can make is the relative high value of the standard deviation, especially for the reaction order. This is due to a relative low quality of the experimental data. We consider that the order of magnitude is acceptable in comparison to the results obtained by a classical non-isothermal analysis (constant heating rate). The only controversial point is the value of the reaction order which is lower than is normally expected. We suppose that these values

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[1] This version of the program does not compute the standard deviation of the parameters; nevertheless, in the output list all the necessary values are given in order to compute it.

result from a different reaction development in the CRTA conditions in comparison to the classical constant-rate decomposition ones.

6. Conclusion

The advantages of this algorithm are:

– does not require an a priori knowledge of the form of the differential conversion function,
– a low sensitivity to experimental errors,
– the evaluation of the activation energy is performed independently of the conversion,
– it permits the observation of decomposition mechanism changes,
– it does not require an initial estimation of the parameters,
– offers good mathematical stability.

The program is written in Microsoft© Visual BASIC 3.0 and 4.0 and can run under MS Windows 3.1x or Windows 95. This program is free of charge for scientific use and may be obtained from the authors on request.

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