Thermochimica Acta, 176 (1991) 49–56
Elsevier Science Publishers B.V., Amsterdam

AN APPROACH TO THE SOLUTION OF THE INVERSE KINETIC PROBLEM IN THE CASE OF COMPLEX PROCESSES.
Part II. Methods relying on one thermoanalytical curve

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(Received 9 April 1990)

ABSTRACT

The development of our previously reported approach to the analysis of complex processes by investigating the character of the dependence of activation energy calculated by the isoconversion method on the degree of transformation. The possibility of realizing this approach in terms of the calculation methods relying on one thermoanalytical curve is considered. Three non-discriminatory methods have been investigated: Piloyan, Šesták–Berggren and exponential multipliers (EM). It was shown that these methods permit the determination of reliable values of activation energy of simple processes. For complex processes the methods of Piloyan and EM identify process type and activation energy at the initial stage of transformation. The results of calculation made using the methods of Piloyan and EM for the same processes are equivalent, which is explained by the common (quasi-isoconversion) assumption underlying these methods. The Šesták–Berggren method fails to provide reliable information on a complex process.

INTRODUCTION

In the first part [1] of this study we proposed an approach to the solution of the inverse kinetic problem in the case of complex processes. As a realization of the proposed approach, the methods of calculating the kinetic parameters (KP) by several thermoanalytical curves were considered. In the present study we investigated the possibilities of employing the methods using one thermoanalytical curve for calculating reliable values of KP of the gross-single-stage (simple) process and the possibility of realizing the previously proposed [1] approach to the analysis of complex processes which relies on a series of curves. As the objects of investigation, we have chosen methods of calculating KP which do not use discrimination: the methods of Piloyan [2], of exponential multipliers [3], and of Šesták–Berggren [4].

0040-6031/91/$03.50

BRIEF CHARACTERISTICS OF THE METHODS

The Piloyan method

The Piloyan method is based on the use of the linear form of the basic equation of non-isothermal kinetics

$$\ln\left[\frac{d\alpha}{dT}\beta\right] = \ln[Af(\alpha)] - \frac{E}{RT}$$

where α is the degree of transformation, T is the absolute temperature, β is the heating rate, R is the gas constant, A is the pre-exponential factor, E is the activation energy and $f(\alpha)$ is the differential form of the formal model of the process. This method permits the effective value of activation energy to be determined without any assumptions being made on the model of the process in the quasi-isoconversion approximation ($f(\alpha) \approx$ constant) which is valid for a narrow range of a small degree of transformation. However, the authors of this method pointed [2] to its applicability in the 0.05–0.8 range. An unjustified widening of the range leads to the violation of the condition $f(\alpha) \approx$ constant, and, therefore, to an erroneous determination of the KP values. In Ref. 5 it was noted that the error in E determined by the Piloyan method can be over 100%.

The method of exponential multipliers

The method of exponential multipliers (EM) is considered in Ref. 3. According to this method, the activation energy is determined by the character of the T dependence of $d\alpha/dT \cdot \exp(\lambda/RT)$, where λ is the zeroth approximation of the activation energy sought. If $\lambda > E$, the above-mentioned dependence decreases and at $\lambda < E$ it increases. This feature serves as the basis for the iterative algorithm for determining the activation energy. Like the Piloyan method, this method is based on the quasi-isoconversion approximation and has, therefore, the same limitations on the range of the degree of transformation used. The common characteristic of the principles underlying these methods makes it possible to assume equivalency of the results of calculations made using them. However, unlike the Piloyan method, the method of EM is based on the non-linear form of the basic equation of non-isothermal kinetics, and hence some differences between the activation energy values calculated by these methods are expected.

The Šesták–Berggren method

The Šesták–Berggren method relies on the generalized description initially proposed in the form $f(\alpha) = \alpha^m(1-\alpha)^n[-\ln(1-\alpha)]^p$ [4]. Later, however, Šesták pointed [6] to the excess number of factors in the representation of $f(\alpha)$ and recommended a form containing the first two of them. The problem of choosing a concrete form of the Šesták–Berggren equation corresponding to the real experimental data has been solved by us in the general form given in Ref. 7. The substitution of $f(\alpha)$ in any of the above-mentioned forms into the basic equation of non-isothermal kinetics with its subsequent linearization by taking the logarithm, reduces the problem of calculating KP and the parameters of the Šesták–Berggren equation to the standard problem of determining the parameters of multiple linear regression.

SIMULATION OF DATA

To test the methods, the kinetic curves for a simple and a complex process were simulated.

(1) Simple (gross-single-stage) process:
$A = 10^{15}$ min^{-1}
$E = 125.46$ kJ mol^{-1}
$\beta = 10°$ min^{-1}
$g(\alpha) = -\ln(1-\alpha)$

(2) Complex process (competing reactions):
$A_1 = 10^{12}$ min^{-1}; $A_2 = 10^{18}$ min^{-1}
$E_1 = 83.64$ kJ mol^{-1}; $E_2 = 146.37$ kJ mol^{-1}
$\beta = 10°$ min^{-1}
$g_1(\alpha) = g_2(\alpha) = -\ln(1-\alpha)$

Simulation of integral kinetic curves ($\alpha - T$) was carried out in accordance with the equations

$$\alpha = 1 - \exp\left[(A/\beta)\int \exp(-E/RT)\,\mathrm{d}T\right]$$

$$\alpha = 1 - \exp\left[(A_1/\beta)\int \exp(-E_1/RT)\,\mathrm{d}T + (A_2/\beta)\int \exp(-E_2/RT)\,\mathrm{d}T\right]$$

for a simple and a complex process, respectively. The integral on the right-hand side was calculated in the Senum–Yang approximation [8]

$$\int \exp\left(-\frac{E}{RT}\right)\mathrm{d}T = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120}$$

where $x = E/RT$. The differential kinetic curves were obtained by substituting into the corresponding form of the basic equation of non-isothermal kinetics of the temperature values and degrees of transformation corresponding to the integral curve.

CALCULATION OF THE KINETIC PARAMETERS OF A SIMPLE PROCESS

The results of our calculations of the activation energy values of the Piloyan method show that in the case where the initial portion of the curve (α up to 5%) is used, a value coinciding with the simulated one (within the error of calculation) is obtained (Table 1). When the working range of the degree of transformation is shifted towards higher values without changing its width (5%), an essential decrease in the activation energy values occurs (Fig. 1) due to the violation of the condition $f(\alpha) \approx$ constant. However, the activation energy value calculated over a wide range of degree of transformation (Table 1) is smaller than the real one by only 8 kJ mol^{-1}. The last fact is the result of the very smooth decrease in the activation energy with increasing degree of transformation for the greater portion of the curve (Fig. 1).

Figure 2 shows the dependences used to determine the activation energy by the method of EM. As can be seen from Fig. 2, the change in the character of the dependence occurs over a certain range of activation energy values, which can be viewed as a confident range and its middle can be viewed as the estimate of the sought value given in Table 1. Comparison of the value obtained in this manner with the activation energy calculated using the Piloyan method confirms our assumption of the equivalency of these methods. This equivalence is also testified by the close activation energy values obtained for the range of degree of transformation from 0 to 99% (see Table 1). Thus, the Piloyan and EM methods yield equivalent results, and permit quite satisfactory values of the activation energy to be obtained for the gross-single-stage process. Furthermore, the reliability of estimations made with these two methods is determined by the closeness of the quasi-isoconversion approximation to the isoconversion one, $f(\alpha) =$ constant, in other words, by the width of the range of degree of transformation.

Also listed in Table 1 are the activation energy values calculated using the Šesták–Berggren method. Obviously, this method permits satisfactory, although less accurate compared with the two other methods, values of the effective activation energy of the gross-single-stage process to be obtained. However, unlike the Piloyan and EM methods, the Šesták–Berggren method

TABLE 1

The activation energy of a simple process calculated using different methods for two ranges of the degree of transformation

Method	Activation energy (kJ mol^{-1})	
	$\alpha = 0$–0.05	$\alpha = 0$–0.99
Piloyan	124.7 ± 0.1	117.1 ± 2.5
EM	124.6 ± 1.7	117.0 ± 4.2
Šesták–Berggren	84.6 ± 11.7	112.9 ± 0.1

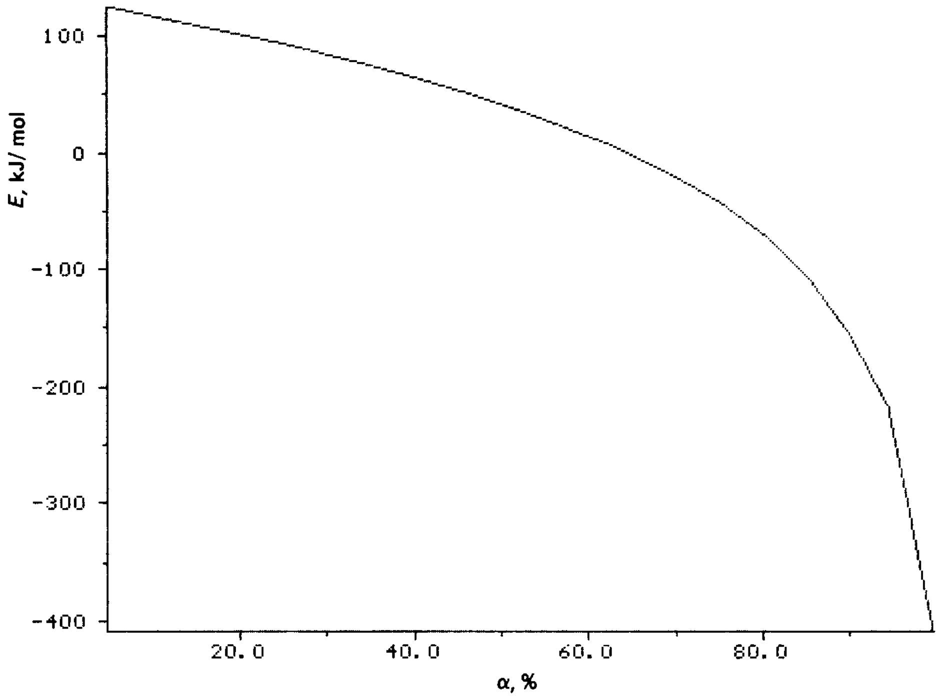

Fig. 1. The dependence of the effective activation energy calculated using the Piloyan method on the degree of transformation for a simple process.

works better the wider this range is. The large errors observed on narrowing the range of the degree of transformation are probably due to the degeneration of the system of linear equations from which the KP and the parameters of the Šesták–Berggren equation are calculated.

CALCULATION OF THE KINETIC PARAMETERS OF THE COMPLEX PROCESS

Figure 3 shows a plot of the activation energy calculated using the Piloyan method vs. the transformation degree. Comparing this figure with Fig. 1, it can be seen that in the range of small values of the degree of transformation there is a slight increase in the activation energy which changes into a decrease, similar to that observed in the case of the simple process which results from the violation of the quasi-isoconversion approximation with increasing α. It was noted previously [1] that the increasing dependence of the activation energy on the degree of transformation is characteristic of a complex process consisting of two competing reactions. Consequently, the application of the Piloyan method makes it possible, in this case, to identify correctly the type of complex process that occurs. As to concrete activation energy values of competing reactions, in this case it is

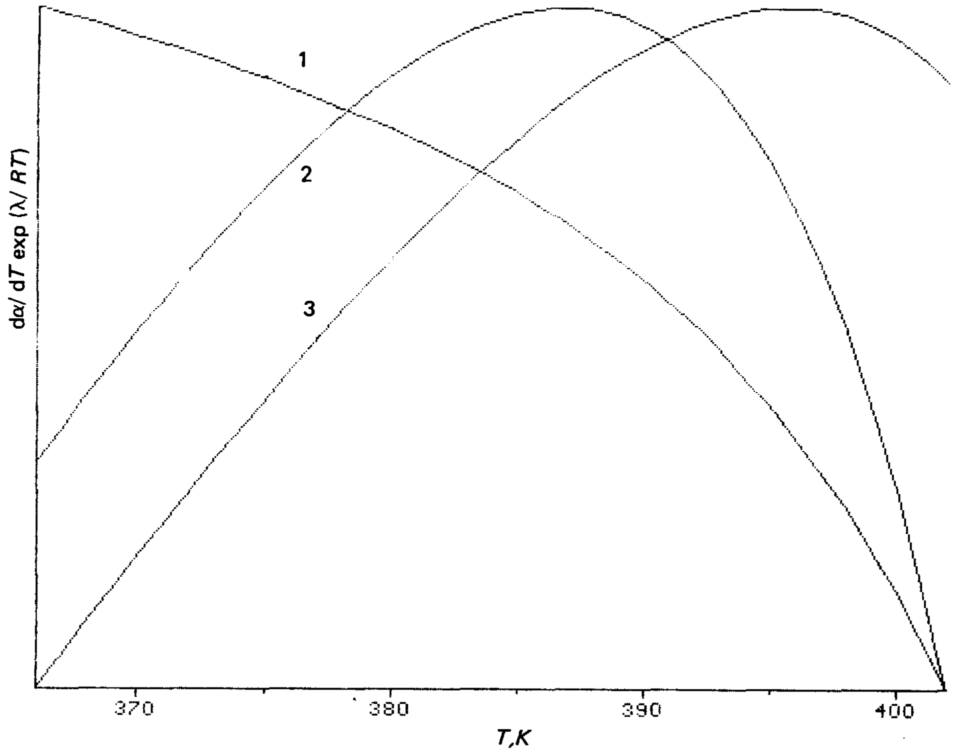

Fig. 2. The temperature dependences of $d\alpha/dT \cdot \exp(\lambda/RT)$ calculated using the method of EM for a simple process. λ(kJ mol^{-1}): (1) 122.9; (2) 124.6; (3) 126.3.

possible to estimate only one value (Table 2), the smallest one, since in the region of low degree of transformation in which this method works the process with the smallest activation energy prevails. As in the case of the gross-single-stage process, the results of calculations made using the method of EM are equivalent to the results obtained with the Piloyan method (Table 2), which points once again to the equivalence of these two methods. If we compare the results obtained with those of our previous calculations [1] done with isoconversion methods relying on several thermoanalytical curves corresponding to different heating rates, a much greater informativeness of the latter is found as compared with the former. In the case of the methods relying on several analytical curves, an undistorted dependence of the activation energy on the degree of transformation is obtained, since the isoconversion assumption holds for all values of α. As a result, identification of the type of complex process is simplified and the possibility of estimating the activation energy of the process prevailing in the region of large values of the degree of transformation appears. We therefore believe that, although the Piloyan and EM methods permit certain information to be obtained about a process in a more economic way (from one thermoanalytical curve),

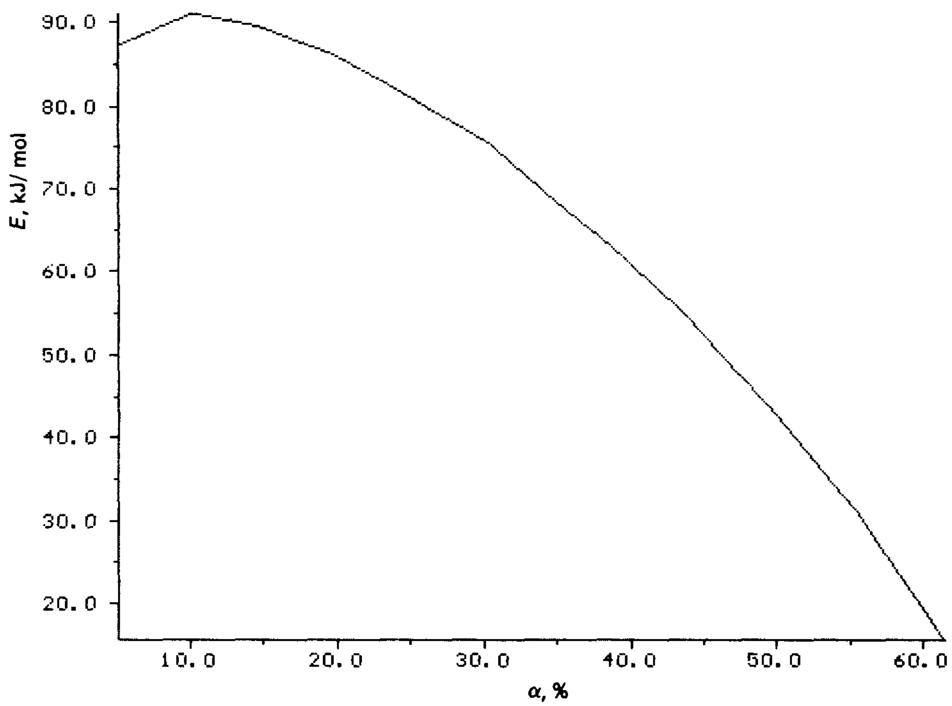

Fig. 3. The dependence of the effective activation energy calculated using the Piloyan method on the degree of transformation for a complex process.

because of the incompleteness of this information these methods can generally only be used for the purposes of express analysis.

Calculation by the Šesták–Berggren method yielded the activation energy value $E = -54.8 \pm 19.6$ kJ mol^{-1} and the parameter values $m = 1.58 \pm 0.41$ and $n = 0.57 \pm 0.07$. In this case one might have expected an intermediate value of activation energy for the competing reactions forming the process; but this was not the case, probably, owing to the fact that in this case the Šesták–Berggren equation appeared to be insufficiently flexible to be able to describe the shape of the thermoanalytical curve (otherwise, one would have obtained the parameter values $m = 0$ and $n = 1$). Naturally, the distortion of

TABLE 2

The activation energy of a complex process calculated using different methods for two ranges of the degree of transformation

Method	Activation energy (kJ mol^{-1})	
	$\alpha = 0$–0.05	$\alpha = 0$–0.99
Piloyan	88.9 ± 0.3	81.6 ± 2.5
EM	87.8 ± 2.1	79.4 ± 4.2
Šesták–Berggren	-41.8 ± 0.6	-54.8 ± 19.6

the parameters of the curve shape (in this case n) leads to the distortion of the value of the parameter of its position (E), since all the parameters are determined from the common system of linear equations. This fact points to potential errors which can arise when using the Šesták–Berggren method, even in the case of the gross-single-stage process, to say nothing of the complex processes to which it is inapplicable.

CONCLUSIONS

The Piloyan and EM methods yield equivalent values of activation energy. In our opinion, the former method is more convenient, since it does not require iterative selection of the value sought.

All the three methods considered here (Šesták–Berggren, EM and Piloyan) make it possible to determine satisfactorily the activation energy of the gross-single-stage process. It should be noted that in the case of the Piloyan and EM methods, the most accurate values of activation energies are obtained when a narrow range of small degrees of transformation is used in the calculations, and the accuracy of the values obtained with the Šesták–Berggren method increases with increasing width of this range.

In investigating complex processes, the Piloyan and EM methods permit adequate information about the type and activation energy of the prevailing process to be obtained within a narrow range of small degrees of transformation, whereas the Šesták–Berggren method is unsuitable for these purposes.

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