Thermochimica Acta, 194 (1992) 221–230
Elsevier Science Publishers B.V., Amsterdam

Potentialities of software for kinetic processing of thermoanalytical data by the isoconversion method

S. Vyazovkin and V. Goryachko

Institute for Physico-Chemical Problems, Byelorussian State University, Minsk 220080 (USSR)

(Received 17 April 1991)

Abstract

The potentialities of the proposed software, which is based on the isoconversion method of calculating the Arrhenius parameters, are compared with software of the Du Pont and Mettler thermoanalysers. Calculations by the model DSC curves for a process involving two parallel independent reactions have shown that the software of the thermoanalysers does not provide reliable information about the kinetics of complex processes. The proposed software makes it possible to establish the complex character of a process and its type, to evaluate the activation energies of parallel reactions and to predict the kinetics of its proceeding outside the experimental temperature range.

In refs. 1–6, it was shown that the correct solution of the inverse problem of non-isothermal kinetics in a general case, was only possible with the use of non-discrimination methods which do not require choosing the formal model of a process for calculating the Arrhenius parameters (AP). Of the non-discrimination methods, the most informative are the isoconversion methods [4], which yield the dependence of the effective activation energy on the transformation degree from the data of several non-isothermal experiments. This is a source of valuable information on the real kinetics of processes investigated by thermoanalytical methods. The approach developed by us [7] offers the possibility of interpreting the form of the transformation-degree dependence of the activation energy in terms of the gross mechanism for both simple and complex (involving several reactions) processes and estimating their corresponding AP values.

On the basis of this approach, software for the kinetic processing of thermoanalytical data has been developed. The present paper compares the potentialities of our software with those of the software used in DuPont thermoanalysers [8], which involves two procedures for calculating AP from the DSC curves. The first procedure is intended for processing data of a single non-isothermal experiment and is represented by the Borchardt–Daniels method [9] according to which AP are calculated by the method of discriminating reaction-order models. Because the software of the Mettler

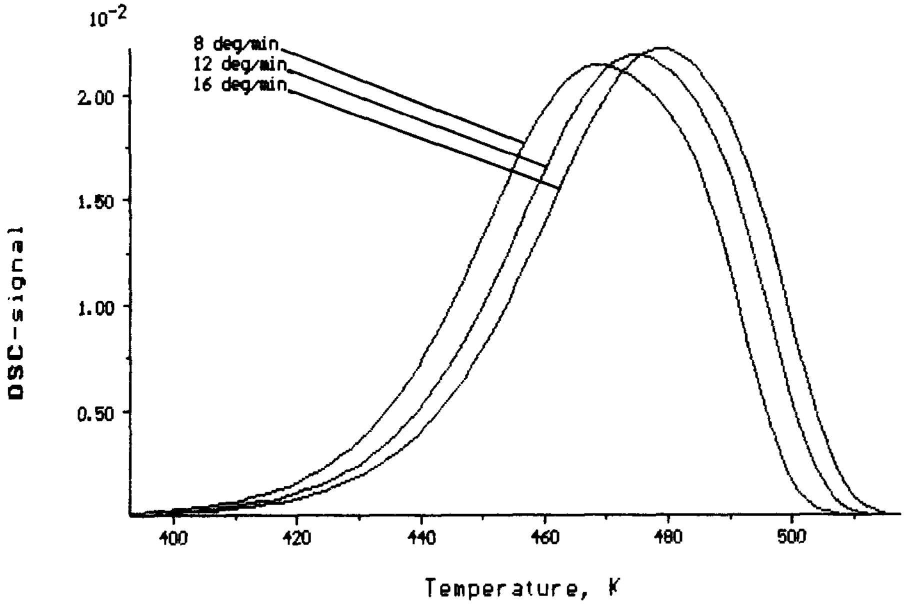


Fig. 1. DSC curves for a complex model process involving parallel independent reactions.

TA 3000 uses a similar procedure of calculating AP [10], the results below obtained by the Borchardt–Daniels method can be ascribed to this software. The second procedure of calculating AP is based on the recommendations of ASTM E698 [11] and is intended for kinetic processing by the Kissinger method of a series of DSC curves obtained at different heating rates [12]. All the figures illustrating the operation of our software are copies of the computer screen.

As an example, consider the kinetic processing of the model DSC curves (Fig. 1) for a complex process involving two parallel independent first-order reactions with the values of activation energy (E) and pre-exponent (A), respectively: $E_1 = 125.4$ kJ mol^{-1}, $E_2 = 167.2$ kJ mol^{-1}, $A_1 = 10^{14}$ min^{-1} and $A_2 = 10^{18}$ min^{-1}. The model DSC curves (heating rates 8, 12, 16 °C min^{-1}) are ordinary bell-shaped curves and, therefore, give no reason to suppose that their corresponding process is complex. The results of calculating the AP values and the order of reaction by the Borchardt–Daniels method are given in Table 1. The activation energy value estimated by the Kissinger method and the logarithm of the pre-exponent value found in accordance with ASTM E698, respectively 133.1 kJ mol^{-1} and 14.59 min^{-1}. As with the shape of the DSC curves, these values give no information on the complex character of the process under consideration. Obviously, considering the kinetic information of a complex process as that of a simple one has no physical meaning. Thus, the methods for calculating AP and,

TABLE 1

The results of calculating the kinetic parameters by the Borchardt–Daniels method

Heating rate (°C min^{-1})	Activation energy (kJ mol^{-1})	Pre-exponent (min^{-1})	Reaction order
8	114.7	12.4	0.944
12	116.6	12.6	0.947
16	118.3	12.8	0.948

consequently, the software based on their application cannot be used for thermoanalytical studies of complex processes.

It should be noted that in the text of ASTM E698, a limited possibility of using the proposed methods of calculating AP by the Kissinger method applied to complex processes is pointed out. However, to question the AP results calculated, one must first have information that the process is complex. But, as we have determined above, the Kissinger method does not provide such information; nor does the Borchardt–Daniels method. Therefore, the results of the kinetic processing of DSC curves with the ordinary bell-shape, which is observed not only for simple but also for many complex processes, can be erroneous if they were obtained by software that does not take into account the potentially complex nature of the process being investigated. As the majority of chemical processes are complex, there are good reasons for supposing that researchers using the software of different

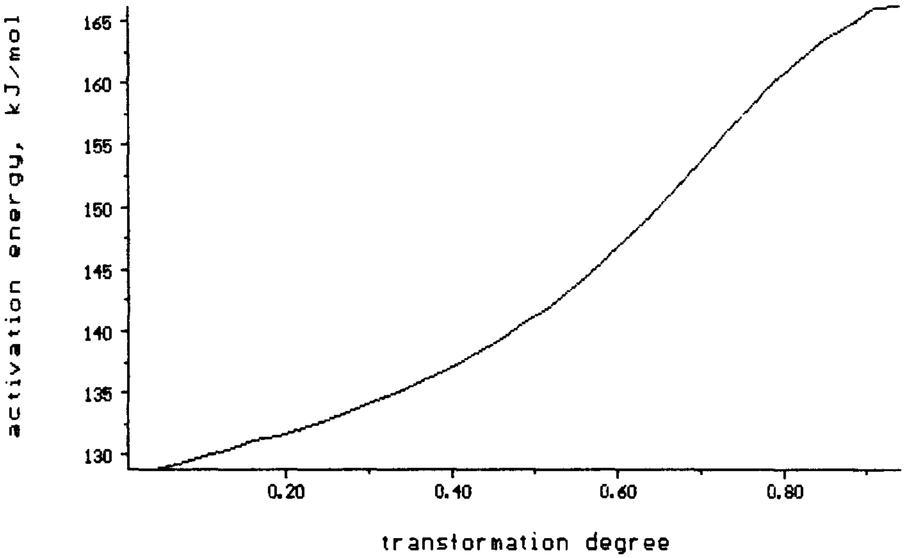
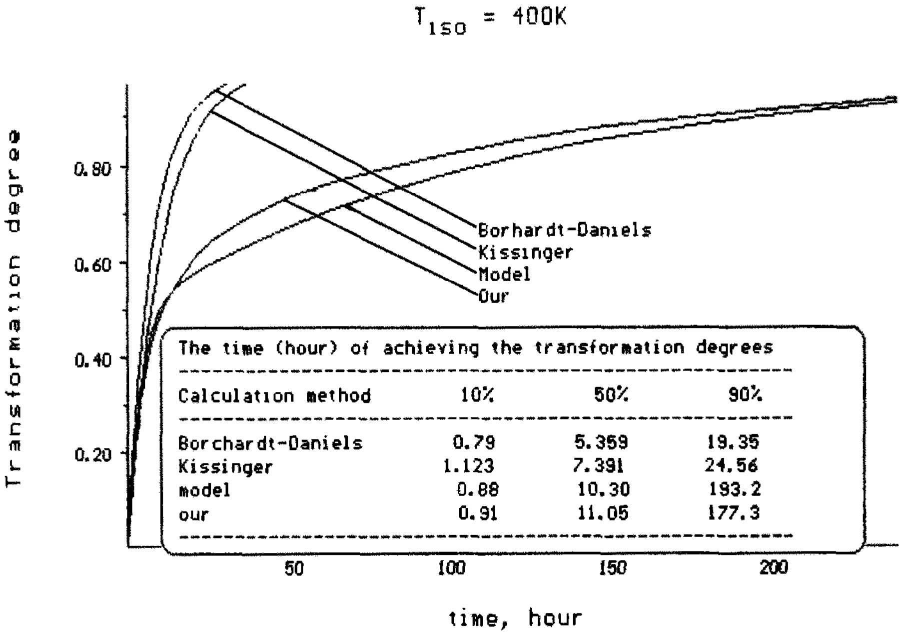


Fig. 2. The transformation-degree dependence of the effective activation energy calculated by the isoconversion method for a model process.

thermoanalysers often obtain unreliable kinetic information, whilst being quite unaware of it. The software developed by us eliminates this misunderstanding, and also permits the solving of practical problems in the case of complex processes. Concrete examples demonstrating the potentialities of our software as compared with the software of the Du Pont and Mettler thermoanalysers, are given below.

The transformation-degree dependence of the effective activation energy calculated for model DSC curves by our software is given in Fig. 2. Interpreting this dependence, we can obtain concrete information about the process being investigated. First of all, the fact of the existence of such a dependence points to the complex character of the process [7,13] (for a simple process the activation energy is constant at any transformation degree). The rising character of the dependence indicates that the reactions forming the complex process are parallel. The activation energy values at transformation degrees close to 0 and 1 are, in this case, estimates of the activation energies of individual reactions and are equal to 128.3 and 165.9 kJ mol^{-1}, respectively. Thus, the approach developed by us [7] and the software created on its basis provide reliable information about the mechanism of a complex process and the activation energy of individual reactions. Examples of interpreting the transformation-degree depen-



The time (hour) of achieving the transformation degrees

Calculation method	10%	50%	90%
Borchardt-Daniels	0.79	5.359	19.35
Kissinger	1.123	7.391	24.56
model	0.88	10.30	193.2
our	0.91	11.05	177.3

Fig. 3. Isothermal kinetic curves (T_{iso} = 400 K) plotted by the results of calculating AP by different methods as against the model curve.

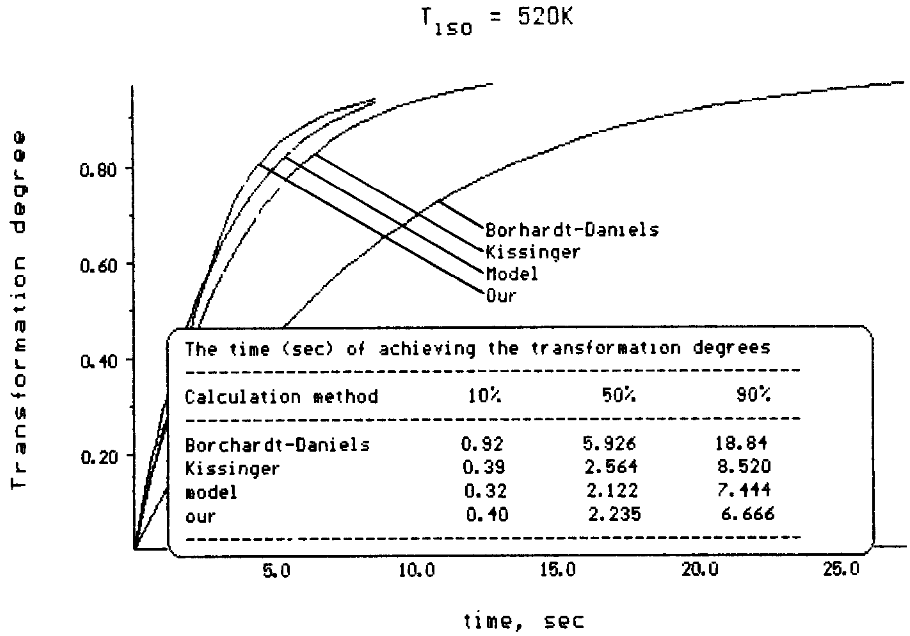
dences of activation energy for real complex processes can be found in our works [14–16].

The question of the reliability of the calculated AP values is especially acute in solving practical problems connected with predicting the behaviour of the process being investigated beyond the experimental temperature range. The solution of such problems is only possible with AP values that reflect correctly the temperature dependence of the rate of the process [6]. To ensure this, let us calculate the AP values by the Borchardt–Daniels and Kissinger methods used in the software of the Du Pont thermoanalyser, as well as by the isoconversion method underlying our software, and, proceeding from the values obtained, try to predict the kinetics of the model process being considered at the temperatures $T_{\mathrm{iso}} = 400$ and 520 K, which are outside the experimental range.

To plot the kinetic curve at a given temperature, T_{iso}, from the AP values and the reaction order calculated by the Borchardt–Daniels method, we use the universally accepted expression

$$t = g(w)/A \exp(-E/RT) \tag{1}$$

where t is the time, w the transformation degree, $g(w)$ the integral form of the equation of the reaction order and R the gas constant. The AP values found by the Kissinger method were substituted into eqn. (1) under the



The time (sec) of achieving the transformation degrees

Calculation method	10%	50%	90%
Borchardt-Daniels	0.92	5.926	18.84
Kissinger	0.39	2.564	8.520
model	0.32	2.122	7.444
our	0.40	2.235	6.666

Fig. 4. Isothermal kinetic curves ($T_{\mathrm{iso}} = 520$ K) plotted by the results of calculating AP by different methods as against the model curve.

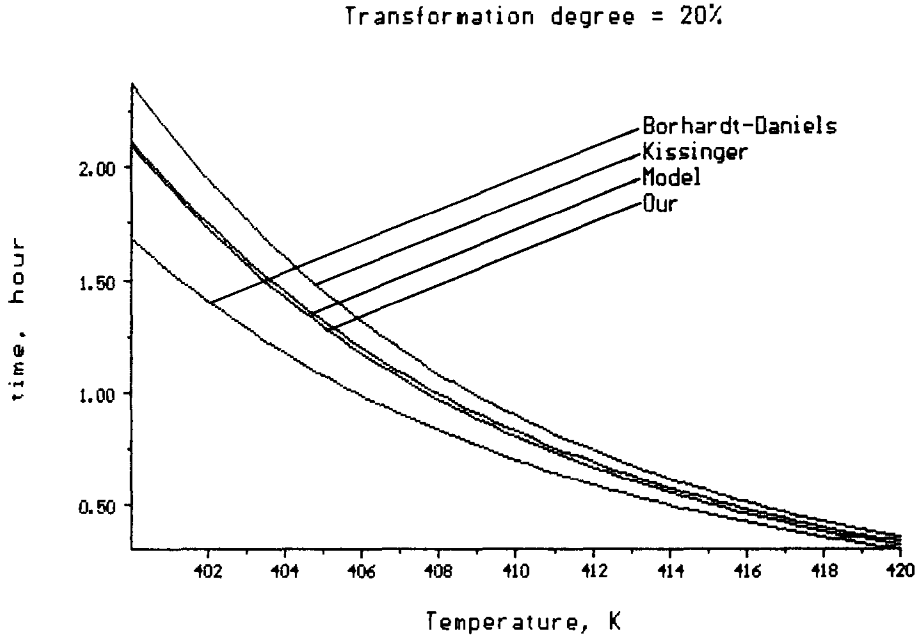


Fig. 5. Isoconversion curves ($w = 20\%$) plotted by the results of calculating AP by different methods as against the model curve.

assumption that the process obeys the first-order equation $g(w) = -\ln(1 - w)$ [8,11]. In accordance with our software, the isothermal kinetic curve is constructed proceeding from the transformation-degree dependence of the activation energy $E = E(w)$ by the previously proposed equation [17,18]

$$t_w = \int_0^{T_w} \exp[-E(w)/RT] \, \mathrm{d}T/q \; \exp[-E(w)/RT_{\mathrm{iso}}] \qquad (2)$$

The value of t_w from eqn. (2) corresponds to the transformation degree, w, reached in the non-isothermal experiment at temperature T_w and heating rate q.

Figures 3 and 4 show the isothermal kinetic curves constructed by the above methods as against the model curves. Comparing the kinetic curves obtained with the model curve, we can see that the Borchardt–Daniels method relying on discrimination of reaction-order models, cannot be used at all for predicting the kinetics of a process beyond the experimental temperature range. The non-discrimination Kissinger method offers more plausible predictions of the kinetics of the proceeding of a complex process than does the Borchardt–Daniels method. However, because the Kissinger method does not take into account the complex character of a process, the results obtained from it are considerably less accurate than the calculations made by our method (eqn. (2)). The isoconversion curves given in Figs. 5–7 indicate that the approach used in our software offers better results in

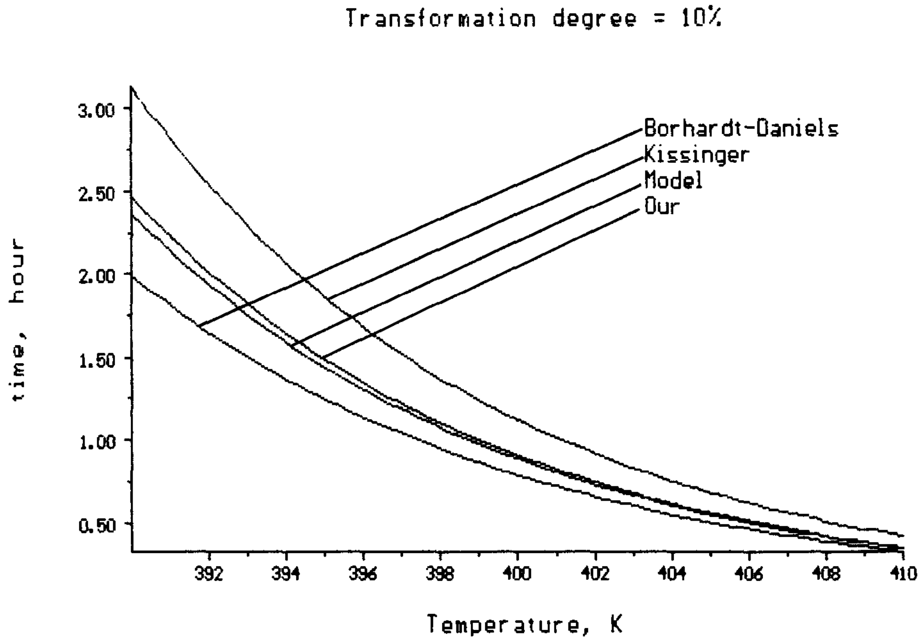


Fig. 6. Isoconversion curves ($w = 10\%$) plotted by the results of calculating AP by different methods as against the model curve.

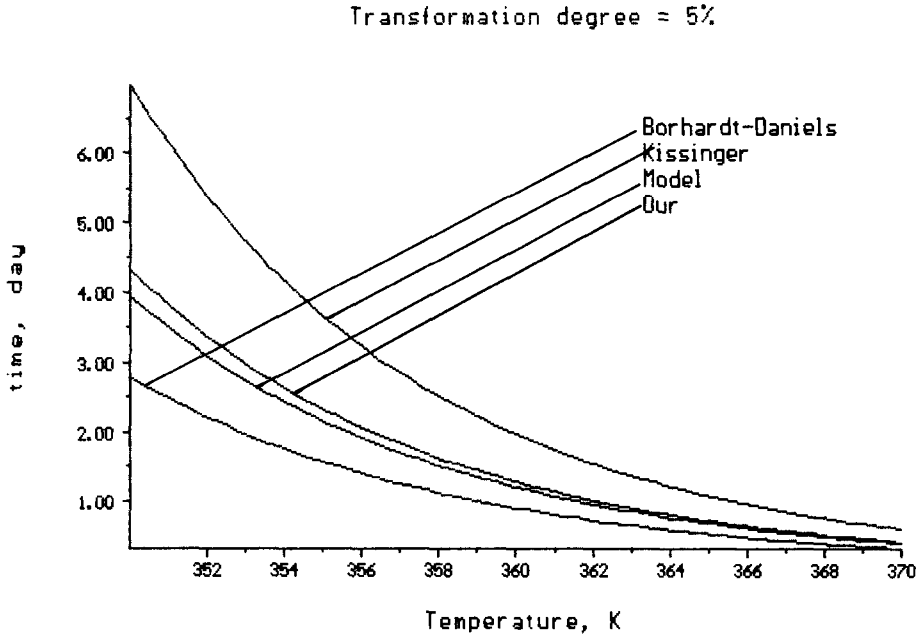


Fig. 7. Isoconversion curves ($w = 5\%$) plotted by the results of calculating AP by different methods as against the model curve.

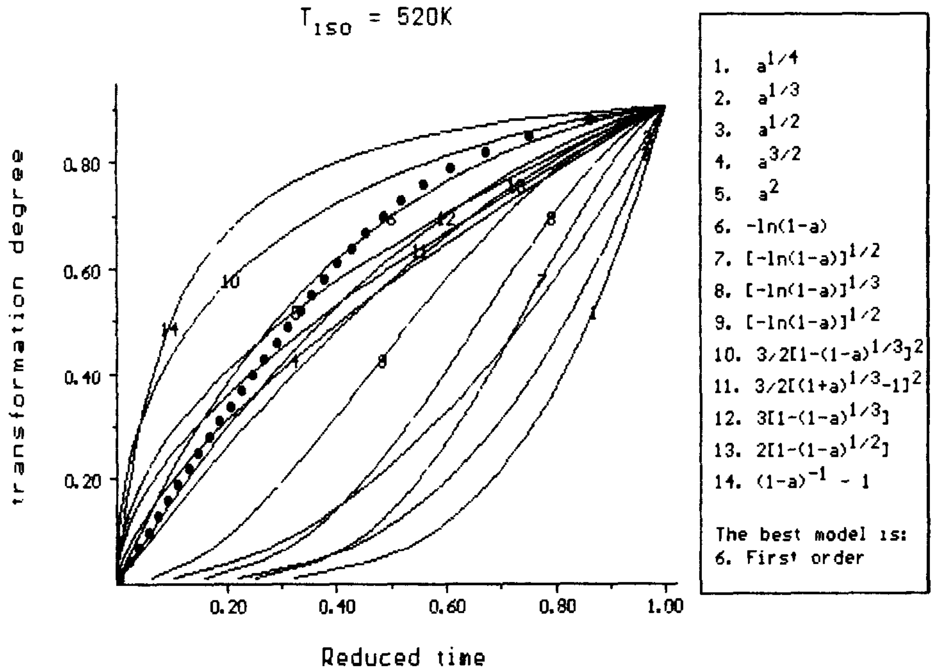


Fig. 8. The thermoanalytical curve (points) transformed to the isothermal form ($T_{iso} = 520$ K) against the background of curves corresponding to various formal models on reduced coordinates.

regions of both large and small transformation degrees. Thus, we may state that the software developed by us copes quite successfully with the kinetic processing of thermoanalytical data in the case of complex processes. It should be noted that it is also applicable to simple processes.

In conclusion, one more feature of our software should be mentioned. Having calculated the transformation-degree dependence of the activation energy and transformed the thermoanalytical curve into the isothermal form, we can choose from the proposed list the most probable model of the process on reduced coordinates, i.e. by the conventional isothermal kinetics method. Figure 8 shows the thermoanalytical curve transformed on reduced coordinates into an isothermal curve, which corresponds to the complex process being considered. It is seen that of the 14 models used, the equation of the first-order reaction best describes the kinetics of this process. However, such a means of choosing the model should be used carefully, as it is substantiated theoretically only for processes whose rate equation can be represented in the form with separable T and w variables [19], i.e. it is correct for all simple and only some complex processes. To be sure that the choice of model is correct, one should transform the non-isothermal kinetic curve to the isothermal form for different T_{iso} temperatures and compare the curves obtained on reduced coordinates. If the

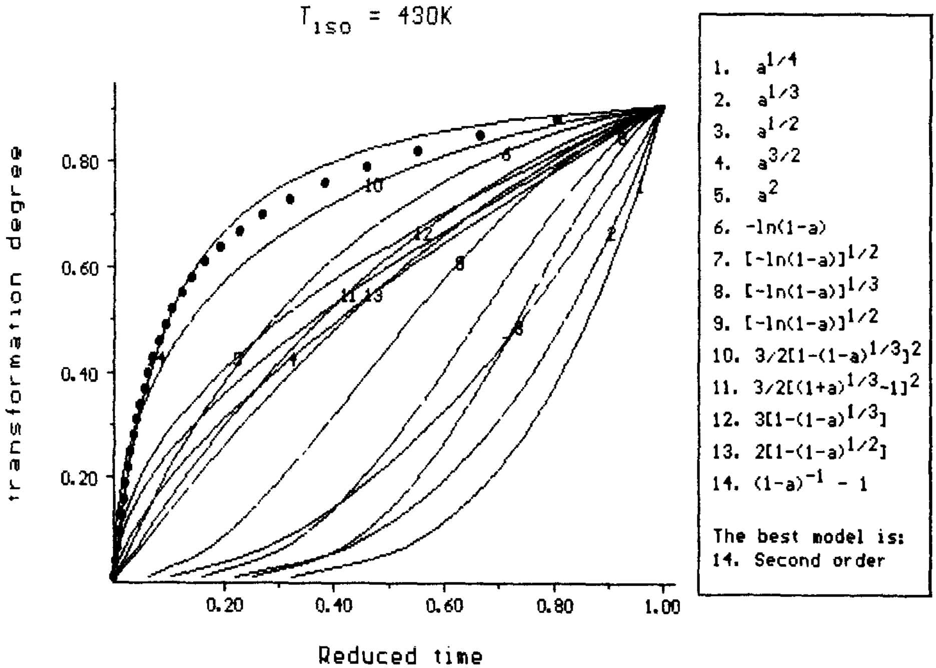


Fig. 9. The thermoanalytical curve (points) transformed to the isothermal form ($T_{iso} = 430$ K) against the background of curves corresponding to various formal models on reduced coordinates.

reduced curves corresponding to different temperatures are the same, i.e. if they are described by one and the same model, the rate of the process being investigated can be described by the equation with separable variables. In this case, the choice of the model should be considered correct. Otherwise the chosen model is a purely formal description of the kinetics of the process in question at a concrete temperature T_{iso}. In particular, the rate equation of the complex process considered in this paper cannot be represented in the form with separable variables; this can be verified by comparing the results of choosing models on reduced coordinates for one and the same thermoanalytical curve transformed into isothermal kinetic curves corresponding to different temperatures (Figs. 8 and 9).

Thus, unlike the software of the Du Pont and Mettler thermoanalysers, for any process our software makes it possible to establish the complex (stage) character of the process; to identify the overall mechanism; to estimate the activation energies of the reactions comprising the process; to predict behaviour outside the experimental temperature range; and to choose the formal model on reduced coordinates.

All our programs are in PASCAL and are oriented to the use of personal computers compatible with an IBM PC, which have EGA / VGA graphics and a colour monitor.

ACKNOWLEDGMENTS

The authors look forward to receiving any comments and any offers concerning the software described in this paper.

REFERENCES

1 S.V. Vyazovkin and A.I. Lesnikovich, J. Therm. Anal., 32 (1987) 909.
2 S.V. Vyazovkin, A.I. Lesnikovich and E.A. Gunin, Thermochim. Acta, 130 (1988) 269.
3 S.V. Vyazovkin and A.I. Lesnikovich, J. Therm. Anal., 35 (1989) 2169.
4 S.V. Vyazovkin and A.I. Lesnikovich, J. Therm. Anal., 36 (1990) 599.
5 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 165 (1990) 11.
6 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 182 (1991) 133.
7 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 165 (1990) 273.
8 Instructions for DuPont 9900.
9 H.J. Borchardt and F. Daniels, J. Phys. Chem., 61 (1957) 1957.
10 Mettler TA 3000, operating instructions, p. 320.
11 ASTM E 698, Arrhenius Kinetic Constants for Thermally Unstable Materials.
12 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
13 S.V. Vyazovkin and A.I. Lesnikovich, Thermochim. Acta, 128 (1988) 69.
14 S.V. Vyazovkin, A.I. Lesnikovich and V.A. Lyutsko, Thermochim. Acta, 165 (1990) 17.
15 S.V. Levchik, E.E. Bolvanovich, A.I. Lesnikovich, O.A. Ivashkevich, P.N. Gaponik and S.V. Vyazovkin, Thermochim. Acta, 168 (1990) 211.
16 S.V. Vyazovkin, V.V. Bogdanova, I.A. Klimovtsova and A.I. Lesnikovich, J. Appl. Polym. Sci., 42 (1991) 2095.
17 S.V. Vyazovkin and A.I. Lesnikovich, Russian J. Phys. Chem., 62 (1988) 2949.
18 S.V. Vyazovkin, A.I. Lesnikovich and V.I. Goryachko, Thermochim. Acta. 177 (1991) 259.
19 P. Barret, Cinetique Heterogene, Gauthier-Villars, Paris, 1973.