A COMPUTER PROGRAM FOR KINETIC ANALYSIS
OF NON-ISOTHERMAL THERMOANALYTICAL DATA

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ABSTRACT

A BASIC program is described which enables the kinetic analysis of thermoanalytical experimental data obtained under non-isothermal conditions. This software has been developed specifically for treating experimental (DSC) data files created by the Perkin–Elmer TADS system. However, it can be easily modified for other computer systems.

The program chooses the best kinetic model for the data and performs a complete quantitative description and kinetic analysis of the process under study, including direct comparison of experimental and theoretically calculated data. Two sets of theoretical and one set of experimental data are presented to demonstrate the application of the program.

INTRODUCTION

The use of non-isothermal data to calculate kinetic parameters of solid state processes has been described in the literature for many years. The kinetic parameters calculation was also one of the earliest to be computerized, and today many kinetic analysis programs are available, even commercially [e.g. 1,2]. However, these programs have their limitations and shortcomings.

Every kinetic evaluation is based on comparison of theoretical and experimental data. The standard kinetic evaluation method is the well known least-squares method

$$\sum_i w_i \left(Y_i^{exp} - Y_i^{calc} \right) = \min \tag{1}$$

where Y_i^{exp} and Y_i^{calc} are the experimental data and their theoretically calculated counterparts, respectively. w_i are optional weight factors. Thus the application of eqn. (1) requires the solution of a differential kinetic equation, which is usually written in the following form

$$Y_i^{calc} = \dot{H}_i = \Delta H \, A \exp(-E/RT_i) \, f(\alpha_i) \tag{2}$$

In practice, this leads to a numerical non-linear regression. However, due to the strong correlation of the kinetic parameters the results of the non-linear

regression depend on the first estimate for the kinetic parameters [3]. Thus kinetic evaluation in thermal analysis is frequently based on simple linearization techniques. It is interesting to note that practically all commercially available kinetic analysis programs are based on linearized multiple regression analysis. Problems and disadvantages associated with these linearization procedures have previously been mentioned [4].

The aim of this paper is to describe kinetic software which has been designed to avoid these shortcomings. Clearly, it is practically impossible to assume a general kinetic model which will be valid for all solid state processes. Thus we will focus our attention on the applicability of the three most frequently used kinetic models, i.e.

(i)   Reaction-order (RO) model [5]

$$f(\alpha) = (1 - \alpha)^n$$

(ii)   Johnson–Mehl–Avrami (JMA) model [6,7]

$$f(\alpha) = n(1 - \alpha)[-\ln(1 - \alpha)]^{1 - 1/n}$$

(iii)   Šesták–Berggren (SB) model [8]

$$f(\alpha) = \alpha^m (1 - \alpha)^n$$

THEORY

The basis for the use of eqn. (2) has been discussed [e.g. 9]. This equation links the heat flow (measured by DSC) induced by the process and the set of kinetic parameters related to the process. The mathematical condition for the maximum of the DSC peak can be written as

$$\dot{H}\left[\beta E/RT_p^2 - Q_p A \exp(-E/RT_p)\right] = 0 \tag{3a}$$

$$Q_p = -[df(\alpha)/d\alpha]_{\alpha = \alpha_p} \tag{3b}$$

This equation can be rewritten, after converting to logarithms, in the form

$$\ln(\beta/T_p^2) = \ln(ARQ_p/E) - E/RT_p \tag{4}$$

The slope of the plot of $\ln(\beta/T_p)$. $1/T_p$ (Kissinger's plot) gives the activation energy. Strictly speaking, this is completely true only in the case of a 'first order' process (i.e. the RO model, where $n = 1$) since $Q_p = 1$. However, it can be shown [10] that whatever the kinetic model, the error in the activation energy estimated in this way is lower than 5% provided $E/RT_p > 10$. Thus the activation energy can be determined by Kissinger's method without detailed knowledge of the kinetics.

Although activation energy is independent of the kinetic model, its value allows the determination of the kinetic model. By rewriting eqn. (2) in a different form we obtain
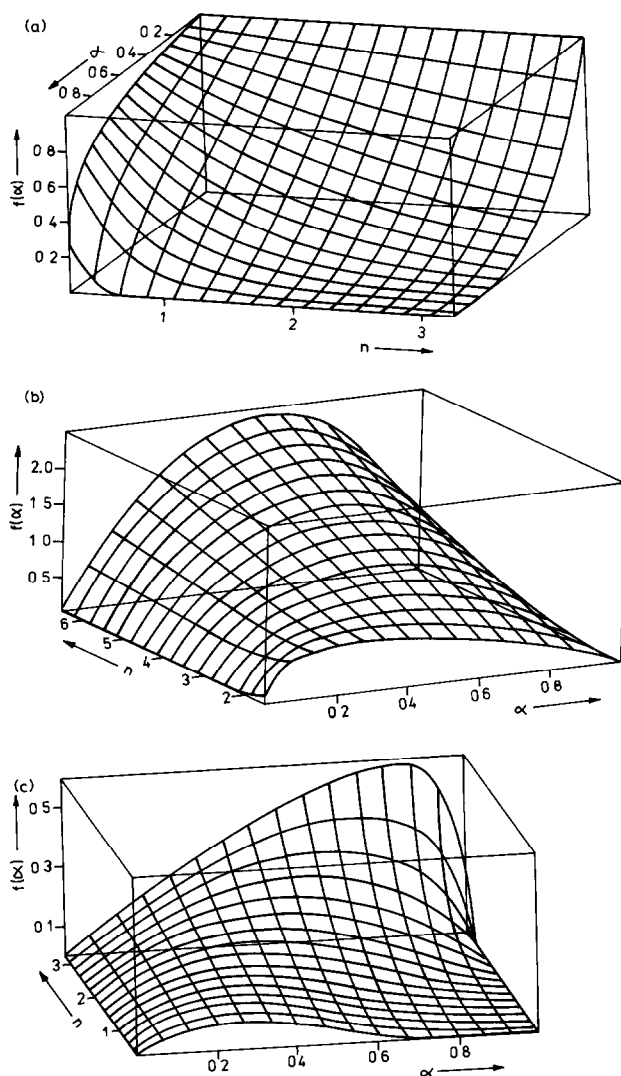
$$y(\alpha) = \dot{H} \exp(E/RT) = A' f(\alpha) \tag{5}$$

Fig. 1. Theoretical relationship between α, n and $f(\alpha)$ for different kinetic models: (a) RO, (b) JMA, (c) SB for $m = 1$.

where $A' = A\,\Delta H$, which is a constant. Thus by plotting normalized $y(\alpha)$ dependence, the shape of the function $f(\alpha)$ can be obtained. $f(\alpha)$ functions calculated for the kinetic models discussed are plotted in Fig. 1. It is clear that the shape of $f(\alpha)$ is significantly different for each model. Thus normalized $y(\alpha)$ dependence can be used to guide the choice of a suitable kinetic model. From this point of view, the following rules are important

(i) If the $y(\alpha)$ function is decreasing steadily (see Fig. 1a), the RO model can be used to describe the process under study. The kinetic parameter n is then calculated iteratively using the equation [11]

$$\alpha_p = 1 - \left[(2nRT_p + E)/(nE + 2nRT_p)\right]^{1/(N-1)} \qquad (6)$$

(ii) If the $y(\alpha)$ function has a maximum and the relation $\alpha_p \approx 0.633$ is fulfilled, the JMA model provides a suitable description of the process under study. The kinetic parameter n is then calculated using the equation

$$n = 1/[1 + \ln(1 - \alpha_M)] \tag{7}$$

(iii) If the $y(\alpha)$ function has a maximum and $\alpha_p \ll 0.633$, then the SB model can be used. The kinetic parameter ratio $p = m/n$ can be calculated using the equation

$$p = \alpha_M/(1 - \alpha_M) \tag{8}$$

Eqn. (1) can be rewritten in the form

$$\ln[\dot{H} \exp(E/RT)] = \ln A' + n \ln[\alpha^p(1 - \alpha)] \tag{9}$$

The kinetic parameter n corresponds to the slope of linear dependence $\ln [\dot{H}\exp(E/RT)]$ vs. $\ln[\alpha^p(1 - \alpha)]$. The second parameter m is then calculated using $m = p \cdot n$.

Finally, a rearrangement of eqn. (3) for the pre-exponential factor yields

$$A = \frac{\beta E}{RT_p^2 Q_p} \exp(E/RT_p) \tag{10}$$

The function Q_p for the kinetic models under discussion can be written as
(i) RO model

$$Q_p = n(1 - \alpha_p)^{n-1}$$

(ii) JMA model

$$Q_p = n[-\ln(1 - \alpha_p)]^{1-1/n} - (n - 1)[-\ln(1 - \alpha_p)]^{-1/n}$$

(iii) SB model

$$Q_p = n\alpha_p^m(1 - \alpha_p)^{n-1} - m\alpha_p^{m-1}(1 - \alpha_p)^n$$

DESCRIPTION OF THE PROGRAM

Figure 2 shows a schematic diagram of the general kinetic analysis program KINET. The program was written in BASIC (PETOS, version A). Experimental data files created by the TADS system (see Experimental) are used in the ALFA subroutine. This incorporates a routine which performs a cubic spline interpolation of the experimental data. A subsequent routine allows the calculation of α values at selected temperatures. This requires user input of peak limits, which delineate where the baseline is to be fitted to the peak. At the conclusion of each run the heating rate T_p and the set of T_i, $\dot{H}_i$ and α_i values are stored sequentially in a new output file.
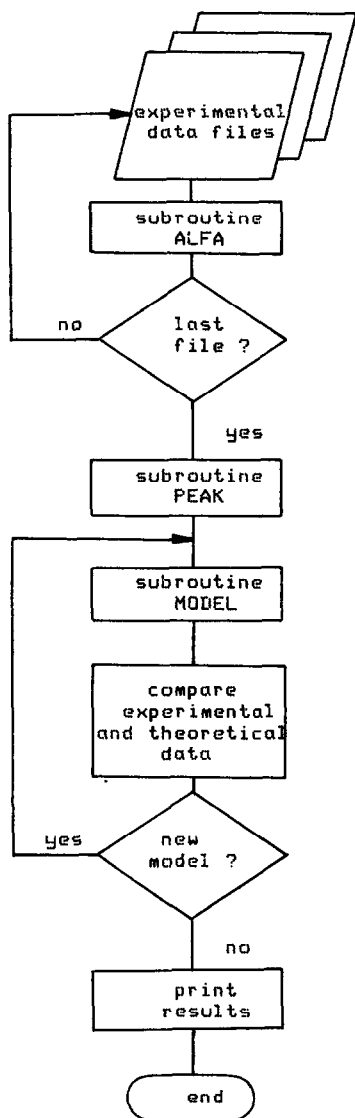
Fig. 2. Schematic diagram of the program KINET.

These new files are used in the subroutine PEAK which calculates the activation energy using a Kissinger's plot. The activation energy is used in subroutine MODEL to generate the normalized $y(\alpha)$ function, according to eqn. (5), to be used for the choice of a suitable kinetic model (see Theory). The kinetic parameters A, $n(m)$ and reaction heat ΔH are calculated for the chosen kinetic model, according to eqns. (6) to (10). The quality of the kinetic results is assessed by comparison of the experimental data with theoretical data $\dot{H}(T)$ calculated using the above-mentioned parameters. If there is systematic divergence of the theoretical from the experimental data,

the operator can then select a different kinetic model. If desired, the calculated kinetic parameters can be printed out, together with both experimental and theoretically calculated DSC curves.

Much has been published about the problems associated with obtaining reliable kinetic parameters. It should be noted that the procedure described cannot be used for kinetic parameters evaluation of complicated simultaneous multiple processes. In any case, efforts should be made to resolve overlapping DSC peaks through the selection of suitable running conditions (e.g. using a slow heating rate). For a simple reaction it would seem reasonable to assume that it will be possible to find the same kinetic parameters using different heating programmes. We recommend that the consistency of the kinetic model applied be assessed by testing the invariance of theoretically calculated kinetic parameters for several scans at different heating rates.

EXPERIMENTAL

In order to test this kinetic analysis software, samples of glassy $GeSe_2$ were run in a DTA–1700 system (Perkin–Elmer) operating in heat flux DSC mode. Raw experimental data were acquired and stored using a Thermal Analysis Data Station (TADS) computer system. Glassy $GeSe_2$ was selected as the test material because it undergoes a thermally initiated crystallization associated with one well defined DSC peak.

The sample was prepared conventionally, as described elsewhere [12]. Freshly prepared powdered glassy samples with an average particle size of 0.1 mm were used for the DSC measurements. To minimize the high reactivity of $GeSe_2$ with oxygen traces at elevated temperatures, all measurements were carried out with the sample placed in the small evacuated ($p \sim 1$ mPa) quartz ampoules fitting into measuring platinum cups. Aluminium oxide powder in an evacuated quartz ampoule was used as the reference sample.

PROGRAM APPLICATION

In order to demonstrate the general applicability of the program, both theoretical and experimental data were used. Theoretical data were calculated for two kinetic models [13] with log A, β, E and ΔH assumed to be 10, 10 K min^{-1}, 200 kJ mol^{-1} and 1000 mJ, respectively. The two kinetic models used were (a) the RO model for $n = 2$ and (b) the JMA model for $n = 3$. The calculated theoretical data were used as input files for the program KINMOD. The normalized $y(\alpha)$ functions for both data sets are plotted in Fig. 3. Curve (a) is decreasing steadily, so the RO model can be
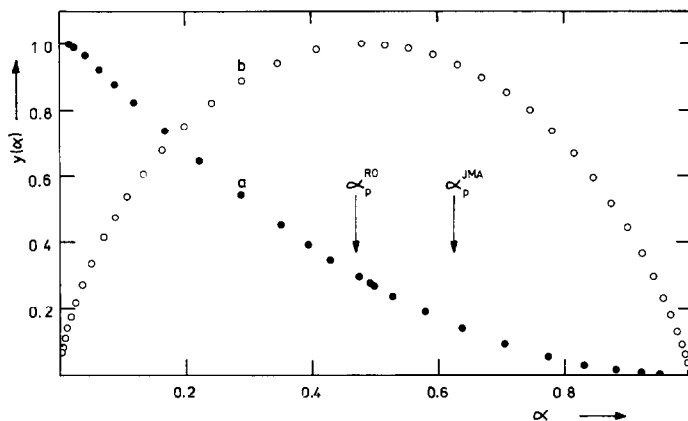
Fig. 3. Normalized $y(\alpha)$ functions for theoretical data: (plot a) RO and (plot b) JMA model. The arrows show α_p for both data sets.

TABLE 1

Kinetic parameters for theoretical data calculated using the program KINET

Model	n	E (kJ mol^{-1})	log A	ΔH (mJ)
RO	1.991	200.0	9.9999	993
JMA	3.003	199.7	10.0004	996

selected in this case. By contrast, curve (b) has a maximum at $\alpha_M = 0.4868$ and $\alpha_p = 0.630$. Clearly, the JMA model is more suitable in this case (see Theory). The kinetic parameters calculated by the program KINET are summarized in Table 1. The theoretical data and recalculated curves for
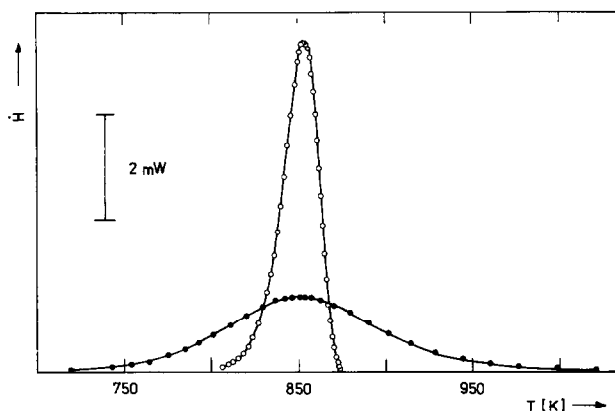

Fig. 4. Theoretical DSC data and recalculated curves for RO (●) and JMA (○) kinetic models. The kinetic parameters are given in Table 1.
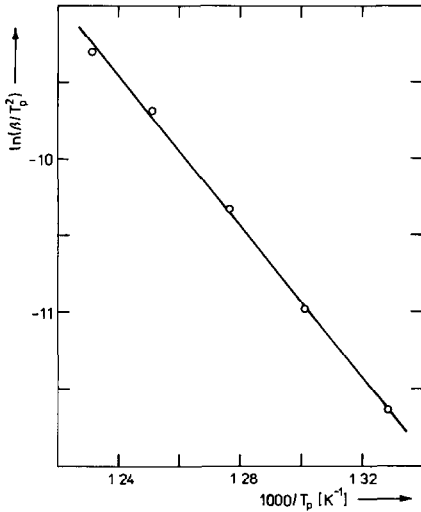
Fig. 5. Kissinger's plot for crystallization of glassy GeSe$_2$.

both kinetic models are presented in Fig. 4. Taking into account rounding errors, the experimental results are in acceptable agreement with the theoretical data.

The program KINET was also used to describe the crystallization process of GeSe$_2$ glass (see Experimental). A Kissinger's plot was calculated using the subroutine PEAK, as shown in Fig. 5. Activation energy was determined to be $E = 204 +/- 7$ kJ mol^{-1}. Figure 6 shows plots of the normalized $y(\alpha)$ functions for three different heating rates. It is evident that these curves are practically identical, and show a common maximum at $\alpha_M \approx 0.36$ for all heating rates. However, the degree of conversion at the maximum of the
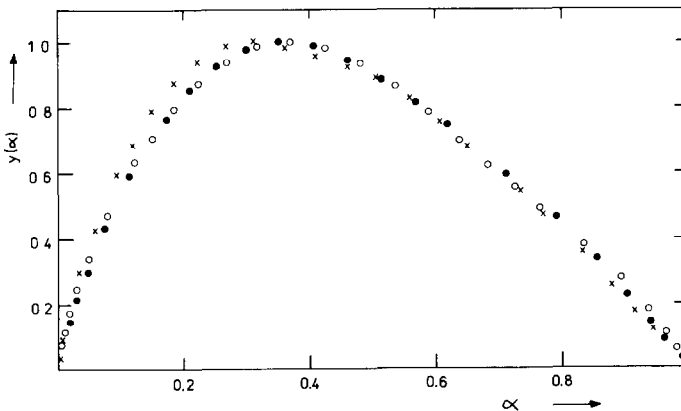

Fig. 6. Normalized $y(\alpha)$ functions for crystallization of glassy GeSe$_2$ at different heating rates: (○) 5, (●) 10 and (×) 20 K min^{-1}.
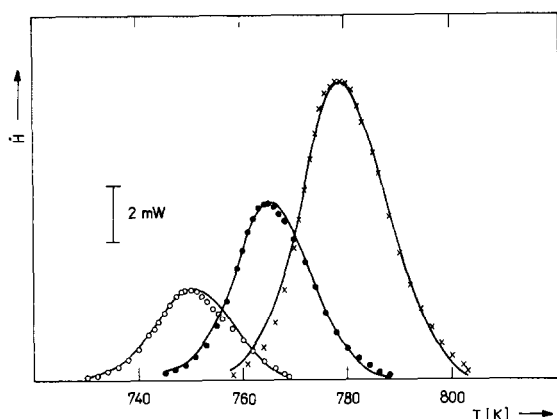
Fig. 7. Comparison of experimental (points) and calculated (full lines) DSC curves for various heating rates, i.e. (o) 5, (●) 10 and (×) 20 K min^{-1}. Corresponding kinetic parameters are given in Table 2.

TABLE 2

Theoretically calculated kinetic parameters for crystallization of GeSe$_2$ glass

β (K min^{-1})	m	n	E (kJ mol^{-1})	log A	ΔH (mJ)
5	0.61	1.01	204	12.971	166
10	0.66	1.10	204	12.899	215
20	0.57	1.09	204	12.382	619

DSC peak varies within the interval $0.40 < \alpha_p < 0.46$. The SB model is therefore suitable in this case. Figure 7 compares measured DSC curves (points) with curves calculated using the SB model (full lines) for the crystallization of GeSe$_2$ glass. The corresponding kinetic parameters are summarized in Table 2. Clearly, the set of kinetic parameters (A, m, n, E) is practically independent of heating rate. Thus the proposed kinetic model is shown to be consistent.

Although the method described allows the quantitative description of solid state processes, it cannot say anything definitive about the real mechanism of these processes. For this your attention is drawn to morphological investigations [14].

LIST OF SYMBOLS

A	pre-exponential factor (s^{-1})
E	activation energy (kJ mol^{-1})
f(α)	general expression of kinetic model
$\dot{H}$	heat flow (mW)
ΔH	heat of process (mJ)
m, n	kinetic power exponents
p	kinetic exponent ratio (m/n)
Q_p	function defined by eqn. (3b)
R	universal gas constant (8.314 kJ mol^{-1} K^{-1})
T	absolute temperature (K)
$y(\alpha)$	function defined by eqn. (5)
α	degree of conversion
β	heating rate (K min^{-1})

Subscripts

i	arbitrary point
p	maximum of DSC peak
M	maximum of f(α) function

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