

POSSIBILITIES OF TWO NON-ISOTHERMAL PROCEDURES (TEMPERATURE- OR RATE-CONTROLLED) FOR KINETICAL STUDIES*

*J. Málek,¹ J. Šesták², F. Rouquerol³, J. Rouquerol⁴, J. M. Criado⁵ and
A. Ortega⁵*

¹JOINT LABORATORY OF SOLID STATE CHEMISTRY OF THE CZECH ACAD. SCI. AND
THE UNIVERSITY OF CHEMICAL TECHNOLOGY, CS. LEGI SQ. 565, 532 10 PARDUBICE,
CZECH AND SLOVAK F.R.

²INSTITUTE OF PHYSICS OF THE CZECH ACADEMY OF SCIENCES, NA SLOVANCE 2,
180 40 PRAGUE, CZECH AND SLOVAK F.R.

³UNIVERSITE DE PROVENCE, PLACE VICTOR HUGO 133 31 MARSEILLE (FRANCE)

⁴CENTRE DE THERMODYNAMIQUE ET DE MICROCALORIMETRIE DU CNRS, 26 RUE
DU 141 EME R.I.A., 130 03 MARSEILLE, FRANCE

⁵INSTITUTO DE CIENCIAS DE MATEMATICAS, C.S.I.C., UNIVERSIDAD DE SEVILLA, 41 071
SEVILLA, SPAIN

The applicability of both conventional Thermal Analysis (TA) and Controlled Rate Thermal Analysis (CRTA) for kinetic analysis is discussed. It is shown that TA method can give a reliable kinetic information and meaningful kinetic parameters especially for solid state transformation. On the other hand the CRTA method is more suitable for decomposition process where one or more gasses are evolved.

A consistent and reliable method of kinetic analysis is proposed for both techniques. This method is illustrated to analyze the crystallization process of chalcogenide glass and the decomposition of dolomite.

Keywords: CRTA, kinetics, TA

Introduction

Nowadays, when reading the literature on kinetics of heterogeneous reactions one may have mixed feelings about the applicability and interest of

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dynamic thermoanalytical methods, as opposed to the isothermal ones. This paper aims to bring some clarification this area and to specify the conditions of a worthwhile dynamic study. The two main routes available for this type of study, namely that of conventional thermal analysis and that of controlled transformation rate thermal analysis will be successively examined.

Fundamental equation

Any kinetic analysis of thermoanalytical data starts from the general expression of the reaction rate of the process under study [1]:

$$(d\alpha/dt) = A e^{-x} f(\alpha) \quad (1)$$

where α is the degree of reaction [dimensionless], A the preexponential factor [1/s] and $x = E/RT$ is the reduced activation energy (E is the activation energy [kJ/mol] and $R = 8.314 \cdot 10^{-3}$ J/mol · K is the gas constant). The function $f(\alpha)$ is the so-called kinetic model of the process. The most frequently cited kinetic models are summarized in Table 1.

Table 1 The kinetic models

Model	Symbol	$f(\alpha)$
Two-parameter model	SB(m, n)	$\alpha^m (1 - \alpha)^n$
Nucleation-growth	JMA(n)	$n (1 - \alpha)[- \ln(1 - \alpha)]^{1-1/n}$
One-parameter model	RO(n)	$(1 - \alpha)^n$
2D-diffusion model	D2	$1/[- \ln(1 - \alpha)]$
Jander model	D3	$3(1 - \alpha)^{2/3}/2[1 - (1 - \alpha)^{2/3}]$
Ginstling-Brounshtein	D4	$3/2[(1 - \alpha)^{-1/3} - 1]$

The aim of the kinetic analysis of TA data is to find the kinetic model which gives the best description the studied process and allows the calculation of meaningful parameters E and A .

There are two non-isothermal procedures used for kinetic studies. The first one is the well-known temperature controlled method i.e. conventional thermal analysis (TA), usually with a constant heating rate and the second one is the rate controlled where, instead of controlling the temperature one controls some other physical or chemical property which is brought to follow a predetermined programme. This is usually chosen to keep constant the transformation rate [2]. This method is called Controlled Transformation

Rate Thermal Analysis (CRTA) following the recent recommendation of the International Confederation on Thermal Analysis.

The applicability of both TA and CRTA methods for kinetical studies is discussed in two following sections with respect to the possibility to evaluate the meaningful kinetic parameters.

Kinetic analysis of TA data

In the last twenty years many papers have been published on the determination of the kinetic parameters from TA data. There are numerous methods aiming to evaluate all kinetic parameters from one TA curve only. We believe that these methods are somewhat problematic and have, therefore, limited applicability.

The main problem of kinetic analysis by means of these methods is a strong mutual correlation of all kinetic parameters in Eq. (1) which can be formulated in the following way:

$$\ln A = a + b E \quad (2)$$

This relationship is sometimes said to express a 'kinetic compensation effect' [3]. It can be derived from the condition for the maximum of TA curve. The constants in Eq. (2) can be expressed as follows: $b = 1/RT_p$ and $a = \ln [-\beta x_p/T_p f'(\alpha_p)]$ where subscript p corresponds to the maximum of TA curve. Thus it seems that it is practically impossible to calculate all kinetic parameters by conventional regression algorithms analyzing one TA or curve only [2] unless the kinetic model is *a priori* known. It is rather surprising that these facts are very often ignored even in the commercially available software packages. This is why a new software package TA-system[©] was developed, based on a method of kinetic analysis of TA data described below, which allows the determination of constants what we tend to call the meaningful kinetic parameters.

Calculation of the activation energy

It is well known that the value of the activation energy E can be determined from multiple scan runs unless the kinetic model has been previously defined. From this point of view it seems that probably the best way of kinetic analysis is first to calculate the activation energy and then knowing this kinetic parameter is possible to determine the kinetic model and calculate remaining kinetic parameters.

The calculation of activation energy is based on multiple scan methods where several measurements at different heating rates are needed. Probably the most popular in this family is the Kissinger method [4] based on the equation derived from the condition for the maximum rate on a TA curve:

$$\ln(\beta/T_p^2) = \ln[-f(\alpha)AR/E] - E/RT_p \quad (3)$$

The activation energy is calculated from the slope of $\ln(\beta/T_p^2)$ vs. $1/T_p$. In fact the first term on the right hand side of Eq. (3) is constant only for first order processes because in this case if $f(\alpha_p) = -1$. Nevertheless, it can be shown [5], that for other kinetic models the error in the activation energy determined by this method does not exceed 5%.

A very similar method of calculation of activation energy is the Ozawa method [6] based on the following equation:

$$\ln \beta = \text{const} - 1.052 E/RT_p \quad (4)$$

The slope of $\ln \beta$ vs. $1/T_p$ plot gives the value of the activation energy. The value of the activation energy determined by the Kissinger and Ozawa methods can be considered as meaningful if the Eqs (3) and (4) are experimentally linear in a broad range of heating rates.

An alternative method of calculation of the activation energy is the Isoconversional method which follows from the logarithmized form of kinetic equation (1):

$$\ln(d\alpha/dt) = \ln\{A f(\alpha)\} - E/RT \quad (5)$$

The slope of $\ln(d\alpha/dt)$ vs. $1/T$ for the same value of α gives the value of activation energy. This procedure can be repeated for various α and, therefore, it easily allows to check the invariance of E with respect to α which is one of the basic assumptions in kinetic analysis.

There is also another method of calculation of the activation energy known as the Freeman-Carroll method [7] which is very popular in the thermoanalytical community. This method is based on the equation:

$$\frac{d \ln(d\alpha/dt)}{d \ln(1-\alpha)} = -(E/R) \frac{d(1/T)}{d \ln(1-\alpha)} + n \quad (6)$$

The Eq. (6) was derived assuming $f(\alpha)$ in particular of RO(n) model, differentiating Eq. (5) and subsequently dividing by $d \ln(1-\alpha)$. The plot of the left hand side of Eq. (6) against $d(1/T)/d \ln(1-\alpha)$ should be a straight line with a slope $(-E'/R)$ and an intercept equal to n' . The E' and n' mean ap-

parent activation energy and reaction order. It should be pointed out that although this method gives straight lines with good correlation coefficients the calculated parameters E' and n' are apparent and they are equal to the true values only for RO(n) model. Therefore the Freeman and Carroll's method cannot be recommended as a general method for the calculation of the activation energy.

Determination of the kinetic model

Once the activation energy has been determined it is possible to find kinetic model which best describes measured set of TA data. It can be shown that for this purpose is useful to define two special functions $y(\alpha)$ and $z(\alpha)$ which can easily be obtained by simple transformation of experimental data. These functions can be formulated as follows [8, 9]:

$$y(\alpha) = (d\alpha/dt) e^{-x} \quad (7)$$

$$z(\alpha) = \pi(x) (d\alpha/dt) T/\beta \quad (8)$$

where $\pi(x)$ is the temperature integral approximation, which it has to be introduced because Eq. (1) cannot be integrated in a closed form. This approximation is usually expressed as rational function and are described e.g. in [2]. According to our experiences it is sufficient by precise to use Senum and Yang [10] approximation in the form:

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (9)$$

which gives errors of lower than 10^{-5} % for $x > 20$.

It can be shown that the $y(\alpha)$ function can be also expressed as follows [9]:

$$y(\alpha) = A f(\alpha) \quad (10)$$

Thus by plotting $y(\alpha)$ dependence, normalized within $\langle 0, 1 \rangle$ interval, the shape of the function $f(\alpha)$ is obtained. Therefore, the shape of $y(\alpha)$ function is characteristic for a given kinetic model and it is without any doubt that this function can be considered as a diagnostic tool for kinetic model determination. From this point of view we can formulate following two rules:

(i) If the $y(\alpha)$ function normalized within $\langle 0, 1 \rangle$ interval decreases steadily, then it has the maximum at $\alpha_m = 0$. Furthermore this function can be convex [$y(\alpha_i) > \alpha_i$], linear [$y(\alpha_i) = \alpha_i$] or concave [$y(\alpha_i) < \alpha_i$]. Convex depend-

ence corresponds to the RO($n < 1$) model, linear dependence to JMA(1) and concave dependence to D2, D3, D4, RO($n > 1$) or JMA($n < 1$) model.

(ii) If there is a maximum of the $y(\alpha)$ function at $\alpha_m \in (0, \alpha_p)$ interval then it corresponds to the SB(m, n) or JMA($n > 1$) model.

It should be pointed out that the maximum coordinate α_m of $y(\alpha)$ function is strongly affected by E . Hence the activation energy is decisive for a reliable determination of the kinetic model because varying the E a particular kinetic data can be interpreted within the scope of several kinetic models. From this point of view the SB(m, n) model can be considered as a general one because all other models (i.e. JMA(n), D2, D3 and D4) can be expressed by means of it for a certain value of apparent activation energy [11]. Of course, this is not true for the fixed value of activation energy [12] determined by the methods described above.

Similarly we can discuss mathematical properties of the $z(\alpha)$ function. This function can also be expressed as follows [8]:

$$z(\alpha) = f(\alpha) g(\alpha) \quad (11)$$

It can simply be shown that the $z(\alpha)$ function has a maximum for all kinetic models summarized in Table 1. For the maximum of $z(\alpha)$ function at α_p^∞ a general condition can be formulated [8]:

$$-f'(\alpha_p^\infty) g(\alpha_p^\infty) = 0 \quad (12)$$

where $g(\alpha) = \int d\alpha/f(\alpha)$. It should be pointed out that the value of α_p^∞ also corresponds to the maximum of a hypothetical DSC or DTA peak for $x_p \rightarrow \infty$. This parameter has a characteristic value [8] for D2, D3, D4 and JMA(n) model as summarized in Table 2. It is interesting that contrary to the maximum of $y(\alpha)$ function α_p^∞ practically does not depend on the value activation energy used to calculate $z(\alpha)$ function (in fact it varies within 1% of the theoretical value).

For both the SB(m, n) and the RO(n) model α_p^∞ depends on the value of the kinetic exponent m or n . On the other hand the maximum of $z(\alpha)$ function for JMA(n) does not depend on the value of exponent n .

It is evident that both the $y(\alpha)$ and $z(\alpha)$ dependencies can be used to guide the choice of a kinetic model which is a completely new way of kinetic analysis. The α_m and α_p^∞ values are especially useful in this respect. Their combinations allows the determination of the most suitable kinetic model as shown by the scheme in Fig. 1.

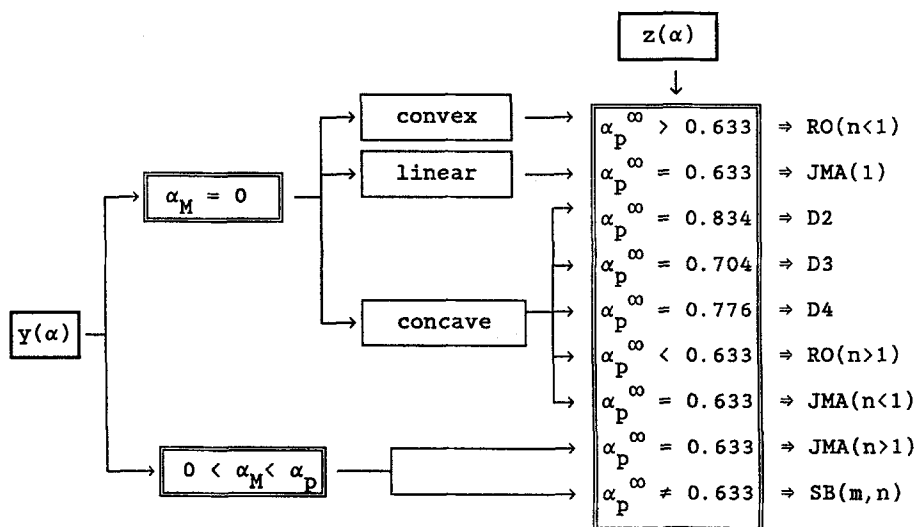


Fig. 1 Schematic diagram of the kinetic model determination

Table 2 Characteristic values of α_p^∞

Model	α_p^∞
JMA(n)	0.633
D2	0.834
D3	0.704
D4	0.776

Calculation of kinetic exponents

Once the kinetic model has been determined the kinetic exponents n (or m) can be calculated for RO(n), JMA(n) or SB(m, n) model. The calculation methods depends on particular kinetic model and are described below.

RO(n) model

The kinetic exponent n for this model is calculated iteratively using the equation:

$$\alpha_p = 1 - \left[1 + \frac{1-n}{n} x_p \pi(x_p) \right]^{1/(n-1)}; \quad n \neq 0 \tag{13}$$

where α_p and x_p correspond to the maximum of DSC peak. This equation was derived originally by Gorbachev [13] for $\pi(x) = 1/(x_p + 2)$.

JMA(n) model

If the $y(\alpha)$ function has a maximum at α_m ($n > 1$) the kinetic exponent n is calculated using the equation [9]

$$n = \frac{1}{1 + \ln(1 - \alpha_M)} \quad (14)$$

If there is no maximum of the $y(\alpha)$ function the parameter n is calculated by means of the Šatava method [14]

$$\ln[-\ln(1 - \alpha)] = \text{const} - nE/RT \quad (15)$$

i.e. from the slope of the plot of $\ln[-\ln(1 - \alpha)]$ vs. $1/T$. An alternative method of calculation is based on the following equation [11]

$$n = \frac{1 - x_p \pi(x_p)}{\ln(1 - \alpha_p) + 1} \quad (16)$$

It is known that the Šatava method gives slightly higher values of parameter n . On the other hand the Eq. (16) gives lower ones. From our experience it seems that an average of these two values is a good approximation of the kinetic exponent.

SB(m, n) model

The kinetic parameter ratio $p = m/n$ is calculated using the equation [9]

$$p = \alpha_M / (1 - \alpha_M) \quad (17)$$

Eq. (1) can be rewritten in the form

$$\ln[d\alpha/dt] e^{-x} = \ln A + n \ln[\alpha^p(1 - \alpha)] \quad (18)$$

The kinetic parameter n corresponds to the slope of linear dependence $\ln[d\alpha/dt] e^{-x}$ vs. $\ln[\alpha^p(1 - \alpha)]$ for $\alpha \in (0.2, 0.8)$. Then the second kinetic exponent is $m = pn$.

Calculation of the preexponential factor

Knowing the value of activation energy and the kinetic model the preexponential factor is calculated using following equation [9]

$$A = - \frac{\beta x_p}{T f(\alpha)} \exp(x_p) \quad (19)$$

Crystallization of chalcogenide glass

This method of analysis of TA data can be demonstrated e.g. in a study of the crystallization kinetics of chalcogenide glass of $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$ composition [11]. By methods of X-ray diffraction and electron microanalysis was confirmed that there is crystallization process of Sb_2S_3 phase in 590–660 K range. Figure 2 shows experimental DSC data (points) obtained by means of the Perkin-Elmer DSC-7/TAS instrument using powdered samples of average particle size of $70\ \mu\text{m}$ in sealed aluminium pans. Low sample mass was used (about 10 mg) to avoid thermal gradients.

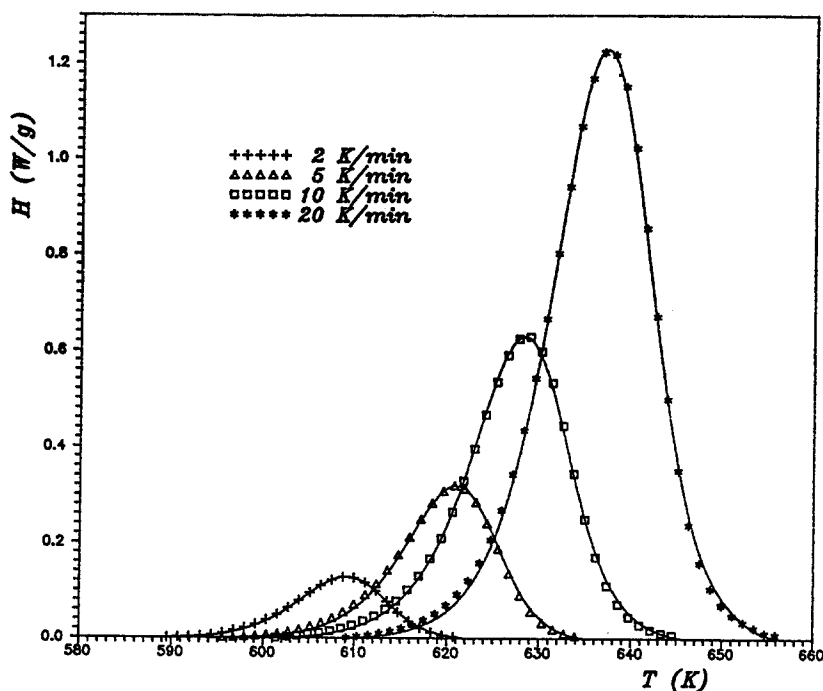


Fig. 2 Experimental (symbols) and calculated DSC curves (full lines) for crystallization of chalcogenide glass of $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$ composition at various heating rates

The values of the activation energy determined by Kissinger and Ozawa methods are 251 ± 10 and 249 ± 11 kJ/mol, respectively. Similar result was also obtained by the isoconversional method ($E = 256 \pm 9$ kJ/mol) where it was also confirmed that this value of activation energy practically does not depend on the α .

Knowing this value of activation energy we can calculate both $y(\alpha)$ and $z(\alpha)$ functions as shown in Fig. 3. Although there is slight scatter of ex-

perimental points it can be concluded that both these dependencies are practically invariant with respect to the heating rate. Maxima of the dependencies can be found for following values: $\alpha_m = 0.41 \pm 0.01$ and $\alpha_p^\infty = 0.57 \pm 0.01$.

Therefore it seems that this crystallization process can be described by the Šesták-Berggren model for following values of kinetic exponents: $m = 0.69 \pm 0.03$ and $n = 0.99 \pm 0.01$. The preexponential factor was determined to be $\ln A = 44.8 \pm 0.04$. It is evident from Fig. 2 that the theoretical DSC curves calculated using these parameters are in good agreement with the experimental data.

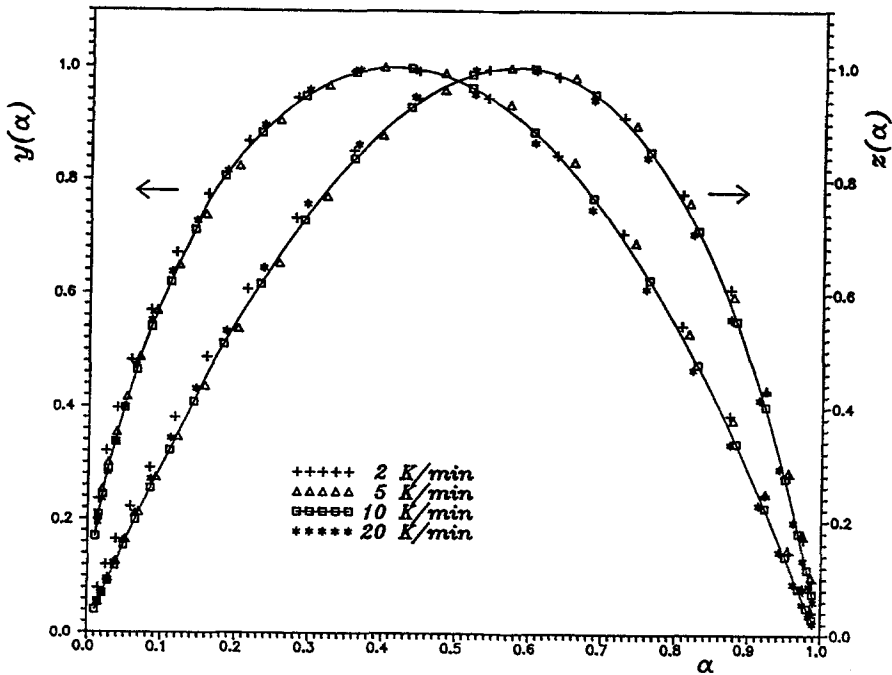


Fig. 3 The $y(\alpha)$ and $z(\alpha)$ functions calculated for DSC data shown in Fig. 2

It should be pointed out that these kinetic parameters cannot say anything definitive about the real mechanism of the process. From this point of view more attention should be drawn to the morphological investigation. Nevertheless the kinetic parameters can be used for the calculation isothermal temperature – transformation curves which are very useful e.g. for the preparation of glass ceramic material with defined properties. Figure 4 shows several isotherms calculated for the studied process using determined values of kinetic parameters.

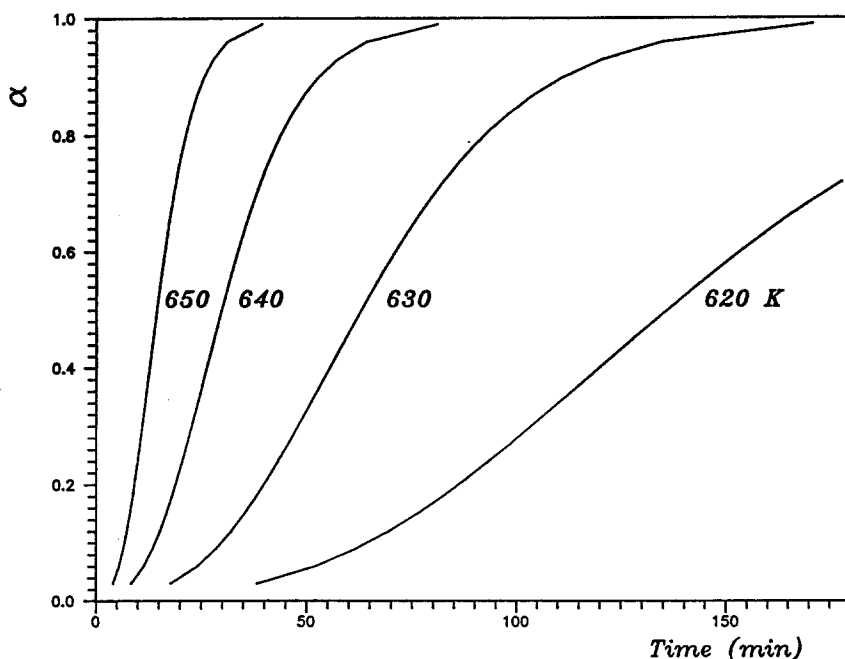


Fig. 4 Isothermal time - conversion curves calculated for the crystallization of $(\text{Ge}_2\text{S}_3)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$ glass at temperatures $T = 620, 630, 640$ and 650 K

As can be seen from the above results, the method of kinetic analysis of TA data described here permits the calculation of kinetic parameters for crystallization kinetics or other solid state transformation processes. Nevertheless, this is not the case of decomposition reactions where the gas phase produced has a feedback to the reaction rate of the process. Therefore the conventional TA often fails to give a reliable result for such processes because of the strong kinetic dependence on the experimental conditions.

Kinetic analysis of CRTA data

The efficiency of CRTA for separating successive steps of dehydration and decomposition of complicated inorganic salts has already been demonstrated [15]. The resolution power of CRTA results from the possibility of controlling the rate of transformation at such a low rate that the remaining temperature and pressure gradients through the sample are themselves low enough to avoid any overlapping of the successive steps. It is of particular interest for kinetic analysis if we compare this method with conventional TA methods.

Determination of the kinetic model

The basic kinetic Eq. (1) can be rewritten for CRTA in the following form:

$$A e^{-x} f(\alpha) = \text{const} \quad (20)$$

By differentiating this equation with respect to α , the conditions for both minima (α_{\min}) and inflex point (α_i) of the CRTA curve can be obtained [16, 17]:

$$\frac{dT}{d\alpha} = -\frac{T}{x} \frac{f'(\alpha_{\min})}{f(\alpha_{\min})} = 0 \quad (21)$$

$$\frac{d^2T}{d\alpha^2} = \frac{T}{x} [f(\alpha_i)]^{-2} \left[[f'(\alpha_i)]^2 \left(\frac{2}{x} + 1 \right) - f(\alpha_i) f''(\alpha_i) \right] = 0 \quad (22)$$

Solution of Eq. (19) does not depend on the value of the reduced activation energy x and for the JMA(n) and SB(m, n) model it is identical with the condition for the maximum of the $f(\alpha)$ function [see Eqs (12) and (15)]. On the other hands, the inflex point of the CRTA curve generally depends on x . The mathematical conditions for the minima and inflex points are summarized in Table 3 for all kinetic model discussed.

Table 3 The values of α_{\min} and α_i for CRTA curves [17]

Model	α_{\min}	α_i
SB(m, n)	$m/(m-n)$	-
JMA(n)	$1 - e^{(1-n)/n}$	-
RO(n)	-	-
D2	-	$1 - e^{(2x-1)}$
D3	-	$1 - \left\{ \frac{8/x + 6}{5 + (4/x + 7)^{1/2}} \right\}^3$
D4	-	$1 - [(2 + 3x)/4x]^3$

It is evident that theoretical CRTA curves can easily be divided into three groups after their general shape [16, 17] as shown in Fig. 5. Thus the general shape of an experimental curve α vs. T as obtained at constant reaction rate is very important for the determination of the actual mechanism and the following rules can be formulated:

(i) The mechanism of nucleation and subsequent growth of nuclei i.e. JMA(n) model but also empirical SB(m, n) model lead to the curves with a temperature minimum. This is a very interesting and unique feature of the CRTA approach.

(ii) The boundary controlled mechanisms (R2 and R3 according to Sharp [18]) as well as 'n-order' mechanisms i.e. RO(n) model give the shape of CRTA curve with no minimum nor inflex points.

(iii) The diffusion processes D2, D3 and D4 lead to curves with an inflex point which location is affected by the reduced activation energy.

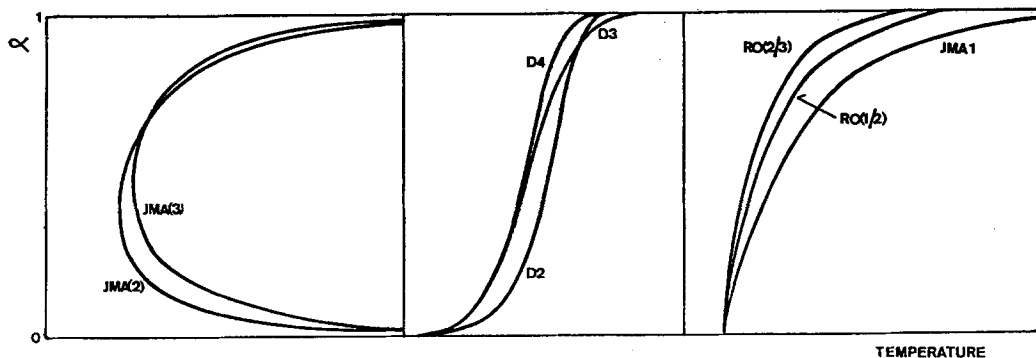


Fig. 5 Typical shapes of CRTA curves for several kinetic models

Calculation of the activation energy

The principle of the method [19, 20] is to bring the rate of reaction to switch between two preset values (with a ratio conveniently chosen as 1 to 3 or 1 to 4). The system which is operated following the CRTA mode, automatically responds by a switching temperature, which is recorded as shown in Fig. 6.

Between 15 to 30 such jumps (and their corresponding drops) are usually performed to analyse one individual step. Each temperature jump allows to determine a separate value of activation energy, since it provides a couple of temperatures (one, T_2 directly measured on the recording and the other, T_1 obtained by extrapolation for exactly the same degree of reaction) and the corresponding couple of reaction rates (whose ratio r is known with a great accuracy, because each may be kept constant as long as needed by a good calibration). Since the degree of reaction remains virtually unchanged during the rate-jump and provided that $f(\alpha)$ is not changed by the corresponding temperature jump (most often in the 5–15 K range) it may be

concluded that the reaction rates are in the same ratio as the rate constants, hence finally:

$$E = \frac{R T_1 T_2}{T_2 - T_1} \ln r \quad (23)$$

where T_1 and T_2 correspond to the same degree of conversion α .

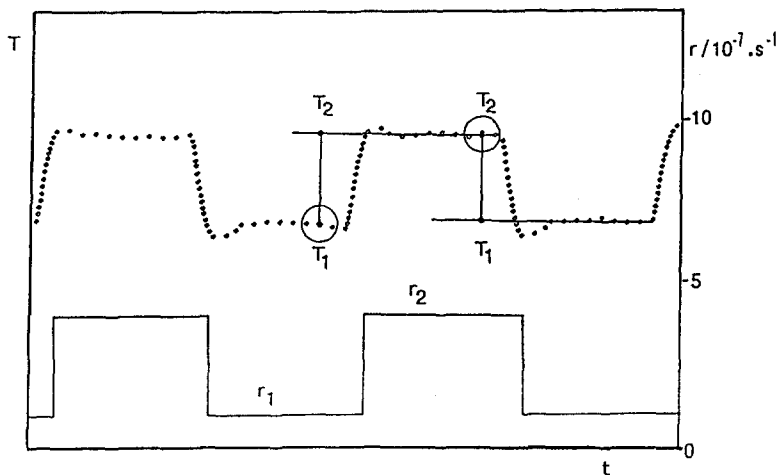


Fig. 6 The determination of E by a rate-jump CRTA experiment

The method described above allows to perform up to 30 independent measurements during one supposed reaction step. Therefore, one may check, a posteriori, by comparing these values if are steady enough to support the use of the Arrhenius law and also to confirm the existence of that individual step.

Decomposition of dolomite

The applicability of the CRTA method for kinetic studies can be demonstrated using the decomposition process of dolomite. The experiments was carried out with powder sample (particle size $<160 \mu\text{m}$) of 50 mg and pressure $2 \cdot 10^{-5}$ mbar). The rate-jump method has been used to determine the activation energy of the decomposition of dolomite [21]. The typical CRTA diagram for two decomposition rates is shown in Fig. 7.

Because the CRTA curve has an inflex point the decomposition process probably corresponds to the diffusion mechanism. The values of the activation energy determined by the rate jump-method are summarized in Table 4.

Table 4 Activation energy of thermal decomposition of dolomite determined by the rate-jump method

α	E (kJ/mol)
0.1	182
0.2	197
0.3	193
0.4	204
0.5	205
0.6	193
0.7	201
0.8	196
0.9	201

The mean value is $E = 197$ kJ/mol. The internal agreement is quite satisfactory except for the first value, which is lower (for $\alpha = 0.1$).

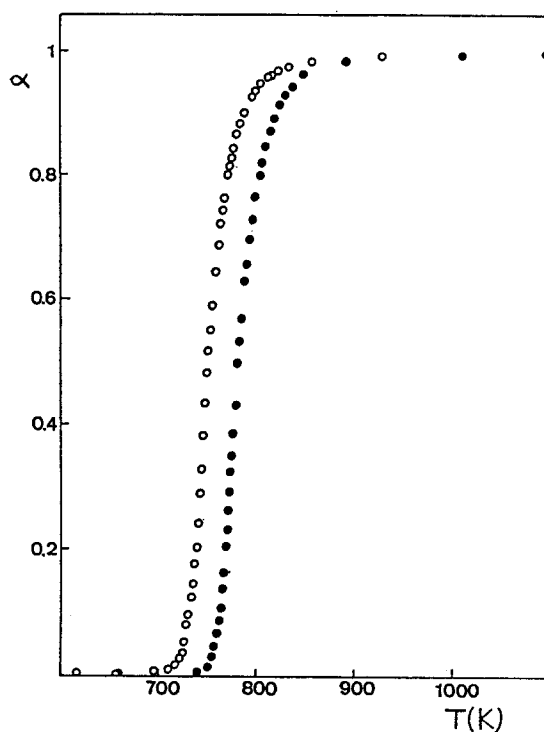


Fig. 7 The CRTA curves for the thermal decomposition of dolomite at two decomposition rates: (○) $3.289 \cdot 10^{-6} \text{ s}^{-1}$ and (●) $1.162 \cdot 10^{-5} \text{ s}^{-1}$

The value of calculated activation energy was checked for different sample mass as well as for various preselected rate ratio. It was found that this method is consistent and the value of activation energy does not depend substantially on the sample mass as well as the decomposition rate ratio.

Therefore we can conclude that CRTA method is very useful for kinetic study of decomposition processes where one or several gases are produced and it allows to determine reliable kinetic parameters for such processes where conventional TA methods can hardly give meaningful kinetic results.

Conclusion

The following conclusions may therefore be easily drawn from the preceding work:

1) It is possible to draw benefit in kinetics, from the easyness and rapidity of the conventional dynamic approach provided two conditions are fulfilled:

(i) the experimental conditions must be chosen to keep relatively low gradients (temperature and/or pressure) in the sample under investigation and

(ii) carefully selected algorithms must be used for calculation of kinetic data. The first condition is usually fulfilled for low sample masses not exceeding 10 mg (as it is fortunately possible with modern TG and DSC instruments) especially if the transformation studied does not produce any gaseous phase (as it is the case of crystallization process presented here).

2) In the case when the sample mass must be larger (for instance for sampling reasons) and especially if the reaction produces one or several gases, then CRTA, at the expense of a slower experiment, provides a satisfactory solution.

3) In these conditions the dynamic method (either of the conventional thermal analysis type or of the CRTA type) have the interest of eliminating the uncertainty found – when using the isothermal methods – in the determination of the starting time of the reaction.

4) It is not correct to use a single curve only for the determination of kinetic parameters. At least one kinetic parameter of $f(\alpha)$ should be calculated independently from a series of TA curves taken at various heating rates. Then the kinetic problem can be solved successfully.

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Zusammenfassung — Es wird die Anwendbarkeit von herkömmlicher Thermoanalyse (TA) und geschwindigkeitsgesteuerter Thermoanalyse (CRTA) bei kinetischen Untersuchungen diskutiert. Die TA Technik kann eine zuverlässige kinetische Information und sinnvolle kinetische Parameter besonders bei Feststoffumsetzungen liefern. Die CRTA Technik ist andererseits mehr für Zersetzungsprozesse geeignet, bei denen ein oder mehrere Gase freigesetzt werden.

Für beide Techniken wird eine einheitliche und geeignete Methode zu kinetischen Analyse vorgeschlagen. Als Beispiel wird diese Methode zur Analyse des Kristallisationsprozesses von Chalkogenidgläsern sowie der Zersetzung von Dolomit angewendet.