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CRTA or TG?

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Abstract

Both the general principle and the historical development of the Constant Rate Thermal Analysis (CRTA) and of the TG technique are described. It is shown that CRTA, whose aim is to reduce at will pressure and temperature gradients inside the sample, has a much more effective control on heat and mass transfer phenomena than conventional TG. The successes and failures of TG is shown.

It is shown also how the field of CRTA is as broad as that of conventional TG since it uses the same technique and the same equipment but in a basically different way: CRTA is in some respects the opposite of TG. © 1997 Elsevier Science B.V.

Keywords: Constant rate thermal analysis; TG

1. Introduction

Before the advent of the TG technique the kinetic analysis of heterogeneous reactions was studied by the isothermal method. This procedure was cumbersome and tedious and one had to compare different samples that had followed different paths at different temperatures. The samples did not necessarily have the same structure, porosity or crystallinity. In this condition the kinetic analysis could not always be satisfactory. In order to avoid this problem the concepts of non-isothermal kinetic were outlined as early as 1930 and ever since there has been rapid development and TG has received considerable attention in the literature.

In general, it is recognised that the TG method permits proper determination of the kinetic constant of heterogeneous reactions. Ninety percent of the kinetic studies found in recent literature have been carried out using the conventional non-isothermal method, but actually there is a large group of scientists having the opposite opinion about the utility of this method for performing kinetic analysis of heterogeneous reactions. The advantages of conventional methods have become questionable owing to the fact that the results show considerable deviations.

The scope of the present paper is to open a controversy about the successes and failures of the TG methods and about the necessity of stimulate the interest of users in the news techniques.

2. Some inevitable failures of TG

Numerous investigators have worked extensively on the kinetics of non-isothermal reactions. Its popularity is due to the fact that both analytical and kinetic data can be obtained simultaneously from a single experiment in a short period of time.

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Unfortunately, different approximative equations have often been used without adequate understanding of their limitations, resulting in an accumulation of unreliable results. The ease with which TG data can be obtained has resulted in increased volume of data and confusion. Every method has its merits as well as disadvantages, but today TG methods have became somewhat questionable. Uncertainties in kinetic studies arise from two important problems:

(a) Problems due to experimental factors (sample mass, particle size, ambient atmosphere, shape of the crucible, heating rate, etc.) that inevitably affect significantly the course of the reaction.

(b) Problems due to uniqueness that unfortunately have generally been ignored.

An example of (a) is the thermal decomposition of calcite.

$$CaCO_3 \leftrightarrow CaO + CO_2$$

which has frequently been studied and the reported values for the activation energy E range from 142 to 3828 KJ/mol [1]. This situation is characteristic of dynamic TG. The reason for such observations is that under different experimental conditions the same compound can have different decomposition mechanisms and different constant parameters. Change in the heating rate, for example, affects the shape of the curve and, hence, the kinetic constant. Since rising temperature conditions can only be imposed by heating the sample in a furnace, one has the problem of creating thermal gradients within the sample itself. This may be minimised by using small samples. However, small samples may not be representative of many systems.

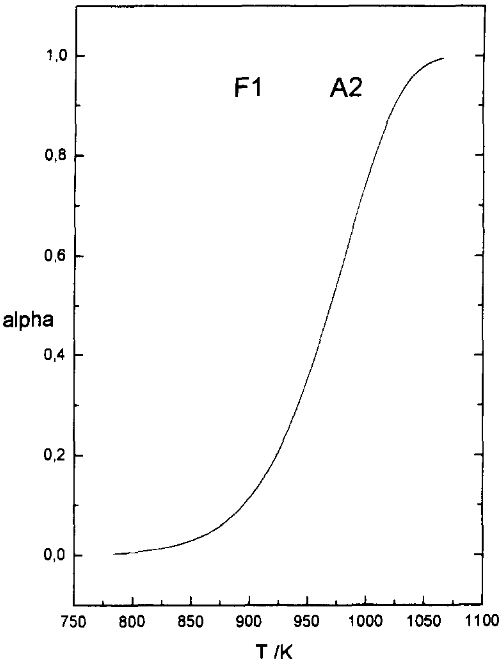

Fig. 1. This curve represents two very different mechanisms: an Avrami–Erofeev (A2) model $E = 76$ KJ/mol, $A = 12\ s^{-1}$ and a first order mechanism (F1) with $E = 167$ KJ/mol $A = 1.6 \times 10^6\ s^{-1}$.

Thus it appears that the kinetic parameters reflect the influence of experimental conditions on kinetics. In this sense they may be regarded as operative parameters under the conditions of investigation. Nevertheless non-isothermal TG continues to be

Table 1
Algebraic expression of the $f(\alpha)$ and $g(\alpha)$ functions commonly used for reaction kinetics

Mechanism	Symbol	$f(\alpha)$	$g(\alpha)$
Random nucleation. Unimolecular decay law (first order)	F1	$(1-\alpha)$	$-\ln(1-\alpha)$
Phase boundary controlled reaction (contracting cylinder)	R2	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
Phase boundary controlled reaction (Contracting sphere)	R3	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/2}]$
Two-dimensional growth of nuclei (Avrami–Erofeev equation)	A2	$2[-\ln(1-\alpha)]^{1/2}(1-\alpha)$	$[-\ln(1-\alpha)]^{1/2}$
Three-dimensional growth of nuclei (Avrami–Erofeev equation)	A3	$3[-\ln(1-\alpha)]^{2/3}(1-\alpha)$	$[-\ln(1-\alpha)]^{1/2}$
One-dimensional diffusion	D1	$\alpha/2$	α^2
Two-dimensional diffusion	D2	$-1/\ln(1-\alpha)$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion (Jander equation)	D3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{-1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (Ginstling–Brounshtein equation)	D4	$3/2[(1-\alpha)^{-1/3}-1]$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

extensively used, given its great experimental simplicity.

With regard factor (b) Fig. 1 shows that a unique TG curve represents two very different kinetic models with different kinetic parameters: a Random Nucleation Unimolecular Decay law, labelled F1 in Table 1, ($E = 167$ KJ/mol, $A = 1.6 \times 10^6\ \mathrm{s}^{-1}$), an Avrami–Erofeev kinetic model, labelled A2, ($E = 76$ KJ/mol, $A = 12\ \mathrm{s}^{-1}$). This shows dramatically the problem of uniqueness and proves that it is impossible to select unambiguously the kinetic function obeyed by the reaction.

The problem arises from the fact that in all cases different kinetic equations appear to fit the same set of kinetic data and researchers may not be able to select the most appropriate one. Identifying the correct form of $f(\alpha)$ is critical to obtaining unique results.

An additional problem has been introduced in the literature by different authors which states that the formal mathematical description of a heterogeneous process is in the form:

$$\frac{d\alpha}{dt} = Kf(\alpha) \tag{1}$$

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

This equation, where n is a semi-empirical constant, is chosen by analogy with that used to describe the homogeneous kinetics of gases. Some authors [2] have pointed out the lack of meaning in n (the reaction order). But the problem arises from the fact that although some methods are available in the literature for performing kinetic analysis of TG data on heterogeneous reactions taking place through mechanisms such as Avrami–Erofeev, Prout and Tompkins etc., most papers consider such reactions as described by the 'n-order' reaction mechanism. This is equivalent to considering the reaction rate to be proportional to the nth power of the amount of undecomposed solid, as in the case of a homogeneous process. However the decomposition of a solid is a heterogeneous process, the description of which with homogeneous equations being a meaningless exercise.

Nevertheless, it is a well-established fact that TG data fit very well the reaction order equation when the values of 0, 1/2, 2/3 or 1 are used. This behaviour might be understood if the established equations needed to perform kinetic analysis of heterogeneous processes in dynamic TG conditions are linearly correlated with those available to analyse n-order reactions.

The application of the integral method involves integrating Eq. (1) to obtain

$$g(\alpha) = \int d\alpha/f(\alpha) = EA/\beta R \int x^{-2}\exp(-x)dx = (EA/\beta R)p(x) \tag{2}$$

where $x = E/RT$ and $p(x)$ is a function which includes the exponential integral.

If we use Doyle's approximation of the $p(x)$ function ($\ln p(x) = -5.33 - 1.05E/RT$), we get the linearizing form:

$$\ln g(\alpha) = \ln\frac{AE}{\beta R} - 5.33 - 1.05\frac{E}{RT} \tag{3}$$

If the function $g(\alpha)$ in Table 1 is correlated with the mathematical function corresponding to n-order, the following relationship holds:

$$\ln g(\alpha) = a \ln h(\alpha) + b \tag{4}$$

where $g(\alpha)$ represents any of the functions used to perform the kinetic analysis of solid-state reactions and $h(\alpha)$ one of the n-order (F1, R2 or R3) functions arbitrarily taken as a reference, and a and b are constant. If the kinetic law actually followed by the reaction satisfies Eq. (4), the experimental data necessarily fit the kinetic equation $\ln h(\alpha)$ from Eq. (3):

$$\ln h(\alpha) = \ln\frac{A_a E_a}{\beta R} - 5.33 - 1.05\frac{E_a}{RT} \tag{5}$$

E_a and A_a are the apparent values of the kinetic parameters obtained by assuming that the $h(\alpha)$ function is obeyed. From Eqs. (4) and (5) we get:

$$\ln g(\alpha) = a\ln\frac{A_a E_a}{\beta R} - 5.33a - 1.05a\frac{E_a}{RT} + b \tag{6}$$

This can be simplified to:

$$\ln g(\alpha) = -1.05\frac{aE_a}{RT} + \text{constant} \tag{7}$$

From a comparison of Eqs. (3) and (7) we can conclude that the activation energy E and the value of E_a taken as reference are related through the relationship:

$$E = aE_a \tag{8}$$

This means that the ratio between the activation energies determined from the different functions

Table 2
Values of a calculated by the least mean squares method according to Eq. (4)

Mechanism	Symbol	a	r
Two-dimensional growth of nuclei	A2	0.50	1.0000
Three-dimensional growth of nuclei	A3	0.33	1.0000
One-dimensional diffusion	D1	1.47	0.9950
Two-dimensional diffusion	D2	1.62	0.9976
Jander equation	D3	1.80	0.9995
Ginstling–Brounshtein equation	D4	1.67	0.9980

$g(\alpha)$ is equal to the ratio between the corresponding values of the constant a. Table 2 shows the values of the constant obtained by Criado et al. [3] for the kinetic model most frequently cited.

We can see that any TG data do necessarily fit the mathematical function which has the form $(1-\alpha)^n$ although the activation energy obtained is strongly dependent on the kinetic law assumed in performing the calculation. This result is important when we use, for example, the method of Freeman and Carroll [4], one of the most popular methods employed in the calculation of the kinetic constants. If it is not taken into account that heterogeneous data can be approximated by n-order kinetic, there is the possibility of making an important error when the method developed by these authors is employed. Thus a reaction taking place through an Avrami–Erofeev or a three-dimensional diffusion mechanism would be erroneously interpreted as first order $(n=1)$ or $n=2/3$ order respectively. This is true regardless of the way of defining the rate constant. Therefore Freeman and Carroll's method cannot be recommended as a general method for the calculation of the activation energy.

3. The exponential integral

The integral methods involve integrating Eq. (9) (see Eq. (2))

$$\int x^{-2}\exp(-x)\mathrm{d}x \tag{9}$$

but Eq. (9) cannot be integrated in closed form and unfortunately gross and inaccurate approximations are used in TG methods. Thus the analysis techniques based upon these equations have often been used without an adequate understanding of their limitations. This still causes considerable confusion and misinformation. Several series of expressions and semi-empirical approximations of $p(x)$ are available in the literature. For large values of x $(x > 60)$ the errors due to approximations are negligible. However, for lower values of interest in thermal analysis, errors resulting from approximation may not be negligible.

Gyulai and Greenhow [5], Doyle [6], MacCallum and Tanner [7] and Coats and Redfern [8] are but a few investigators who have used different methods to evaluate the integral $p(x)$, and have therefore provided different approaches to non-isothermal kinetics. There has been much discussion of the possibility of determining kinetic parameters, a significant amount of information in the literature is based on poor approximation in the calculation of the activation energy. The E values may be comparable from various approximations and the error yielded in this parameter is, in all cases, lower than 10% (for $E/RT > 20$) in spite of giving poor accuracy when they are used for calculating the $p(x)$ function. However, all these methods make important errors in the calculation of the pre-exponential factor A. For example, the Coats and Redfern approximation yields an error of $\approx 98\%$ in the pre-exponential factor A for $E/RT < 20$.

4. The kinetic compensation effect

This is a characteristic problem in dynamic temperature; it causes the kinetic parameters E and A to be linked, such as shown by Fig. 2. The literature of this problem has hundreds of positions; the discussion about the mutual relation between E and A has divided scientists into two groups: those who affirm that the observation of this relation has potential for predicting the effects of experimental factors on kinetic parameters and those who believe that it is an artefact resulting from the mathematical form of kinetic equations [9]. The relationship between E and A may be simply stated as follows:

$$\ln A = aE + b$$

where a and b are characteristic of the system.

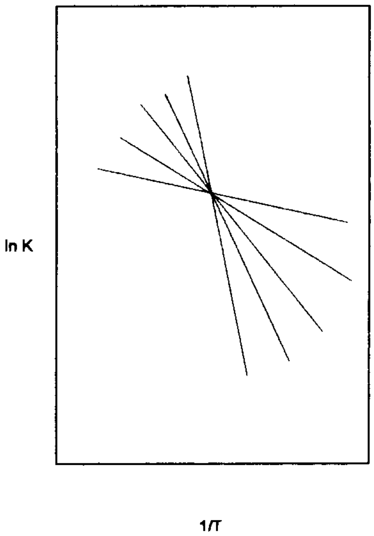

Fig. 2. Link between $\ln A$ and E in the Arrhenius plot.

Owing to this relationship numerous values of E may fit the TG experimental data. The knowledge of the values of E and A is not sufficient when one tries to connect the kinetic calculations with the real course of the process. There are numerous difficulties in finding the proper mathematical solution to determine E and A and in using these mathematical parameters correctly. At present nobody has proposed a physical meaning of the kinetic parameters in solid-state reactions despite considerable progress in heterogeneous reactions.

We conclude that the problem of the kinetic compensation effect, in dynamic conditions, is still unsolved and there still exists much controversy concerning its mathematical treatment.

5. An alternative approach: The Controlled Rate Thermal Analysis (CRTA)

The literature data have shown that the reliability of TG data is influenced by the experimental parameters such as sample mass and shape, particle size, ambient atmosphere etc. The existence of these significant effects has led several authors to conclude that there is a real limit to our kinetical understanding and to a consistent interpretation of heterogeneous reactions.

Technology demands that we evaluate the kinetics of heterogeneous reactions as best we can. The dream of many scientists involved in TA is:

> to obtain kinetic parameters which would be independent of the reaction environment.
> to identify the correct form of $f(\alpha)$.

In this author's opinion the above wishes can be satisfied by an alternative approach which could be described as reaction-determined temperature control. This approach is, in some respects, the opposite of the conventional technique which could be described as program-determined temperature control where the temperature program is decided upon in advance.

The new procedure has its beginnings when J. Rouquerol [10] in Paris and F. Paulik [11] in Bucharest independently had the idea of automating the ultra-slow heating procedure used at that time by a few researchers in order to ensure, if possible, quasi-equilibrium conditions and to increase the resolution of thermal analysis. Rouquerol's idea was to heat the sample in such a way as to control, at any time, the flow of self-generated gas in what is now called Evolved Gas Detection (EGD) equipment. Paulik's idea was to control the signal of the derivative unit of a balance for controlling the reaction rate. The first experiment was carried out by Rouquerol. This author has proposed the name of Controlled Rate Thermal Analysis (CRTA) and the ICTA council has approved this term for those techniques which monitor the temperature versus time profile needed to maintain a chosen, fixed rate of change of a property of a sample in a specified atmosphere.

In CRTA instead of the usual control of the furnace heating to follow a temperature program a quantity directly related to the decomposition rate is kept constant. This quantity may be, for instance, a gas flow or a signal of derivative TG. In Ref. [12] Rouquerol represents schematically the principle of CRTA.

In conventional TG analysis three basic parameters are measured simultaneously as shown by Fig. 3: the sample temperature T (by the thermocouple), the time (by the chronometer) and the weight (by the balance). The first two parameters are associated by means of the heating control loop in order to follow a predetermined T versus t program ($T = f(t)$) which is most often linear and which is therefore not necessarily

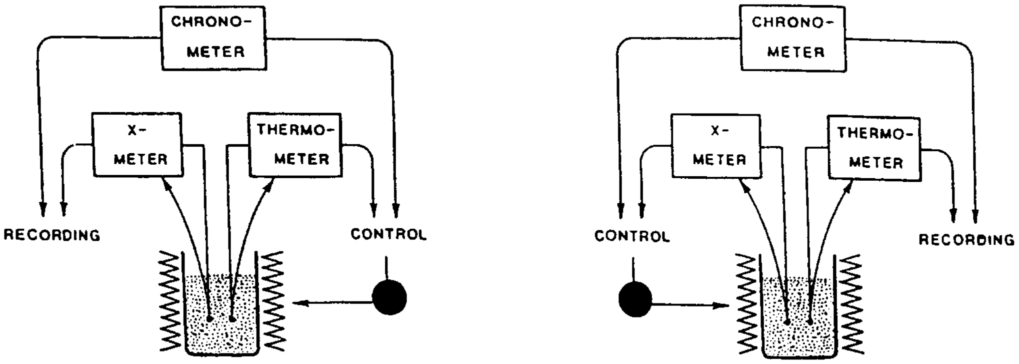

Fig. 3. (a) Principle of conventional thermal analysis (TG); (b) Principle of controlled rate thermal analysis (CRTA).

recorded. The corresponding value of weight is recorded versus t or T to deliver the proper thermal analysis curve. The CRTA approach is very close to TG analysis but is in some respect the opposite as Fig. 3 shows. Here the physical property (weight) is brought to follow a predetermined program.

Comparison between the CRTA approach and the conventional TG methods has been systematically carried out and is reported in several papers [13–16]. The principal advantages of the technique CRTA can be summarised as follows:

to reduce the influence of mass and transfer phenomena.
to obtain kinetic parameters which are independent of the starting sample mass
to identify the correct form of the $f(\alpha)$ function.

The kinetic of solid-state reactions is probably the most recent field in which CRTA has been applied. It is well known that the validity and significance of the kinetic analysis of solid-state reactions depends on our exact knowledge of both the 'influencing parameters' and of their values at any point of the reacting system. This means that any unknown gradient in temperature, gas composition or pressure is a real limit to our kinetical understanding of the reaction. It has been shown [17] that CRTA allows considerably better control of the heat transfer than conventional methods. By way of example Table 3 shows the activation energies of the thermal decomposition of sodium bicarbonate with different sample weights.

We can see that the values obtained by TG depend on the sample weight and changes in a random fashion. This trend is not observed with CRTA experiments; the activation energies have the same values despite the wide range of sample weight used, the small differences are within experimental errors. In TG experiments the transport phenomena reflect the experimental conditions under which the curve was obtained.

Table 3
Values of the activation energy with different sample weights

Sample weight (mg)	20	40	80	150
TG (KJ/mol)	90	110	162	130
CRTA (")	94	93	92.5	94

Criado [18] has shown the influence of the experimental conditions (pumping rate and sample size) on the thermal decomposition of the alkaline-earth carbonates. The scope of his work was to study the reaction in such a way that the effects of mass and thermal transport may be, if possible, separated. The TG traces move towards higher temperatures when the sample size is increased, while maintaining a constant pumping rate. If the pumping rate is decreased, while maintaining the sample size and heating rate constant (i.e two important parameters in the control of heat transfer) the TG traces move towards higher temperatures while the CO_2 pressure around the sample increases. If the thermolysis was heat-transfer controlled, the increase in pressure (and therefore in surrounding thermal conductivity) would cause the TG curves to move towards lower temperatures (which is not observed). We therefore conclude that even in vacuum experimental conditions, the residual pressure is a major rate-controlling parameter which does not act through a heat transfer process but through the control of a reversible reaction, and may be also through a mass transfer, diffusion, process.

However, the data obtained by means of CRTA show that the activation energy is independent of both CO_2 residual pressure and the decomposition rate. This behaviour seems to indicate that the reaction is not influenced by any mass transfer, heat transfer or equilibrium pressure phenomenon. These results are surprising if we bear in mind the strong effect exerted by the pumping rate on the kinetic parameters as calculated from the TG curves, recorded, apparently, in a similar pressure range. It was necessary to work with 2 mg (!) of the sample to obtain by TG the same activation energy as that calculated from CRTA with various samples weighing up to 300 mg.

The efficiency of CRTA for separating successive steps of dehydration and decomposition of complicated inorganic salts has already been demonstrated [19]. 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 gradients through the sample are themselves low enough to avoid any overlapping of the successive steps. The literature data show that the kinetic parameters calculated from CRTA are independent of both the starting weight and the constant rate selected over all the range investigated. This fact points out that the kinetic parameters obtained do not seem to be influenced by heat and/or mass transfer phenomena which are in good agreement with previous works which state that the CRTA technique leads to a more effective control of these phenomena than conventional TG.

6. Determination of the correct form of the $f(\alpha)$ function

The basic kinetic equation can be rewritten for CRTA in the following form:

$$A\exp(-x)f(\alpha) = \text{constant} \tag{10}$$

where $x = E/RT$ by differentiating this equation with respect to α the conditions for both minima (α_{min}) and point of inflection (α_{i}) of the CRTA curve can be obtained.

$$\frac{\mathrm{d}T}{\mathrm{d}\alpha} = -\frac{T}{x}\frac{F'(\alpha_{\mathrm{min}})}{f(\alpha_{\mathrm{min}})} = 0 \tag{11}$$

$$\frac{\mathrm{d}^2T}{\mathrm{d}\alpha^2} = \frac{T}{x}[f(\alpha_i)]^{-2}\left[[f'(\alpha_i)]^2\left(\frac{2}{x}+1\right) - f(\alpha_i)f''(\alpha)\right] = 0 \tag{12}$$

The point of inflection of the CRTA curve generally depends on x. The mathematical conditions for the minima and points of inflection are summarised in Table 4 for all kinetic models discussed.

It is evident that theoretical CRTA curves can easily be divided into three groups after their general shape [20] as is shown in Fig. 4.

Thus the general shape of an experimental α vs. T curve as obtained at a constant rate is very important for the determination of the actual mechanism. The following rules can be formulated:

the T vs. α plots obtained for reactions following the Avrami–Erofeev mechanism (growth of nuclei) yield a temperature minimum. This is an interesting and unique feature of the CRTA method.

the n-order reactions (boundary controlled mechanism) R2, R3 and F1 lead to curves with neither maxima nor minima nor point of inflection.

the diffusion-controlled reactions (D_n) give the shape of CRTA curve with a point of inflection.

Therefore, a mere glance at the shape of a CRTA curve provides an easy way to discriminate between the three families of isokinetical models; in particular, the shape of the Avrami–Erofeev model is very char-

Table 4

Kinetic model	α_{min}	α_{i}
Growth of nuclei	$1-\exp\nu((1-n)/n)$	—
n order	—	—
D2	—	$1-\exp(2/x-1)$
D3	—	$1-\{(8/x+6)/[4/x+5+(4/x+7)^{1/2}]\}^3$
D4	—	$1-[(2+3x)/4x]^3$

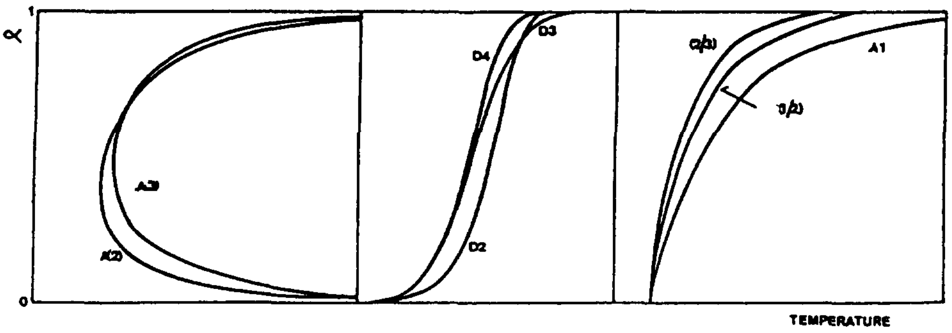

Fig. 4. Typical shapes of CRTA curves for several kinetic models.

Table 5
Kinetic analysis of nickel nitrate by conventional TG

Mechanism	E (KJ/mol)	r
R2	138	0.99
R3	146	0.99
Fl	159	0.99
A2	79	0.99
A3	46	0.99
D1	251	0.99
D2	272	0.99
D3	301	0.99
D4	284	0.99

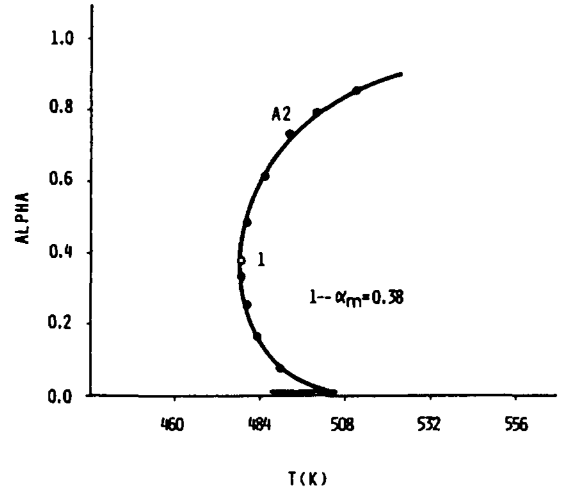

Fig. 5. Experimental CRTA curve for the thermal decomposition of anhydrous nickel nitrate. $C = 2.5 \times 10^{-3}\ \mathrm{min}^{-1}$.

acteristic. Thus the question 'how do you know that you have the correct form for $f(\alpha)$?' has been solved in good part in CRTA where one discovers a completely new picture. Nickel nitrate is a case where it is difficult to distinguish the kinetic law by means of conventional TG analysis [21] such as shown in Table 5 , because all the kinetic equations fit the thermoanalytical data very well. The advantage of CRTA can be demonstrated if we examine the shape of the curve in Fig. 5: we can see that the thermal decomposition of nickel nitrate gives rise to a typical U-shape which corresponds to the mechanism controlled by nucleation and growth of nuclei.

To go one step further, that is, to discriminate among the various mechanisms forming one given family, one must, of course, try to fit a theoretical curve with the experimental one. Nevertheless, here again, the job is made easier because of the availability of the energies of activation obtained by the 'rate-jump' method.

7. Calculation of the activation energy

It is possible to analyse a single linear temperature experiment and obtain the kinetic parameters, E and A, using any of the conventional methods of kinetic analysis. However, these methods have many shortcomings that stem from the fact that they must identify the correct form of $f(\alpha)$ function. But, in conventional analysis, the problem arises from the fact that in all cases different kinetic equations appear to fit a set of kinetic data and that researchers may not be able to select the most appropriate one. On the other hand, the activation energy obtained is strongly dependent on the kinetic law assumed in performing the calculations, such as shown by Table 5. The above difficulties encountered with the analysis of conventional rising

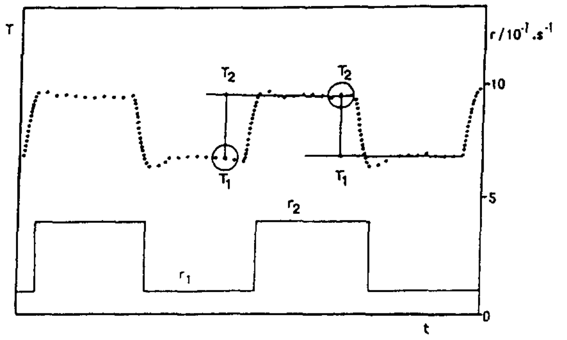

Fig. 6. The determination of E by a rate-jump CRTA experiment.

temperature experiments are virtually eliminated if the experiments are carried out by CRTA using the 'rate-jump' method, because this method does not need any assumption about the so-called 'function of α.'

The principle of the method is to bring the rate of reaction to switch between two preset values with a ratio conveniently chosen between 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 20 and 30 such jumps are usually performed for analysing one individual step. Each temperature jump allows the determination of a separate value of activation energy, since it provides a couple of temperature (one, T_2 directly measured on the recording and the other, T_1 obtained by extrapolation for exactly the same degree of conversion) 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 good calibration). Since the degree of reaction remains virtually unchanged during the rate-jump and provided that the function $f(\alpha)$ is not changed by the corresponding temperature jump (most often in the 10–15 K range), it may be concluded that the reaction rates are in the same ratio as the rate constant, hence finally:

$$E = \frac{RT_1T_2}{T_2 - T_1}\ln r \qquad (13)$$

The method described above allows the performance of up to 30 independent measurements during one supposed reaction step.

The applicability of the 'rate-jump' method for kinetic studies can be demonstrated using the decomposition process of dolomite. The experiment was carried out with a powder sample sieved between 30 and 160 μ. The rate-jump method was used to determine the activation energy of this solid-state reaction. Fig. 7 shows a typical rate-jump diagram for dolomite. From Fig. 8 it can be seen that the

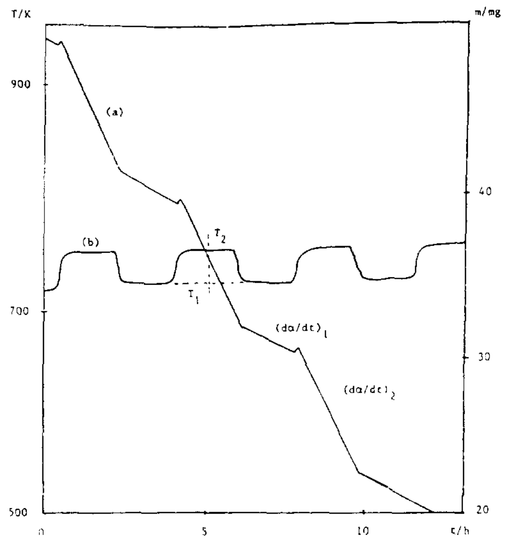

Fig. 7. Typical rate-jump diagram for dolomite thermolysis. Curve (a), m vs. t; curve (b), T vs. t.

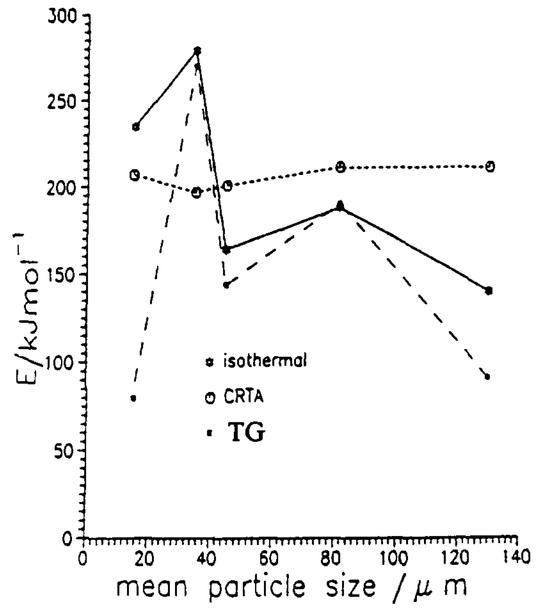

Fig. 8. Activation energies as a function of the particle size for the thermal decomposition of dolomite.

activation energy changes in a random fashion when the kinetic analysis was carried out by means of conventional methods (TG or isothermal). These trends were not observed with CRTA experiments, in this case the activation energies have the same values despite the wide range of particle size used. There is a small difference within experimental errors.

8. Conclusion

The conventional dynamics techniques of thermal analysis offer attractive ways to determine kinetic parameters. There is an obvious convenience and economy in making a single set of measurements in a short time but these advantages are actually counterbalanced by experimental uncertainties leading to apparent activation energies, depending on the experimental conditions. There are still numerous difficulties in finding the proper mathematical solution for the determination of E, A and $f(\alpha)$ and in trying to correlate them with real processes. This is not to say that CRTA is a panacea and that conventional methods cannot be used to good effect but it does provide a powerful new technique in thermal analysis.

The following conclusions may therefore be drawn:

It is possible to draw benefit from the rapidity of the conventional dynamic approach if the experimental conditions are chosen to keep relatively low gradient in the sample. This condition is usually fulfilled for low sample masses not exceeding 10 mg. In the case when the sample mass must be larger then CRTA provides a satisfactory solution. Carefully selected algorithms must be used for calculation of kinetic parameters.

The increase in control brought by CRTA makes it much easier and safer to derive an energy of activation and to determine the most probable mechanism.

The CRTA was specially developed to lower at will the gradient through the sample and to allow the performing of more meaningful experiments.

Using the CRTA approach instead of TG technique a much greater sensitivity can be achieved.

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