

THE KINETICS OF HETEROGENEOUS SOLID STATE DECOMPOSITION REACTIONS;
A NEW WAY FORWARD?

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Abstract

Some of the problems associated with measuring kinetic parameters for solid state decomposition reactions are discussed. It is proposed that the problem lies mainly in the choice of the experimental method. The nature of a thermoanalytical experiment is discussed and it is proposed that Constant Rate Thermal Analysis has certain advantages over conventional methods. The use of the Arrhenius equation is defended on theoretical grounds. The theoretical and practical advantages of the Rate Jump method of measuring activation energies are outlined. A novel method of identifying the α function called the reduced temperature plot is described and its advantages outlined. It is suggested that Constant Rate Thermal Analysis should be more widely used for a variety of reasons.

There is a great deal of uncertainty surrounding the significance of kinetic parameters measured for the thermal decomposition reactions of the type solid - solid plus gas. Dollimore, Galwey and Brown, in their comprehensive review of this field [1], underlined the reasons for this uncertainty when they observed that, "the kinetic parameters most frequently used to provide information about the (reaction) step identified as rate limiting are A and E. Values for nominally the same chemical change often show significant deviations". The A and E referred to are the preexponential constant and activation energy of the Arrhenius equation with which most chemists are familiar in the context of the

energy barrier model of chemical kinetics. These 'significant deviations' are exemplified by the reported values for the activation energy of the thermal decomposition of calcium carbonate which ranges from 142 to 3828 kJ/mol [2].

Since the publication of the above observation in 1980 little has changed, yet agreement between different research groups on experimentally determined parameters must be regarded as a sine qua non before researchers in this field can consider their work to be on a sound scientific footing. Some authors have concluded that meaningful values for kinetic parameters cannot be obtained for solid state decomposition reactions because their behaviour is dominated by mass and thermal transport problems or even that the Arrhenius equation is inapplicable [3,4].

How then are these questions to be resolved so that the study of heterogeneous kinetics of this type can either be recognised as simply an empirical exercise in curve fitting, or elevated to the level of homogeneous gas phase and solution kinetics ?

It is the purpose of this article to propose that pessimistic conclusions about the applicability of the Arrhenius equation are ill founded. Further we wish to propose that the heart of the problem is the choice of experimental method. Inadequate experimental methods and inappropriate methods of analysing experimental data will inevitably lead to a wide scatter of results and can lead to the invalidation of a correct theoretical model or the validation of a false one.

First let us consider the component parts of a thermoanalytical experiment. It can be considered as comprising three elements;

- 1) a method of measuring reaction rate
- 2) a method of temperature control
- 3) a method of controlling the reaction environment

In thermal analysis the method of measuring reaction rate could be a balance, a calorimetric signal etc.. Decomposition reactions of the type being considered here involve the evolution of a gas and consequently a weight loss, they are therefore most frequently studied using thermogravimetry and/or evolved gas analysis (EGA). For these types of reaction, control of product gas partial pressure is crucial because of its influence on the back reaction and we shall concentrate on methods that centre around EGA. For our purposes we can consider that modern instruments can usually provide accurate and reliable techniques for measuring gas concentrations in vacuum and flowing atmospheres.

The methods of temperature control familiar to most thermal analysts involve a device for heating and cooling the sample and a temperature programmer that can be used to subject the sample to a predetermined temperature programme. The most common programmes are either isothermal or linear rising temperature. This approach could be described as programme determined temperature control; the temperature programme is decided upon in advance and proceeds independently of any reaction undergone by the sample. There is an alternative

approach which could be described as reaction determined temperature control. In this method the temperature of the sample is altered in response to the measured reaction rate. If the sample does not react or the parameter being measured is insensitive to the progress of the reaction no true programming is achieved. Ideally this should be done in such a way as to maintain the reaction rate constant i.e maintain some measured reaction parameter that is proportional to the reaction rate at a constant value thereby maintaining the reaction rate itself constant. This approach was first proposed in a general way by Rouquerol [5] in which he said "instead of the usual control of the furnace heating to follow a temperature programme, a quantity directly related to the decomposition rate is kept constant. This quantity may be, for instance, a gas flow, thermal flow or a signal of derivative thermogravimetry". The method is most widely known as Constant (or Controlled) Rate Thermal Analysis (CRTA). An equivalent method has also been proposed by Paulik and Paulik [6], who developed their method independently, called Quasi Isothermal Quasi Isobaric Thermal Analysis, these two methods are essentially identical. Most of the examples given here will be based upon the approach adopted by Rouquerol who chose as the controlled reaction parameter the pressure of product gas within a continuously evacuated reaction chamber. A pumping system connected to a vessel in which the pressure is maintained constant should pump away gas at a constant rate. Thus if the sample is heated in such a way that the pressure in the reaction chamber, and therefore above the reacting sample, is kept constant this results in a constant rate of gas evolution and therefore reaction rate. This system has been coupled to thermogravimetry so that rate of mass loss can be monitored simultaneously [7].

One of the advantages of CRTA becomes apparent when we consider the control of the reaction environment. This centers around the control of product gas pressure and the reduction of temperature gradients within the sample bed. Control of product gas pressure is generally attempted by removing product gases from the sample environment by use of a purge gas or a vacuum pump. The usual approach is to keep the partial pressure of the product gases within the reaction environment as low as possible by continually removing them. With programme determined temperature control the rate of gas evolution changes during the course of the reaction, therefore, if the rate of pumping or gas flow remains constant, the pressure of product gases in the sample environment changes as the reaction proceeds. In contrast, with CRTA, the product gas pressure remains constant during the whole course of the experiment. This is illustrated by fig.1 which gives typical results for all of the methods discussed so far using mass loss and EGA measurements. It is, of course, possible to devise other methods of controlling product gas pressure, however, the problem finds a natural and elegant solution once programme determined temperature control is abandoned in favour of Constant Rate Thermal Analysis.

The problem of temperature gradients is usually tackled by using small sample sizes which reduces thermal transport problems within the sample bed. Another important factor is reaction rate; the higher the reaction rate of an endothermic decomposition reaction the greater the chance of significant temperature gradients across the sample bed. This poses special problems for isothermal experiments because the dangers of too high a reaction rate at the beginning of an

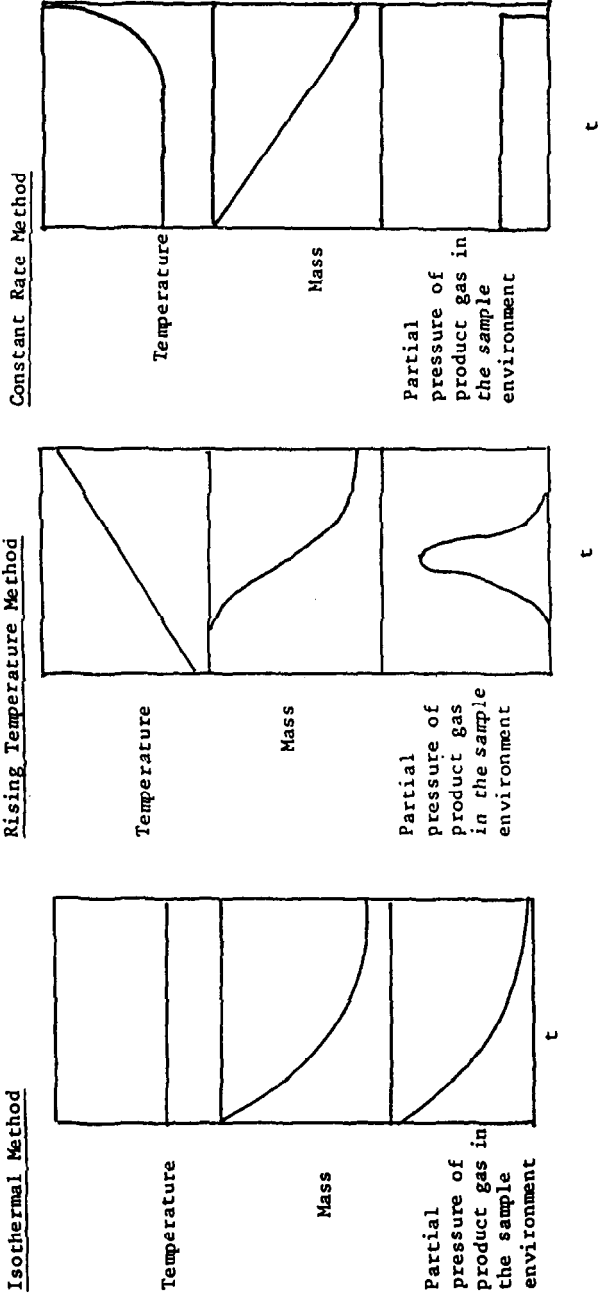


Fig. 1 Typical Results for Various Methods of Temperature Programming

experiment must be balanced against the problems of too slow a reaction rate near the end of the reaction leading to incomplete reaction over a realistic time scale. This problem becomes particularly acute when examining the higher temperature behaviour of a sample that decomposes in several poorly differentiated steps over a wide temperature range. Although the situation is better with linear rising temperature experiments a similar problem exists. The rate generally goes through a maximum somewhere near the mid-point of the reaction. Adjusting the heating rate to limit the maximum rate can also give rise to very long experiments with most of the reaction occurring at much lower rates. Once a rate is chosen that is sufficiently low to avoid excessive temperature gradients, the Constant Rate method ensures that the experiment takes the minimum time and that the reaction goes to completion. There are, therefore, purely pragmatic advantages to using this method.

Thus it can be seen that Constant Rate Thermal Analysis provides some advantages over more traditional methods by providing a much greater degree of control over the reaction environment and thereby over sources of experimental error.

At this point it is appropriate to discuss the model that might be used to describe solid state decomposition kinetics. By far the most popular approach can be expressed in the form:

$$\frac{d\alpha}{dt} = f(\alpha) A e^{-E/RT} \quad \dots(1)$$

Where: t = time

α = fraction reacted

A = preexponential constant

T = temperature

E = the activation energy

R = universal gas constant

This model may be divided into two parts;

- 1) the relationship between reaction rate and temperature, here given by the Arrhenius equation
- 2) the relationship between rate and extent of reaction expressed through $f(\alpha)$

Garn [3] maintains that in the solid state " the lack of a statistical distribution rules out the the use of the Arrhenius equation" he assumes that " a substantial difference from the average energy is not achievable within the crystal". However the Boltzmann distribution is at the basis of the successful statistical theory of heat capacity in the solid state [10]. Also the Arrhenius equation is used to model the kinetics of vaporization in sublimation processes [11]. These would seem sufficient reasons for assuming that the Boltzmann energy distribution exists within the solid bulk and thus at the interface. Deactivation of an excited molecule may be rapid, thus allowing little time for the internal energy of the excited species to be rearranged (so that sufficient energy is distributed into the reaction co-ordinate for reaction to ensue), however, excitation is also rapid thus in unit time the probability that a number of excited molecules will have their energy distributed in such a manner as to allow dissociation to occur is correspondingly high.

There are many different equations used to describe the course of thermal decomposition reactions. Here we consider a

selection of the more commonly used expressions given in table 1. They may be divided into three classes. The first includes models that assume the formation of sparse nuclei that grow, resulting in an accelerating reaction rate, then merge. Under isothermal conditions this results in a sigmoid shaped α vs t curve, these expressions are known as Avrami Erofe'ev equations (equations 1-3). The second assumes that the surface is rapidly covered with diffuse overlapping nuclei whereafter the interface proceeds through the sample particle, these are known as order or geometric expressions (equations 4-6). The third contains expressions that assume diffusion to be the rate limiting process (equations 7-10).

The equations are given in a differential form and the integral form $g(\alpha)$ where :

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) \quad \dots\dots(2)$$

Under isothermal conditions we can write the classical expression:

$$g(\alpha) = kt \quad \dots\dots(3)$$

$$k = A e^{-E/RT} \quad \dots\dots(4)$$

When considering these equations it should be remembered that they assume that either one particle of a particular shape is decomposing or that a number of particles all of the same shape and size are all decomposing in a similar manner. In practice this may be experimentally difficult to achieve. Also these expressions are idealised and may not be adhered to during the whole course of the reaction. In general, obedience to these expressions cannot be taken as proof that

the postulated mechanism is correct in detail without corroboration from another technique such as microscopy.

Two things must be determined, the activation energy and the form of the α function. We shall consider these separately.

First let us consider measuring the activation energy.

Both programme and reaction determined temperature control can be used in a continuous mode, in which case any change in the controlled quantity can be described by a continuous function, or a jump mode, in which case the controlled quantity is changed in a sudden discontinuous manner. When considering programme determined temperature control we need only consider the temperature jump experiment which consists of jumping from one isothermal regime to another. From the two reaction rates and their corresponding temperatures at the instant of the jump the activation energy can be calculated viz:

$$-E = \frac{R \ln \left[\frac{(d\alpha/dt)_1}{(d\alpha/dt)_2} \right]}{\left[\frac{T_2 - T_1}{T_1 T_2} \right]} \quad \dots\dots(5)$$

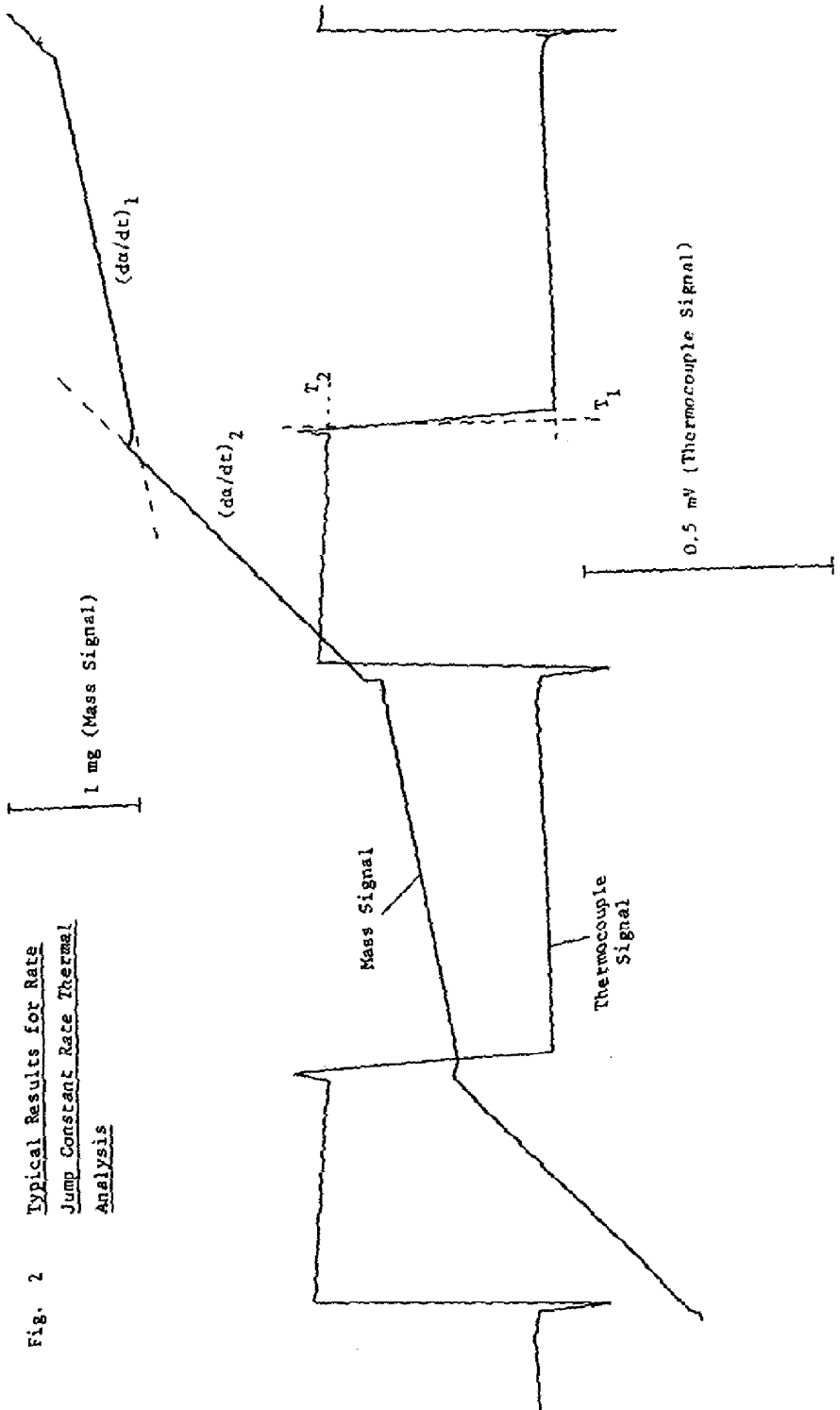
This assumes no significant change in α during the temperature jump itself. The advantage of this method is that the activation energy can be determined without knowing or assuming the α function. Also all the measurements are made on the same sample thus avoiding errors introduced by sample differences when using methods that require several discrete experiments using several different samples. Further, it is possible that the thermal history of the sample can affect the form of the α function, under this condition a jump method is the only way of reliably

measuring the activation energy. This then is the programme determined temperature control method that makes the least assumptions and therefore offers, in theory at least, the best method of measuring activation energies.

It is appropriate at this point to consider the analysis of single rising temperature experiments. Ostensibly it is possible to analyse a single linear temperature experiment and obtain the activation energy, the α function and preexponential factor using the method of Coats and Redfern [8] and its many variants. However these methods have many shortcomings that stem from the fact that they must identify the correct α function in order for the other quantities, A and E, to be correct, whereas this may not be possible either because the correct function is not amongst those considered, or because the method of discrimination between candidate equations is not sufficiently sensitive when set against the experimental errors. The great danger with these methods is that the experimenter can obtain a linear Arrhenius plot but, nevertheless, derive the wrong results. Much of the present difficulty with the measurement of these kinds of parameters stems for the incautious use of these methods.

The disadvantage of the temperature jump experiment is that the pressure of product gas above the sample undergoes a step change along with the reaction rate unless there is a sensing system that controls a pumping rate or a gas flow rate. The CRTA analogue to this method is the rate jump method. Here the rate of reaction, which is being held constant, is suddenly increased and the corresponding temperature increase is measured. Fig.2 gives an example of the kind of results

Fig. 2 Typical Results for Rate
Jump Constant Rate Thermal
Analysis



that are obtained using the CRTA apparatus described above, equation 5 is again used to calculate the activation energy. The advantage of this method compared to the temperature jump approach is that the parameter that is being kept constant is the pressure above the sample, thus the pressure above the sample is the same before and after the rate jump (the rate jump is achieved by suddenly increasing the pumping rate). Fig.2 is an accurate tracing of a chart recording. It can be seen that the errors involved in making the short interpolation over the actual rate jump itself are small (the sample size was 100mg). We have shown [2] that by using CRTA that reproducible values for the activation energy for the decomposition of calcium carbonate can be obtained over a range of sample sizes from 10mg to 500mg, a range of temperatures from 740K to 990K and a range of decomposition rates that extends from a rate which corresponds to a total reaction time of 1.5 hours to 31 days. This suggests that the theoretical advantages of this approach given above can translate themselves into real experimental advantages that enable the experimenter to make more reliable measurements safe in the knowledge he has made the minimum possible assumptions

One very popular method of identifying the α function is the reduced time plot [9]. Taking the time elapsed up to $\alpha=0.9$ to be $t_{0.9}$ for isothermal experiments we may write.

$$\frac{g(\alpha)}{g(0.9)} = \frac{t}{t_{0.9}} \quad \dots\dots(6)$$

A series of master plots of α against $g(\alpha)/g(0.9)$ may be drawn for the different $g(\alpha)$ s, examples of these plots for the equations given in table 1 are given in Fig.3. It is not possible to construct similar plots for rising temperature

experiments but it is for constant rate data. Taking $T_{0.3}$ to be the temperature at $\alpha=0.3$ and adopting a similar convention for $T_{0.9}$ it can be shown from equation 1 that:

$$\frac{\frac{1}{T} - \frac{1}{T_{0.9}}}{\frac{1}{T_{0.3}} - \frac{1}{T_{0.9}}} = \frac{\ln f(\alpha) - \ln f(0.9)}{\ln f(0.3) - \ln f(0.9)} \quad \dots (7)$$

$$\therefore \frac{a - T_i}{\frac{aT_i}{b}} = \frac{\ln f(\alpha_i) - q}{d} \quad \dots (8)$$

Where

$$a = T_{0.9}$$

$$b = \frac{T_{0.9} - T_{0.3}}{T_{0.9} T_{0.3}}$$

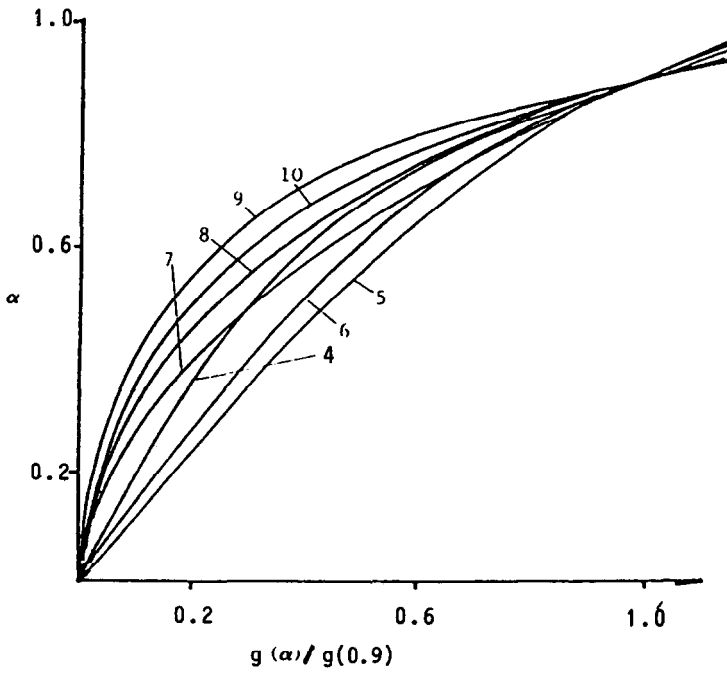
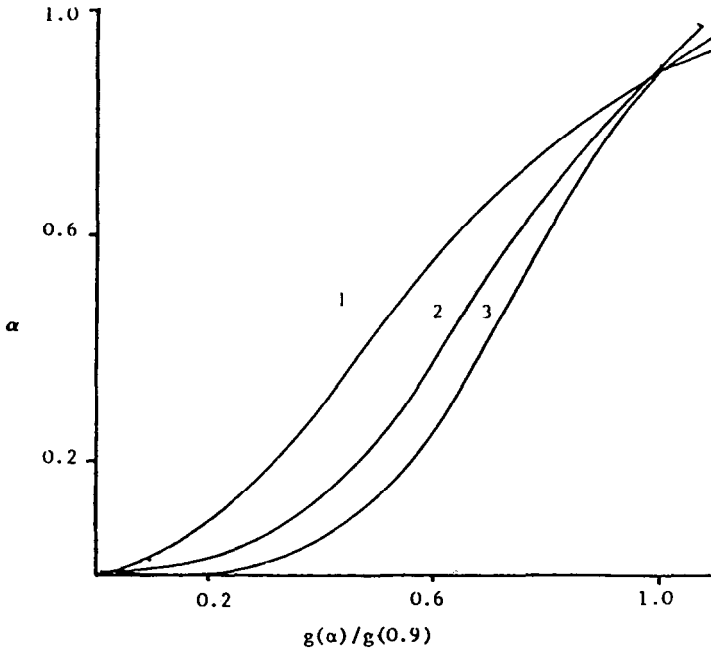
$$q = \ln f(0.9)$$

$$d = \ln f(0.3) - \ln f(0.9)$$

Table 1

Commonly Used Kinetic Equations

No.		$f(\alpha)$ [$=(d\alpha/dt)/k$]	$g(\alpha)$ [$= kt$]
	<u>Sigmoid Rate Equations</u>		
1		$(1-\alpha)(-\ln(1-\alpha))^{\frac{1}{2}}$	$2[-\ln(1-\alpha)]^{\frac{1}{2}}$
2	Avrami Erofe'ev	$(1-\alpha)(-\ln(1-\alpha))^{\frac{2}{3}}$	$3[-\ln(1-\alpha)]^{\frac{1}{3}}$
3		$(1-\alpha)(-\ln(1-\alpha))^{\frac{3}{4}}$	$4[-\ln(1-\alpha)]^{\frac{1}{4}}$
	<u>Deceleratory</u>		
4	first order	$(1-\alpha)$	$-\ln(1-\alpha)$
	<u>Based on Geometric Models</u>		
5	Contracting area	$(1-\alpha)^{\frac{1}{2}}$	$2[1-(1-\alpha)^{\frac{1}{2}}]$
6	Contracting volume	$(1-\alpha)^{\frac{2}{3}}$	$3[1-(1-\alpha)^{\frac{1}{3}}]$
	<u>Based on Diffusion Mechanism</u>		
7	One dimensional diffusion	α^{-1}	$\frac{1}{2}\alpha^2$
8	Two dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
9	Three dimensional diffusion	$[1-(1-\alpha)^{\frac{1}{3}}]^{-1}(1-\alpha)^{\frac{2}{3}}$	$\frac{3}{2}[1-(1-\alpha)^{\frac{1}{3}}]^2$
10	Ginstling Brounshtein	$[(1-\alpha)^{-\frac{1}{3}}-1]^{-1}$	$\frac{3}{2}[1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}]$

Fig.3 Reduced Time Plots. Numbers from Table 1.

and a, b, q and d are constants. Thus in a similar manner to reduced time plots a series of reduced temperature master plots of

$$\frac{\ln f(\alpha) - q}{d} \text{ against } \alpha$$

can be drawn. Examples of these plots using the equations given in table 1 are given in Fig.4. It should be noted that equations of the type $(1-\alpha)$ can not be distinguished between by this method but can be distinguished between once the activation energy has been determined by plotting $\ln(1-\alpha)$ against $1/T$ from which the ratio E/n can be found thus n can be determined. However when considering order expressions the isothermal reduced time plots show a degree of discrimination that CRTA cannot. Also it can be seen that they can easily distinguish between Avrami Erofeev (sigmoid) and other equations (see fig.3) but the distinction between order expressions and diffusion control expressions is much less clear. In contrast the reduced temperature plots very easily distinguish between the three classes of expression considered here (see fig.4). When the comments made above regarding the differences that may arise between the theoretical description of a function and the practical reality are taken into account perhaps the most useful and meaningful thing that can be said about the mechanism of many decomposition reactions is whether the reaction rate is controlled by nuclei growth, sample geometry (order expressions) or diffusion. In making distinctions of this type CRTA shows more discrimination than alternative methods. Fig.5 shows the results of tests of two candidate equations against

Fig. 4 Reduced Temperature Plots Numbers from Table 1

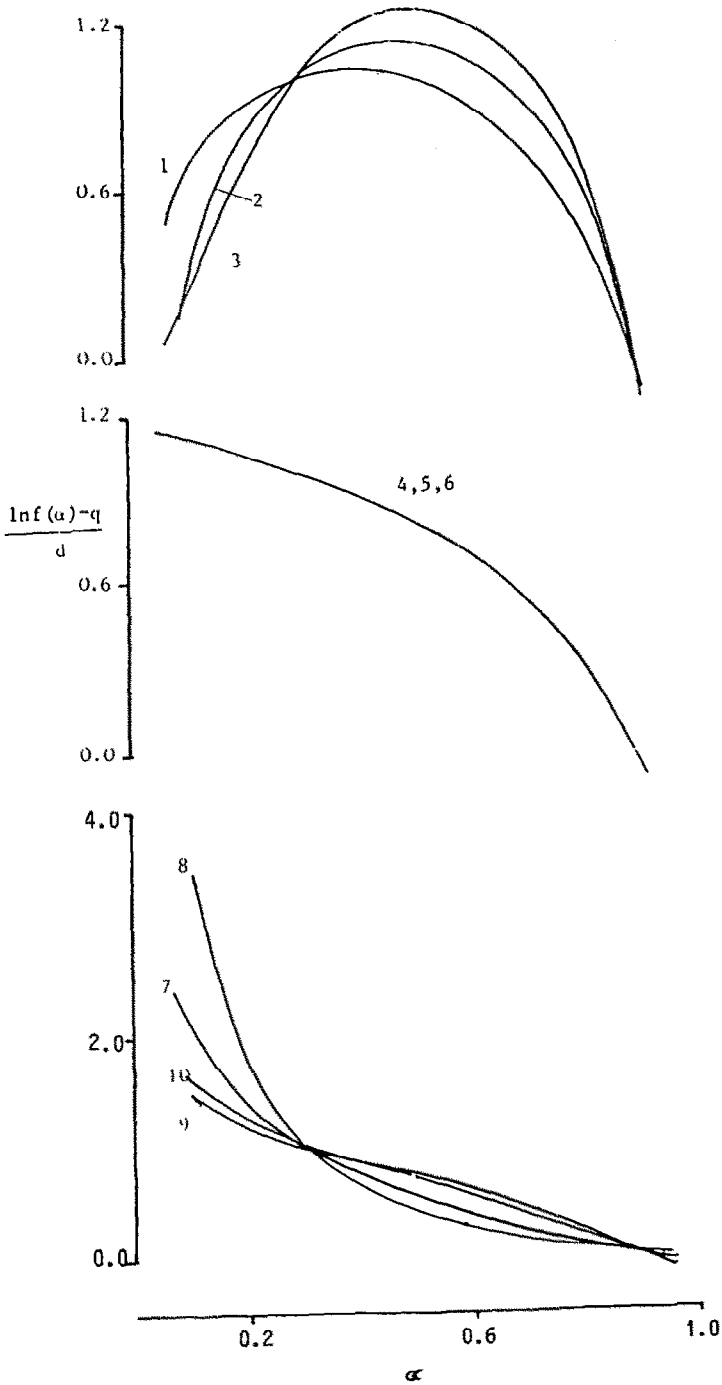


Fig. 5

Isothermal Results 10 mg CaCO₃ Under Vacuum

Fig. 3.24 Test for $g(\alpha)$

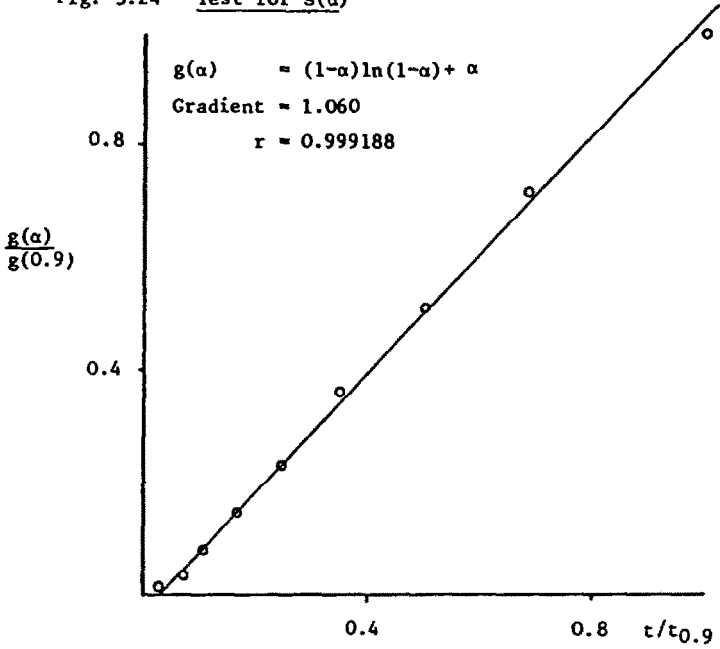
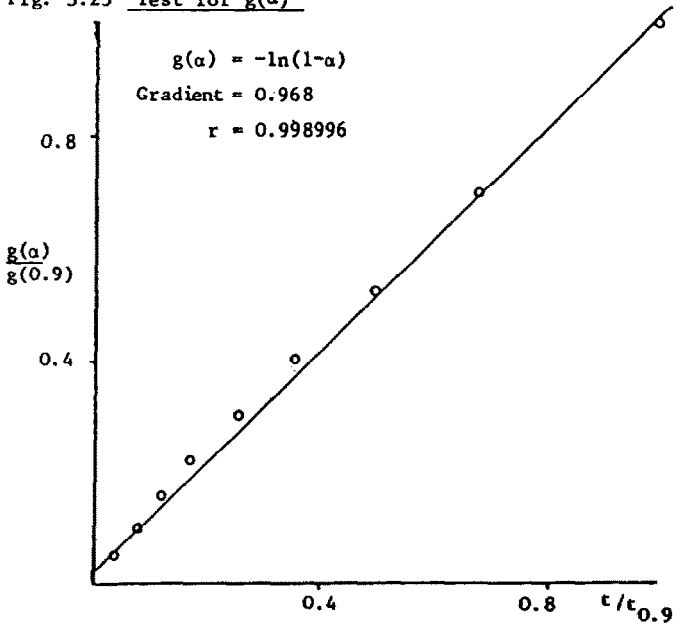


Fig. 3.25 Test for $g(\alpha)$



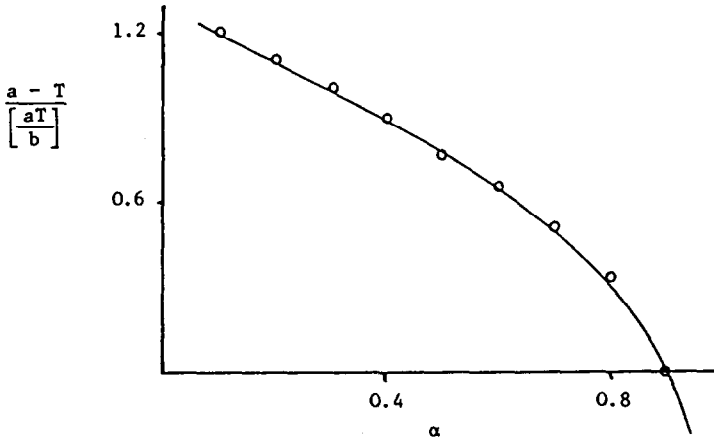
experimental reduced time data for the decomposition of calcium carbonate under vacuum. It can be seen that both a diffusion expression and an order expression give good fits. Fig.6 gives the reduced temperature plot for the same material, simple inspection is sufficient to determine that a diffusion expression is not appropriate.

In this discussion some of the potential advantages of CRTA when carried out using EGA as the method of following the progress of the reaction have been presented. It is not possible within the scope of this article to give an exhaustive list, they include control over surface properties, potential for dealing with complex reactions that evolve more than one gas simultaneously, very high resolution when there are overlapping reactions, ability to examine near equilibrium conditions and many more. The areas of application are considerable, extending from the decomposition of organic materials to preparation and characterisation of catalysts [12,13,14].

The greater control this approach can give over reaction conditions, the strengths of the rate jump method and the reduced temperature plots can, we believe, give the chemist the means of obtaining high quality kinetic data that should enable the elimination of the significant deviations referred to in the opening paragraph except where they reflect real mechanistic differences. 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 weapon in the thermal analyst's armoury that may enable us to elevate the kinetics of heterogeneous decomposition reactions to the level of universal acceptance that homogeneous gas and liquid

Fig. 6

Constant Rate Results 10 mg CaCO₃ Regulated Pressure =
5 x 10⁻⁵ torr Rate = 2.671 x 10⁻⁵ sec⁻¹

Fig. 3.30 Reduced Temperature Results

phase kinetics presently enjoys, despite the much greater experimental obstacles.

In conclusion it must be said that, if CRTA has failed to gain the acceptance it deserves it is, at least in part, because the necessary equipment is not commercially available. Modern micro processor based controllers make the construction of the necessary instrumentation a comparatively straightforward affair. If this article has stimulated the interest of both users and manufacturers in the thermoanalytical world perhaps those of us interested in kinetics can look forward to a brighter future.

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