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# The application of thermal analysis in studying the thermal decomposition of solids

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## Abstract

The basic principles applying to the application of thermal analysis to the thermal decomposition of solids are outlined. The importance of considering the nature of the surface is considered. Thermodynamic and kinetic factors are discussed.

## INTRODUCTION

Thermal analysis covers a series of techniques in which a property of a material or a system is measured as a function of temperature, the system being subjected to a controlled temperature regime. In thermal analysis, the property is measured at the temperature imposed on the system. In other studies, the properties may be measured on the sample at room temperature after the sample has been heated to a pre-determined temperature and then cooled back down to ambient. It should also be recognized at the start that the majority of studies in thermal analysis are on materials which are solid at ambient temperature. Typical properties and techniques where the measurement is at room temperature include surface area determinations, porosity, particle size, optical and electron microscopy, and strength. Typical measurement techniques where the measurement is made at the programmed temperature include, thermogravimetricy (TG), differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermomechanical analysis and dilatometry.

The fact that the temperature is altered in thermal analysis means that special considerations must be given to thermodynamic and kinetic factors. Thermodynamics deals with the equilibrium condition at any temperature. In kinetics, the emphasis is on the rate of reaction. The conventional

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday chemist tends to report experiment studies carried out at a constant temperature. In connection with these two observations, in typical laboratory experiments the limiting feature imposed is the "Socially Conformable Experiment" whereby the experiment is started and finished during the working day usually in the afternoon after the experiment has been set up in the morning! The socially conformable experiment (SCE) is an important design feature built into many automated thermal analysis instruments.

Industrial processes often involve rising temperatures whereas, as noted, the laboratory supporting investigations often involve studies at constant temperature, with a choice of studying equilibrium at a given temperature (thermodynamic features) or the rate of change at a given temperature (kinetic factors). These isothermal studies are then repeated at a series of different temperatures.

Whereas the laboratory studies may be designed to conform with principles of the SCE, the industrial processes do not, the expedient of shift working enabling the processes to be carried out over long periods of time or continuously. Such industrial processes may employ systems in which the temperature is changed, such as the carbonization of coal, the production of carbons, the manufacture of cement and glass production. The firing of ceramics involves a complicated sequence of temperature programming as does catalyst and transducer manufacture.

Thermal analysis can prove valuable in providing scaled-down information on behavior which involves complicated temperature programming even if the scheme of study has to be altered to conform with the principles of the SCE. The equipment used in thermal analysis can be operated in a conventional isothermal mode or in a controlled temperature regime, enabling data to be collected for systems with regard to such phenomena as thermal stability, aging processes and explosion dangers. There are certain rules regarding the reporting of data but it should always be initially the signal measuring the property, plotted against the temperature. These rules are promulgated by committees of the International Confederation for Thermal Analysis (ICTA) and widely reported [1,2]. Thus, in thermogravimetry, the plot is usually mass plotted against temperature.

However, experiments are usually required to provide information on equilibrium or kinetics. The experiments in which the system is exposed to a controlled temperature regime, need careful examination to decide whether the information refers to kinetic or equilibrium features. In solid-state decompositions, there are features which enable one to argue that there is no such thing as a truly isothermal experiment. However, the real reason for persevering with thermal analysis techniques from the industrial point of view is the saving of time and the ability to mould studies into experimental programs which conform to the practice of the SCE.

There is an analytical application of rising temperature techniques which is implicitly recognized in the name thermal analysis and in the name given to some of the techniques. However, a wider educational consideration of thermal analysis techniques indicates that its use transcends this limited application and that it can be used to demonstrate principles of chemistry and science in all branches of scientific teaching.

## STRUCTURAL CONSIDERATIONS — THE SOLID STATE

In many industrial practices and in most thermal analysis studies, the starting material is a solid at the onset. Later, possibly during and because of the heat treatment, it may be possible that a transition occurs either completely or partially to a liquid or a gas phase and it seems important to recognize this special position of the solid phase. There are several possibilities

$$\text{A(solid)} \xrightarrow{\Delta} \text{A(liquid)} \xrightarrow{\Delta} \beta\text{(solid)} + \text{gas/gases}$$

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$$\text{A(solid)} \xrightarrow{\Delta} \text{gas(gases)}$$

$$\text{A(solid)} \xrightarrow{\Delta} \beta\text{(liquid)} + \text{gas/gases}$$

$$\text{A(solid)} + \text{gas} \xrightarrow{\Delta} \text{gas/gases}$$

In multi-stage decompositions, the possibilities are more extended. However, wherever a liquid phase intrudes, the structural processes can be explained in terms of a homogeneous rearrangement of structures within the liquid phase. This happens in certain dehydrations [3,4] and also occurs in nitrate decompositions where material appears to melt. In such cases, it is a mute point whether this is described as dehydration with the material dissolving in the liberated molecules of liquid water or simply saying the material melts.

The case of complete gasification also provides a simple case of gasification from an external surface. This would seem justified as an a priori hypothesis in reactions of the type:

$$\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO(g)/CO}_2\text{(g)}$$

This type of gasification in carbon blacks represents gasification from an external surface [5,6]. In porous carbons, gasification may take place from a proportion of the porous structure as well as from the exterior surface [7]. Again a realistic model is to confine structural changes to this surface involved in the gasification.

However, in a solid (reactant) – solid (product) transformation, there is a real mechanistic problem present from the initiation of the reaction. The easy way and probably the most common method of dealing with structural changes in solid-state decompositions, is to explain them on the basis of nucleation followed by the advance of an interface (a reaction interface) in which the changes are taking place. The alternative is to assume a homogeneous process distributed throughout the volume of the solid reactant [8]. It is probable that both these two variations occur but the concept of nucleation, nucleation growth and the advance of the reaction interface seems to be dominant [9]. However, dehydration of zeolites and clays through channels from cavities or layers seem to be models which, if not homogeneous, do not draw on the concept of an advancing reaction interface [10,11].

To appreciate what is possible and what is not, the nature of the solid structure must be considered. First the following properties associated with the solid have to be noted: (i) the solid is a rigid structure; (ii) the solid reactant may occupy a different volume to the solid product; (iii) solid structures may be almost stoichiometric or possess a notable degree of defectiveness resulting in non-stoichiometry; (iv) diffusion of chemical species through the structure is possible under certain conditions; (v) heating without decomposition causes sintering (the coalescence of particles); (vi) the forces which hold constituent chemical species in a particular position in the bulk of the solid structure are unbalanced at the surface; (vii) the solid as characterized can have either a long-range order or only possess a disordered long-range structure with order only apparent in the context of the neighborhood species around any particular species considered.

The concept of a rigid structure would seem, at first sight, to make a solid-state decomposition a catastrophic event which is only partially minimized by the consideration of its being localized at a reaction interface. However, the nature of certain lattice structures, e.g. in the case of zeolites and layered clay structures, makes it possible to visualize loss of species in the decomposition without disruption of the basic structure. In the case of layered clay structures, it is possible to cope with alterations in volume (between the solid reactant and solid product) on the basis that the layer distances are altered. In general, however, and wherever a reaction interface is involved, the difference in volume between solid reactant and solid product is bound to produce a strained structure. This strained structure often results in fragmentation of the original particles leading to the production of active solids which can be recognized by their high chemical reactivity and surface area. This aspect is covered by Gregg [12] and, as an example, the decomposition of nickel oxalate may be cited [13]. In nitrogen this material decomposes in two stages

$$NiC_2O_4 \cdot 2H_2O(s) \rightarrow NiC_2O_4(s) + 2H_2O(g)$$

and

$NiC_2O_4(s) \rightarrow Ni(s) + 2CO_2(g)$

The nickel produced is so reactive that it is pyrophoric, catching fire at room temperature when exposed to air.

It is fairly easy to demonstrate sites of different energy within the bulk structure of a solid. Almost always these result from a departure from true stoichiometry. It can be argued that beyond a certain size a crystal is bound to have defects and a loss of stoichiometry. Defects can be found both at the surface and within the bulk structure.

Besides being the sites for initial nucleation, the resultant vacancies found in the bulk structure together with the availability of suitable interstitial holes, allows diffusion to occur both at the surface and within the bulk structure. The diffusion processes contribute to sintering and are temperature dependent [14]. The fragmentation process, due to the difference in solid reactant and product volumes, can also influence the stoichiometry of the solid product. The result is often a loss of long-range order resulting in products which are amorphous. The term amorphous is preferred here to vitreous because the connotation for this latter term implies that its loss of long-range order is a result of cooling from a true liquid state. The fragmentation process to produce the "active solid" in its amorphous form need not coincide with complete decomposition. There may be regions of undecomposed reactant solid present which certainly alters the kinetic features [15].

In an endeavor to elucidate the movement of constituent ions in thermal decomposition, Goodman studied brucite using an electron microscope from which electron diffraction data could also be obtained [16]. The results were very encouraging but because transmission electron microscopy was used, it can be said to be applicable only to thermal decomposition in thin films, a condition which would allow greater freedom of movement than in bulk particles.

## SURFACES

In the majority of solid-state decompositions, a surface is involved. Three surfaces can be identified — the external surface area, the porous structure and its contribution to the area, and the reaction interface. The external area and the porous structure can often be identified from adsorption studies, and optical and electron microscopy. The reaction interface most often has to be inferred from kinetic modeling. The initiation, i.e. the nucleation process, can however be followed by microscopy [17]. The reaction interface is rarely identified with the external surface area. The exception to this may be the gasification reactions. In studies on carbon black oxidations in air, the rate of gasification per unit surface area

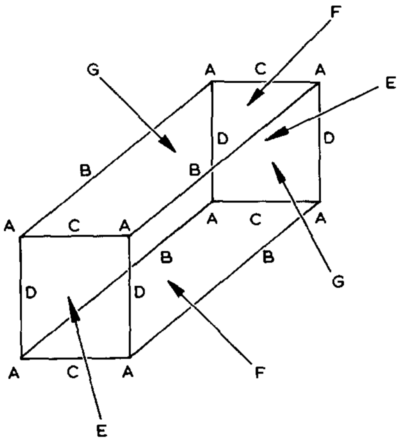

Fig. 1. Simple rectangular crystal structure and different environmental surface conditions. (For description of surface see text.)

allows an identification of two types of surface [5,6,18]. In these studies the carbon surface can be shown to be composed of clusters of graphite rings with, in one case, the basal plane exposed to the surface and, in the other, the edge atoms exposed [19,20]. The edge atoms oxidize many times faster than the basal plane surfaces.

The above example also illustrates the heterogeneous nature of most surfaces. This is in contrast to the symmetry and order present in most solid structures. Even a perfect crystal with no distortion at the surface shows different surface environments and energetics. Figure 1 shows a simple rectangular crystal structure and indicates these different conditions. Even in a perfect crystal, one can discern seven different positions for ions or constituent species which are of varying energetic and environmental condition. These are: corner atoms, marked A in diagram; edge atoms: long edge, marked B; short edge, two types marked C and D; face atoms, three types marked E, F, and G.

If we now add to these, positions of difference due to each kind of defect present in the crystal, the list can be extended considerably. More complicated crystal shapes will also extend the number of energetically different sites which can be cited. Some of these defects, if due to non-stoichiometry, can be controlled by doping. There are several instances which can be quoted showing that doping or the presence of impurities affects the course of decomposition [21,22].

These comments refer to a structure where the normal distribution of atoms is simply terminated at the surface. In fact depending on the relative polarizability of the species considered, the surface condition represents a considerable imbalance of forces which is partially ameliorated by polarizability of chemical species and actual movement of ions. Thus many oxides present an array of oxide ions at the surface (as evidenced by the fact that their heats of immersion are all of the same order of magnitude [23]). The fact that surfaces of large surface-area carbons show considerable bonding with heteroatoms also supports this contention [24].

The change in available area on heating prior to the onset of decomposition may be important. Without decomposition, a material will sinter. This means that the reaction interface initiated at the external surface may not be represented by an area determined on the original material, because that area will have been diminished by the sintering process. Three temperature dependent processes of sintering have been recognized [25]. In the description applied to materials that melt, sintering occurs by points of contact being fixed up to $\tau = 0.33$, by surface diffusion between $\tau = 0.33$ and 0.5 and by bulk diffusion beyond $\tau = 0.5$ where $\tau = 1$ represents the melting point. The point $\alpha = 0.5$, the Tamman temperature, is important because it would seem to imply that at temperatures beyond this the concept of an advancing interface in mechanistic modelling of the solid-state decomposition process is unrealistic. Now it is true that many oxysalts and oxides have no realistic melting point but the Tamman temperature can be recognized by virtue of a solid losing its extreme rigidity and possibly losing some long-range order [26]. There are at least two solid-state mechanisms for decomposition where the advancing reaction interface is unrealistic. The first of these has already been noted, e.g. by channeling as in zeolites or loss of water from layered structures (e.g. clays). The second is from systems which decompose above the Tamman temperature. In this latter case, diffusion processes may be rate determining, or the actual process of decomposition may be rate determining.

## THERMODYNAMIC FACTORS

It must be noted that as far as thermodynamic factors are concerned with reactions which occur in the liquid state, a conventional textbook approach is possible. The solid phase is, however, dominated by its prehistory. This presents problems when considering the thermodynamics of solid-state decompositions which for all practical purposes means the equilibrium state. The fact that the solid-state is the only phase where one has to cite its prehistory is due to the structural and surface features of that state as already discussed. It is difficult to bring about rearrangement in the solid-state because of its rigid nature. This means that high-temperature solid forms can exist in lower temperature regions where they should have transformed to a lower temperature form. Fenner's [27] original work on silica can be noted (Table 1). This concept forms the basis of quenching systems from high temperature to subambient temperature in order to ascertain the high-temperature form. However, the product solid-state form in a solid-state decomposition is often formed in an amorphous or energy-rich state owing to the inability of the solid phase to contain the

TABLE 1

Various forms of silica

| Temperature of transition (°C) | Type of transition |
|---|---|
| 117 | $\alpha T \rightleftharpoons \beta_1 T$ |
| 163 | $\beta T \rightleftharpoons \beta_2 T$ |
| 198–241 | $\beta C \rightarrow \alpha C$ |
| 220–275 | $\alpha C \rightarrow \beta C$ |
| 570 | $\beta Q \rightarrow \alpha Q$ |
| 575 | $\alpha Q \rightarrow \beta Q$ |
| 870 ± 10 | $Q \rightleftharpoons T$ |
| 1470 ± 10 | $T \rightleftharpoons C$ |
| 1625 | $\beta C \rightarrow$ silica glass |

Key: T, tridymite; C, cristobalite; Q, quartz; $\alpha$ and $\beta$ indicate forms stable at low and high temperature respectively [27].

stresses involved in rearrangement and possible volume change. It is best to retain the term "amorphous" for this state of affairs and to use the term "vitreous" to apply to a super-cooled liquid. In both cases, only short-range order exists and long-range order is lost. These "metastable" states existing at temperatures lower than usual owe their existence to the kinetic factor. The rate of change is lowered with a drop in temperature and if the "metastable' solid phase is brought successfully to a temperature where the rate of change is negligibly slow, then to all intents and purposes it has to be regarded as stable.

First we have to recognize that the forms of the equations relating to equilibrium conditions or rates of kinetic change are similar. For a phase change, e.g. liquid to vapor

$$\log p = \frac{-\Delta H}{RT} + \text{constant}$$

where $p$ is the equilibrium vapor pressure above the liquid, $T$ is the temperature in kelvin and $\Delta H$ is the latent heat of vaporization. A similar equation holds for the equilibrium between a solid and a vapor.

For the equilibrium condition for a solid phase decomposition, calcium carbonate is often quoted in the text books

$$\log p_{CO_2} = \frac{-\Delta H}{RT} + \text{constant}$$

where for the reaction

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

$p_{CO_2}$ is the equilibrium pressure of $CO_2$ at temperature $T$. Calcium carbonate decomposition is commonly quoted as being reversible but

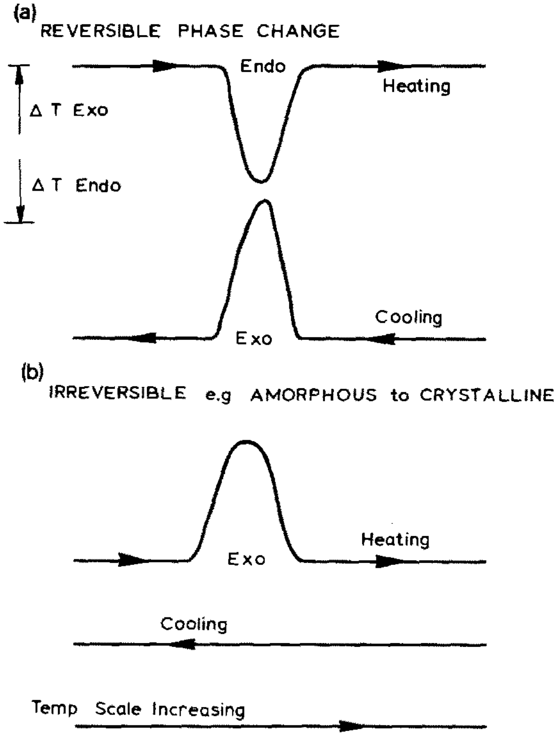

Fig. 2. Schematic DTA data on phase changes: (a) reversible phase change; (b) irreversible, amorphous to crystalline.

almost certainly with various limestones some different results will be obtained although the validity of the form of the equation can be shown. In many dehydrations, reversibility can be demonstrated [28] and in some carbonates the oxides may be recarbonated [29] but in other systems reversibility may be absent. Taking carbonates, then, two systems can be cited: reversible systems, $MCO_3(s) \rightarrow MO(s) + CO_2(g)$ and $MO(s) + CO_2(g) \rightarrow MCO_3(s)$; and non-reversible systems where carbonization of the oxide does not take place.

The reason for reversibility or non-reversibility in the carbonation reaction must be in the nature of the carbonate layer initially produced; if it prevents further access of $CO_2$ to the oxide layer then realistic progress of the carbonization is impeded and the process is eventually non-reversible.

Some of these points can be portrayed schematically using DTA traces. Figure 2 shows schematic illustrations of a reversible phase change, usually solid to liquid. This is endothermic on the heating curve and exothermic on the cooling curve. Runs of this kind distinguish the amorphous-to-crystalline transition which is exothermic and irreversible. In studying single-stage decompositions, consider calcium carbonate dissociation as the example. Figure 3 sets out the trend schematically. Similar results would be seen for

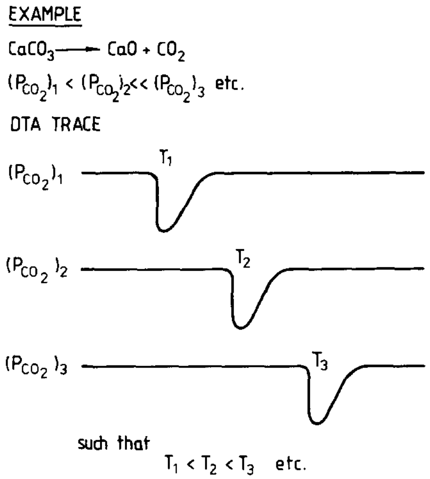

Fig. 3. Schematic DTA plots for single-stage decomposition carried out in increasing pressure of product gas.

oxide dissociation in the presence of increasing pressures of oxygen. However for such simple systems and phase changes, a controlled atmosphere manometer experiment would probably produce the same results more cheaply and simply, but the endothermic (or exothermic) character of the transition would not be immediately apparent. In two-stage decompositions, the DTA is superior to manometer systems. The behavior is shown in outline in Fig. 4. This would hold for oxide dissociation or dehydration sequences. As the pressure of product gas is increased, so both stages of dissociation are moved to higher temperatures. In manganese oxide dissoci-

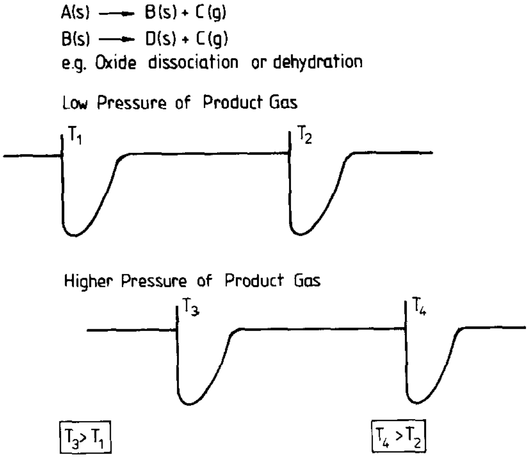

Fig. 4. Schematic DTA plots for two-stage decomposition carried out in increasing pressure of product gas.

ations, there are several steps involved [30]: $MnO_2 \rightarrow Mn_2O_3$; $Mn_2O_3 \rightarrow Mn_3O_4$; and $Mn_3O_4 \rightarrow MnO$. All these dissociations are pressure dependent. Phase changes of the solid–solid type occur which are well-characterized in the $Mn_2O_3$ form. These solid–solid transitions are invariant with regard to pressure. All the phases characterized here by formulae are in fact capable of sustaining a high degree of non-stoichiometry.

The variability found in these type of measurements is basically related to a kinetic ingredient which cannot be separated from a true equilibrium condition.

## KINETIC FEATURES

It should be noted that unlike thermodynamics, kinetic features are pathway-dependent. Many of the constraints imposed on solid-state decomposition kinetics have already been outlined. The normal process of following the kinetics of a reaction is to operate the experiment at a series of temperatures. This is the isothermal method and in solid-state decompositions the reaction is followed by plotting fraction decomposed $\alpha$ against time $t$, keeping temperature constant, and repeating such an experiment at several different temperatures. This enables the reaction mechanism to be identified and the specific reaction rate constant $k(T)$ to be determined at each temperature. By plotting log $k(T)$ versus $1/T$ where $T$ is the temperature in kelvin of the corresponding isothermal experiment, the Arrhenius terms, namely the pre-exponential term $A$ and the activation energy $E$ can be established.

There is no concentration term in solid-state decomposition kinetics, therefore appropriate models have been set out and possible mathematical relationships established between the fraction decomposed and the time of heat treatment. As already indicated, most of these kinetic models for solid-state decomposition use the concept of the formation of nuclei, and their subsequent growth via a reaction interface. It is in this reaction interface that the structural rearrangement occurs. The idea that this reaction interface should be considered as a reaction zone having a definite volume was explored by Hill [31] and there are textural features which would support this concept. A consequence of experimental treatment is that nucleation most often occurs at the crystal surface. The progress of the reaction interface then reflects the geometry of the crystal shape as the interface contracts inward away from the surface [9]. Other workers, particularly in the field of ceramics, have explored the effect of the additional process of the diffusion of species away from or towards the reaction interface [32].

It has become usual to associate particular mathematical relationships with particular models. Table 2 sets out a variety of such relationships in differential and integral form; this is excellent and can be used advanta-

TABLE 2

Broad classification of solid-state rate expressions

| | | $g(\alpha)=kt$ | $f(\alpha)=1/k(\mathrm{d}\alpha/\mathrm{d}t)$ |
|---|---|---|---|
| (1) Acceleratory $\alpha-t$ curves | | | |
| P1 | Power law | $\alpha^{1/n}$ | $n(\alpha)^{(n-1)/n}$ |
| E1 | Exponential law | $\ln \alpha$ | $\alpha$ |
| (2) Sigmoidal $\alpha-t$ curves | | | |
| A2 | Avrami–Erofeev | $[-\ln(1-\alpha)]^{1/2}$ | $2(1-\alpha)(-\ln(1-\alpha))^{1/2}$ |
| A3 | Avrami–Erofeev | $[-\ln(1-\alpha)]^{1/3}$ | $3(1-\alpha)(-\ln(1-\alpha))^{2/3}$ |
| A4 | Avrami–Erofeev | $[-\ln(1-\alpha)]^{1/4}$ | $4(1-\alpha)(-\ln(1-\alpha))^{3/4}$ |
| B1 | Prout–Tompkins | $\ln[\alpha/(1-\alpha)]+C$ | $\alpha(1-\alpha)$ |
| (3) Deceleratory $\alpha-t$ curves | | | |
| (3.1) Based on geometrical models | | | |
| R2 | Contracting area | $1-(1-\alpha)^{1/2}$ | $2(1-\alpha)^{1/2}$ |
| R3 | Contracting volume | $1-(1-\alpha)^{1/3}$ | $3(1-\alpha)^{2/3}$ |
| (3.2) Based on diffusion mechanisms | | | |
| D1 | One dimensional | $\alpha^2$ | $1/2\alpha$ |
| D2 | Two dimensional | $(1-\alpha)\ln(1-\alpha)+\alpha$ | $(-\ln(1-\alpha))^{-1}$ |
| D3 | Three dimensional | $[1-(1-\alpha)^{1/3}]^2$ | $3/2(1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$ |
| D4 | Ginstling–Brounshtein | $(1-2\alpha/3)-(1-\alpha)^{2/3}$ | $3/2((1-\alpha)^{-1/3}-1)^{-1}$ |
| (3.3) Based on "order" of reaction | | | |
| F1 | First order | $-\ln(1-\alpha)$ | $1-\alpha$ |
| F2 | Second order | $1/(1-\alpha)$ | $(1-\alpha)^2$ |
| F3 | Third order | $[1/(1-\alpha)]^2$ | $0.5(1-\alpha)^3$ |

geously in identifying the equation which will describe the kinetic data when incorporated in the appropriate treatment. To identify the equations with models is a wrong approach, however, and does less than justice to the people postulating the model. The models used by Mampel [33], Erofeev [34] and Avrami [35] show that each model can give rise to numerous mathematical relationships. To label an equation as the Erofeev–Avrami equation obscures the fact that the Erofeev model is totally different from that of Avrami. The model used by Avrami deals with phase transformations and has no direct connections with the thermal decompositions of solids.

The fact is that totally different models can give rise to the same type of kinetic relationship and this can be demonstrated very easily. A starting point is to make the assumption that the rate of decomposition per unit area of interface can be considered to be constant. A variation in the experimental rate per unit mass is then a result of variation in shape and size of the reaction interface area. Thus

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=kRs(t)$$

where $\alpha$ is the fraction decomposed, $t$ is the time of heating, $k$ is a proportionality constant and $Rs(t)$ is the area of the reaction interface at time $t$. If the crystal is a plate-type crystal, then on the assumption that there is a constant rate per unit area and that contributions from the edges are negligible, it follows that

$$\frac{d\alpha}{dt}=k$$

or

$$\alpha=kt$$

This kind of reaction is shown by silver mellitate [36]. In the oxidation of carbon blacks, however, the edge atoms react many times faster then the basal plane atoms [8]. This model still predicts a zero-order reaction. Other kinds of zero-order reactions are based on still different geometrical models, e.g. the dehydration of cobalt oxalate [37]. Thus obedience to a particular mathematical kinetic relationship does not necessarily identify the model by which the decomposition is taking place and other supporting observations are necessary.

In the case of the decomposition of cylindrically shaped crystals, the normal contracting cylinder equation results

$$kt=1-(1-\alpha)^{1/2}$$

But if the particles are large, then a first-order relationship develops

$$\frac{d\alpha}{dt}=k(1-\alpha)$$

The same is true for the contracting sphere model. In both cases, as the particle size diminishes, the model predicts first a zero-order, then a first-order relationship and, finally, a contracting cylinder or contracting sphere equation. Thus, we have different models giving the same equation and the same model giving perhaps two, three or more alternative expressions. Thus, the analysis of an isothermal TG curve gives only a mathematical relationship and does not identify a model.

There is a strong case for asserting that there is no such thing as an isothermal solid-state thermal decomposition experiment. The reaction may be endothermic or exothermic and this can affect the temperature of the reaction. In experiments on gasification of carbon, the temperature may run many degrees above the nominal experimental temperature [38]. The design of modern TG equipment makes it difficult to produce an isothermal run where the initial temperature rise to the desired temperature does not have a significant impact on the resulting data. This is one reason for choosing a rising temperature method of kinetic analysis. The main reason, however, is that obtaining the data from a single rising temperature experiment makes equipment and experimental design equate to the principles of the socially conformable experiment discussed in the introduction. Almost all established kinetic analysis techniques can be adapted to a rising temperature experiment. The single factor which in thermal analysis has generated several hundred papers, is that most experimenters prefer to use integral kinetic equations and, in the rising temperature kinetic analysis, one is then faced with the integration of the function

$$\int \exp(-E/RT)\,\mathrm{d}T$$

This proves to be intractable by normal analytical procedures and various alternatives have to be sought. In the procedure outlined here, the differential equations are used. The reluctance to use this more simple approach is offset by the fact that computer programming provides easier analysis than hitherto. The procedure is relatively simple. Three basic equations are involved. The first is the linear temperature regime imposed on the sample

$$T = T_0 + bt$$

where $T$ is the temperature (K), $T_0$ is the starting temperature (K), $b$ is the heating rate and $t$ is the time of heating. The second equation is the Arrhenius equation

$$k(T) = A\exp(-E/RT)$$

and the differential form of the kinetic equation is also used

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)F(\alpha)$$

where $f(\alpha)$ is specified as one of the differential functions in Table 2. Noting that

$$b = \frac{\mathrm{d}T}{\mathrm{d}t}$$

then

$$k(T) = (\mathrm{d}\alpha/\mathrm{d}T)b/f(\alpha)$$

and

$$\begin{aligned}\ln((\mathrm{d}\alpha/\mathrm{d}T)b/f(\alpha)) &= \ln k(T)\\ &= \ln A - E/RT\end{aligned}$$

and the values of $A$ and $E$ can also be calculated if $f(\alpha)$ is known. This approach transfers the problem in rising temperature kinetic analysis to that of correctly identifying the function $f(\alpha)$. The easiest method is to inspect the differential plot of the $\alpha$–$T$ date (Fig. 5). Each type of reaction equation gives a characteristic peak [39]. These assertions have been tested

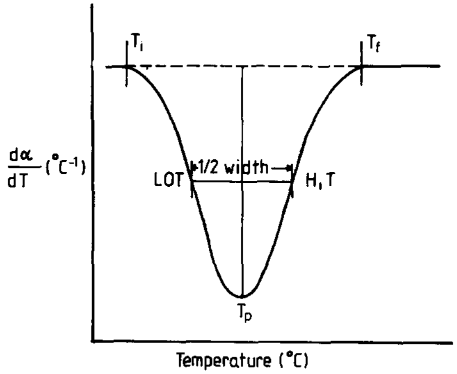

Fig. 5. Differential plot of $\alpha-T$ data (schematic representation).

exhaustively beforehand by use of computer programs which plot the $\alpha-T$ curve if the mechanism and both $A$ and $E$ are entered into the program. Extensive use of idealized created curves of this kind enable the characteristic features of the derivative curve of $\alpha$ versus $T$ to be established for any specified mechanistic equation. This plot of $d\alpha/dT$ versus $T$ is shown in Fig. 5 together with appropriate features and labelling that are needed in the characterization. This approach makes identification of the mechanistic equation possible. Figure 6 provides the outline of the scheme, using the characteristic features of the $d\alpha/dT$ versus $T$ diagram already shown in

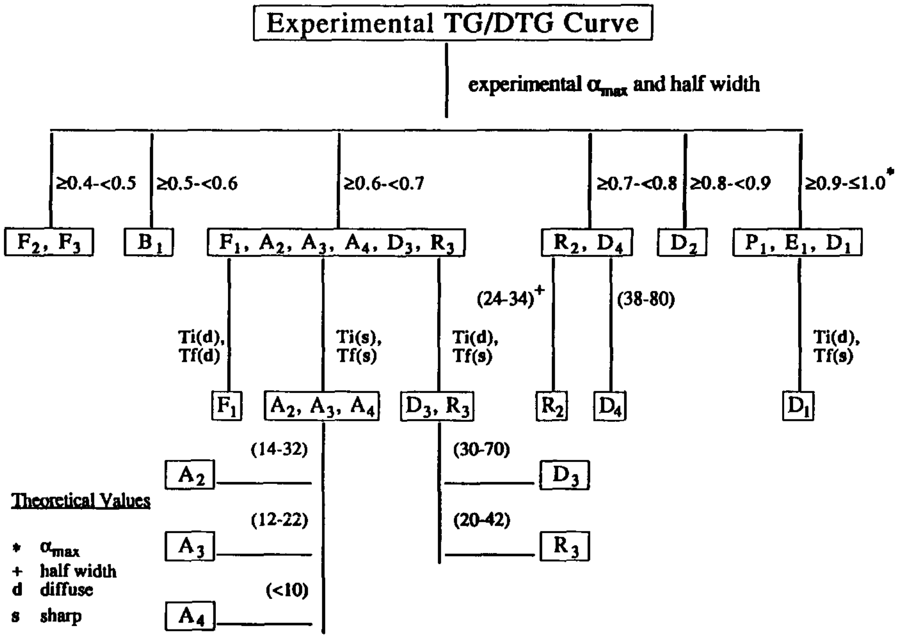

Fig. 6. Outline of scheme to identify kinetic mechanism from plots of $d\alpha/dT$ versus $T$.

Fig. 5. The method is flexible and other schemes embodying features of the $d\alpha/dT$ versus $T$ data are possible.

## COMMENT

It can be seen that determining the thermodynamic properties is possible for thermal decomposition reactions using thermal analysis techniques. The kinetic data can also be ascertained by use of rising temperature techniques. It must be remembered, however, that most decomposition processes studied are solid-state processes and it is emphasized that this is the only phase where the prehistory of the sample must be known. It is shown that the surface and interface surfaces of the sample undergoing degradation should be studied in order to interpret the mode of the decomposition process.

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