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THERMODYNAMIC, KINETIC AND SURFACE TEXTURE FACTORS IN THE PRODUCTION OF ACTIVE SOLIDS BY THERMAL DECOMPOSITION

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The production of an active solid by thermal decomposition of some precursor material usually an oxysalt is only one way of producing such a material. The activity of any solid resides at the surface albeit some of the surface may be internal or in the decomposition process a reaction interface. The peculiar property of any solid phase is that to describe it properly one must cite the pre-history of the material, and it can be shown that the pre-history of any solid phase is mainly that of altering the surface and textural properties. This fact influences the application of thermodynamic and kinetics to processes involving the solid phase. This becomes more evident in the case of active solids where a larger proportion of chemical species than usual resides at or near the surface. This is evidenced by the existence of many or more active solids in an amorphous phase and the possible co-existence of different types of solid phase. In this review, the usefulness of normal solid phase structural determination is discussed and the manner in which thermal analysis can be used to determine thermodynamic and kinetic parameters.

Keywords: active solids, kinetic,thermodynamic

Introduction

The production of an active solid by thermal decomposition of some precursor material, usually an oxysalt is only one way of producing such a material. By careful control of precipitation or the crystallization conditions one can initiate the production of an active solid from solution but in this route a heating stage is usually required to finish off the process. It is reasonably obvious that the activity of a solid resides at the surface albeit some of the surface may be an internal porous structure or in the decomposition itself the activity resides at a reaction interface.

It would be a mistaken notion to think that an active solid is necessarily stoichiometric. The most active particulate material may be produced in the

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decomposition stage prior to complete decomposition or the presence of dopant material may be necessary to induce the maximum activity.

While the liquid and gaseous states for particular materials are defined by citing certain properties, such as volume concentration and pressure this is not true for the solid state. In the case of a solid the pre-history has to be cited as well. Examples easily come to mind, thus the various crystallographic forms of silica can be cited, i.e. quartz, crystobalite and tridymite, or the different crystalline states of calcium carbonate, i.e. calcite, aragonite, vaterite, etc. All of these forms co-exist at room temperature (and at other temperatures), transition temperatures are quoted in the literature but the transformations may be accompanied by a significant kinetic factor [1, 2]. Indeed the process of quenching to freeze a high temperature phase so that it co-exists at a lower temperature is simply a recognition of the fact that in considering the solid phase the pre-history must be noted. The co-existence of these phases at the lower temperatures is simply due to the kinetic factor operating-namely that the rate of transformation is occurring at such a slow rate that the observed phase in reality must be considered stable.

However to quote definite crystal forms as examples of the solid state is to ignore the fact that many solids exist with a disordered long range arrangement of constituent species. The nomenclature associated with these solid phase structures has changed over the years. The amorphous form would have been the general term used, with the glassy state reserved for a supercooled liquid in which long term order is also absent. Now there is a tendency to use the term ‘the glassy state’ as the general term with the amorphous state hardly mentioned. Whatever the name, these forms must be regarded as unstable and an enhanced surface area must render them even more unstable because often such change are initiated by surface defects. All these points render any changes in the physical form of a solid as having both thermodynamic and kinetic aspects.

There are research workers who believe that the equilibrium state is rarely if ever reached in studies on the solid state. The reason for this is ultimately that only the surface of the solid phase is involved in any change. The logical conclusion would be a restatement of thermodynamic concepts to cope with materials (solids), which are stable (in practical terms), probably near to but not at the equilibrium stable state. It is not clear how such treatments would vary from kinetic studies involving a very slow kinetic approach to an equilibrium condition from a starting point near to that of the equilibrium position. The opposite position, i.e. a kinetic study from a situation far removed from the equilibrium position has been studied; this is the Smith-Topley effect

[3–5]. The limitation in this latter approach is its restriction to dehydration studies although some investigators may have stumbled onto other systems such as silver carbonate which meet this condition without realizing it [6]. There are two other areas of kinetic study which have to be mentioned with respect to the solid phase. These concern the methods of studying the kinetics. In the first the rate of reaction is held constant with respect to the particular component or property measured [7, 8]. This rather involved statement is necessary as for example in the following, the oxidation of carbon, the rate of production of CO could be held constant, but alternatively the rate of producing CO_2 could be held constant or the rate of loss of carbon could be kept constant. The results would probably be different in all three cases. The other innovation replaces the normal experimental approach of a series of isothermal studies at different temperatures with a single experiment of a programmed temperature regime [9]. There are analytical problems concerned with these new approaches including the question as to whether such experimental techniques should give results which agree or are different from the more classical approach.

In any case the kinetic interpretation studies ignore much structural information. The concept of a continuous progression of a reaction interface does not hold in those instances where the production of an active solid (i.e. fragmentation of the original material) occurs before decomposition is complete. This makes it imperative to discuss surface structural features and the changes which occur during decomposition.

Such a task of examining all these problems involves writing a book. In this review only the salient points can be noted and this opens up areas which required further exploration and study.

The solid state

The conventional view of the solid state is to define structures, and construct phase diagrams of condensed systems. This ignores speculation as to how such changes are possible in rigid structures and ignores the special features of the surface.

X-ray studies leading to elucidation of crystal structures is becoming increasingly available with the introduction of the newest automated equipment. However, the use of such structural determinations, in elucidating reaction mechanisms is a naive exercise in many cases, which ignores the fact that such data refers to the solid state while the reactions being considered occur in the liquid phase (e.g. dehydration of many nitrates or degradation of some polymer systems). Even if the reactions being considered are in the solid phase or involve the solid phase any deductions drawn from bulk state structures must be viewed with caution as the reaction between a liquid and a solid, or between two solid phases must take place at an interface. The structure at the interface of the solid phase is represented by a distorted structure reflecting the unbalance of forces at the surface and the polarizability of the species appearing at the surface. Thus in most oxides the real surface is represented by an array of oxide ions (witnessed by a similarity in the heats of wetting of such oxides with respect to unit surface area).

This unbalance of forces at solid surfaces leads to alteration both in the extent of the surface (an extensive property) and the surface energetics associated with that surface (intensive). This results in aging or sintering of solids. Aging usually refers to the increase in particle size and reduction in surface area at or around ambient temperatures whilst sintering refers to the same process at elevated temperatures. In its simplest form this represents a tendency to reduce the total surface energy. These sintering processes are temperature related and operate by mechanisms which have been clearly elucidated over the years.

Hüttig's findings on sintering can be summarized in terms of temperature [10], expressed as

$$\tau = \frac{T}{T_m}$$

where T is the absolute temperature of the solid and T_m is the melting point. Then,

1. Below $\tau = 0.23$, a process of adhesion between particles occurs with a reduction in surface area.

2. In the region $\tau = 0.2 \sim 0.36$ surface diffusion occurs leading to an initial increase in surface activity when surface area and capillaries are enlarged.

3. In the region $\tau = 0.33 \sim 0.45$ the surface diffusion results in sintering.

4. In the region $\tau = 0.37 \sim 0.53$ internal lattice diffusion occurs and may initially lead to activation. In this region the last traces of occluded votalile materials are often expelled.

5. In the region 0.45–0.80 lattice diffusion continues with further sintering. It is in this region that single crystals may be formed.

6. Above $\tau = 0.8$ a light reactivation may occur before melting.

In oxides the above statements may be simplified as follows:

1. Below $\tau = 0.33$ sintering occurs by adhesion between particles giving permanent junctions at the points of contact.

2. In the region $\tau = 0.33 - 0.45$ sintering takes place by surface diffusion. In this process coalescence of particles occurs through surface migration of chemical constituents.

3. Above $\tau = 0.5$ sintering occurs by diffusion of species through the bulk material.

Most of the above summaries result from observations on metals and oxides particularly ceramics. In many such systems the value $\tau = 0.5$ is so important and visible it can easily be recognized. It often is given the title 'The Tamman Temperature' [11, 12]. In many systems the small rearrangements producing transitory activation are absent.

In sintering process there is probably a relaxation effect. However sintering experimentally can often be shown to follow expressions of the kind (at constant temperature)

$$\frac{dS_t}{dt} = -k_s (S_t - S_f)$$

where S_t is the surface area at time; t and S_t is the surface area at $t = \infty$ when the rate has diminished to zero and k_s is a rate constant [13, 14]. Integration gives;

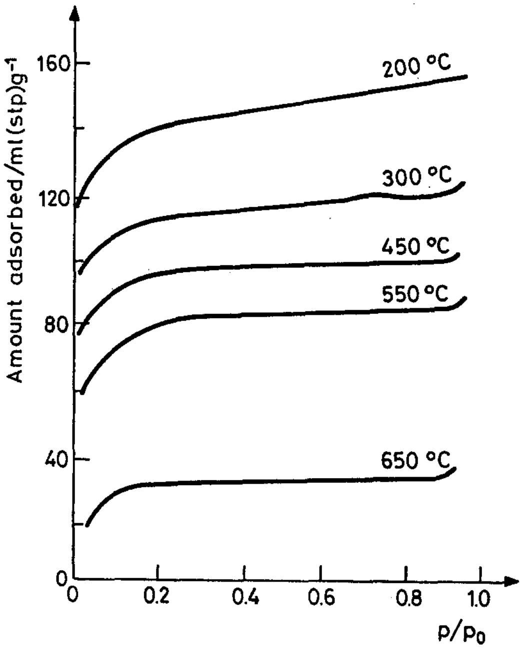

Fig. 1 Sintering studies of microporous silica. Adsorption isotherm (Nitrogen) plotted (Ref. 17)

$$\ln(S_t - S_f) = -k_s t + \text{const.}$$

This kind of expression applies to many oxide systems and zinc oxide can be cited as an example [15]. In many studies on metals the particle size of spherical particles is cited [16]. The relationship between the two measurements is apparent from the equation

$$R = \frac{3}{S\rho}$$

where R = radius of the particle
S = specific surface area

and ρ = density of material. The variations of the surface area with heat treatment of silica [17] and of zinc oxide are shown in Figs 1 and 2. The studies on zinc oxide encompass temperature regions where both surface and bulk diffusion occurs when each region is characterized by its own energy of activation (Fig. 3).

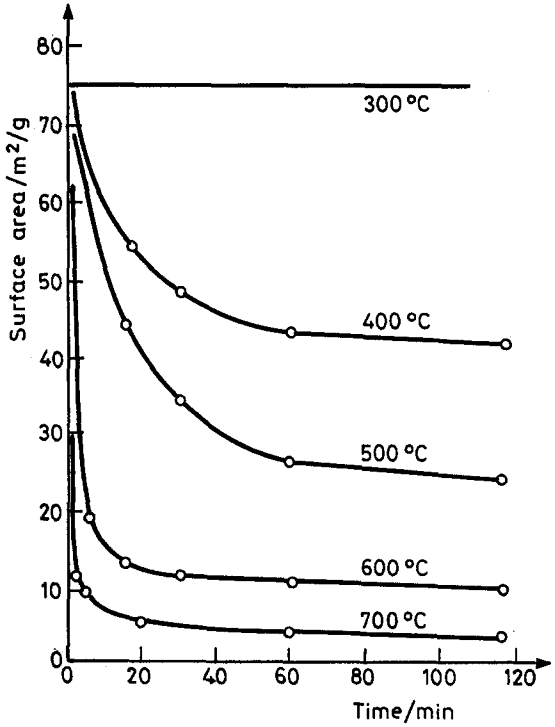

Fig. 2 Sintering studies of zinc oxide heated in 6 cm N_2 pressure. Surface area plotted against time for sample heated at indicated temperatures (Ref. 15)

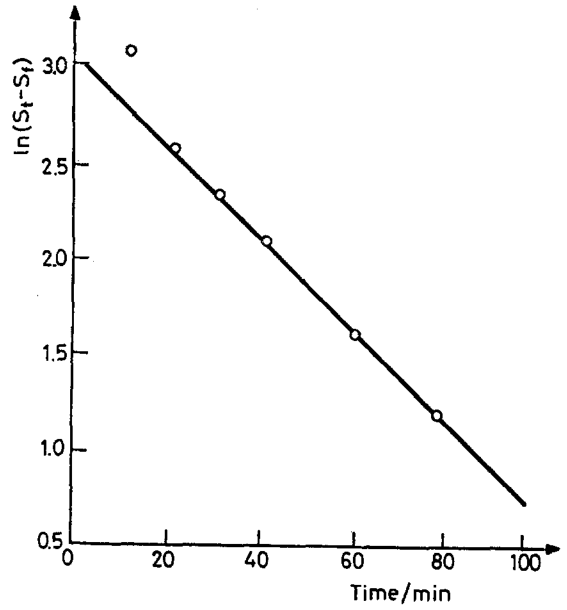

Fig. 3 Plot of ln $(S_t{-}S_f)$ against time for sintering of zinc oxide at 723 K in nitrogen

In studies on polymers and glasses a second order transition is observed called the glass-transition point (T_g point) below which the solid phase is brittle and above which it is plastic, rubbery or liquid like [18]. At first inspection any resemblance between the Tamman temperature and the glass transition temperature seems superficial. However the fact is that below the T_g point there is littel transitional motion of the polymer molecule or movement of the segments of the chain. Motion of the constituent atoms is seemingly restricted to movement of a very few atoms in the main chain or of side groups together with vibrational movement of atoms about an equilibrium position. Above the T_g point transitional motion of the entire molecule is possible with movement of segments of the chain to allow flexing and uncoiling [19]. When considered in this manner and on the basis of observed behavior a reasonable resemblance between the Tamman temperature and the glass-transition temperature is to be seen. Whether a solid material undergoing reaction is in a temperature region where surface or bulk diffusion is possible would seem to be a pertinent point to consider in terms of possible mechanisms.

Thermodynamic considerations

The thermodynamic consideration of solid state processes must take into account two factors:

1) The activity and that change is an any change is located at an interface and

2) The activity is conditioned by the pre-history of the solid phase.

The first point regarding the activity residing at the surface can be overcome by logically defining a dividing interface between two phases and then following the treatments outlined by Gibbs [20]. In the associated field of adsorption chemistry this leads naturally to the Gibbs Adsorption Equation and the developments originated by the Polanyi Treatment of Adsorption [21] and its most recent restatements [22]. In an overview of this nature one can only indicate the method of treatment but it is not the absolute answer for it ignores the second factor; namely the effect of prehistory.

The effect of the pre-history of the solid phase means that the sample material may be removed significantly from its equilibrium state. The lower the temperature the less is the rate of conversion to the thermodynamically stable phase and any study of geology indicates the existence of such 'metastable' forms, and that the rate of conversion is to all intents zero. Of course in many processes involving the solid phase the rate of conversion or reaction is significant and an end solid product can be the form stable at that temperature. In such instances the 'classical' thermodynamic treatment appears to fit usually with one exception, namely, that due to the location of the process at the reaction interface the reverse of the process may become impossible. Thus in the decomposition of calcium carbonate, the recarbonation of the oxide can be achieved but in the decomposition of magnesium carbonate the recarbonation of the oxide is very difficult and may be confined to the surface layers only.

One method of dealing with the difficulty of the 'pre-history' of a solid phase is to eliminate the history of the sample. This technique is practiced widely in polymer science and technology. The method is straightforward-simply take the sample temperature up to produce the liquid state and cool back down to the solid phase region. The history can then accurately be defined in the solid phase by controlling the rate of cooling. At one extreme, quenching preserves a glassy phase whilst annealing will produce a more crystalline form depending on the rate of cooling.

In spite of the points outlined above a surprising number of processes show an obedience to the form required by classical thermodynamics. This

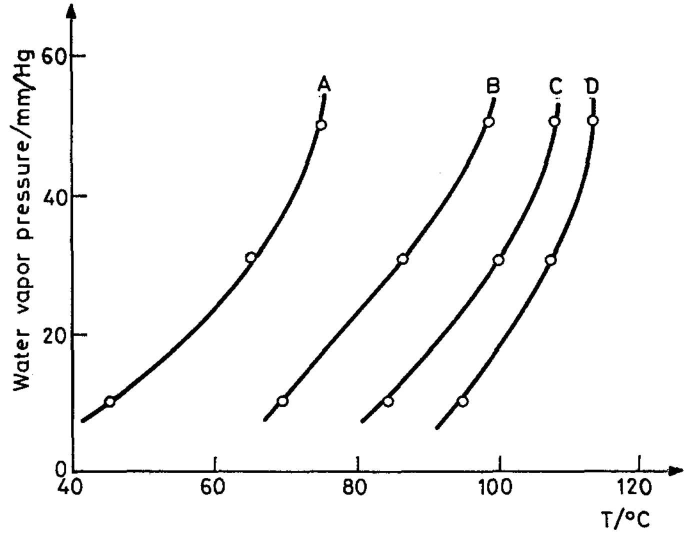

Fig. 4 Relationship between onset of peaks on DTA plots for
A. $Al_2(SO_4)_3 \cdot 16H_2O \rightarrow Al_2(SO_4)_3 \cdot 14H_2O + 2H_2O$
B. $Al_2(SO_4)_3 \cdot 14H_2O \rightarrow Al_2(SO_4)_3 \cdot 12H_2O + 2H_2O$
C. $Al_2(SO_4)_3 \cdot 12H_2O \rightarrow Al_2(SO_4)_3 \cdot 9H_2O + 3H_2O$
D. $Al_2(SO_4)_3 \cdot 9H_2O \rightarrow Al_2(SO_4)_3 \cdot 6H_2O + 3H_2O$

can be illustrated by reference to dehydration processes. In Fig. 4 the DTA, peak temperatures for the dehydration of $Al_2(SO_4)_3 \cdot 16H_2O$ are plotted for various pressures of water vapor above the sample [23]. These results can be expressed in the form;

$$\log P_{atm} = A + \frac{B}{T_p}$$

where P_{atm} represents the pressure in atmospheres of the product gas above the sample, T_p is the initial temperature of the peak as defined above for any particular dehydration stage and A and B are constants. Such plots were reported by Berg [24] for the complicated system arising during dehydration of $CoSO_4 \cdot 7H_2O$ (Fig. 5). This shows a non-linear relationship between $\log p$ and $1/T$ for many stages of dehydration and shows that in systems where dehydration produces liquid water the peak temperature is virtually constant with the vapor pressure of the product in the atmosphere. Three invariant points can also be discerned. The similar plots for dehydration of $CuSO_4 \cdot 5H_2O$ shown in Fig. 6 were also originally reported by Berg [25].

The above equations can be translated into the easily recognized forms:

$$\ln K\mathrm{p} = \frac{-\Delta H}{RT} + \mathrm{const}$$

or

$$\ln P\,\mathrm{g}_{\mathrm{atm}} = \frac{-\Delta H}{RT} + \mathrm{const}$$

where ΔH represents the standard heat of reaction.

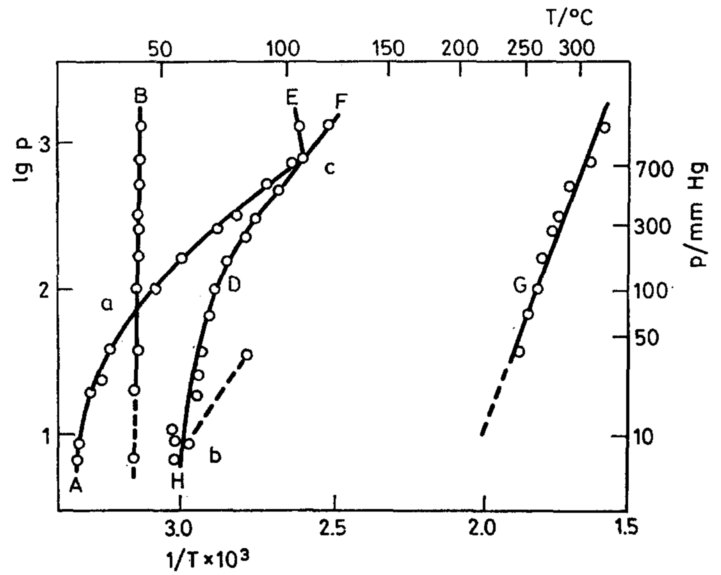

Fig. 5 Relationship between the water-vapor pressure P and the peak DTA temperature for the dehydration of $CoSO_4 \cdot 7H_2O$

A. $CoSO_4 \cdot 7H_2O \rightleftarrows CoSO_4 \cdot 6H_2O$ + vapor

B. $CoSO_4 \cdot 7H_2O \rightleftarrows CoSO_4 \cdot 6H_2O$ + solution (45°C)

C. Solution $\rightleftarrows CoSO_4 \cdot 6H_2O$ + vapor

D. $CoSO_4 \cdot 6H_2O \rightleftarrows CoSO_4 \cdot H_2O$ + vapor

E. $CoSO_4 \cdot 6H_2O \rightleftarrows CoSO_4 \cdot H_2O$ + solution (107°C)

F. Solution $\rightleftarrows CoSO_4 \cdot H_2O$ + vapor

G. $CoSO_4 \cdot H_2O \rightleftarrows CoSO_4$ + vapor

H. $CoSO_4 \cdot 6H_2O \rightleftarrows CoSO_4$ + vapor

Three invariant points:

a) $CoSO_4 \cdot 7H_2O + CoSO_4 \cdot 6H_2O$ + solution + vapor at T = 45°C, p = 65 mm Hg

b) $CoSO_4 \cdot 6H_2O + CoSO_4 \cdot H_2O + CoSO_4$ + vapor at T = 65°C, p = 12 mm Hg

c) $CoSO_4 \cdot 6H_2O + CoSO_4 \cdot H_2O$ + solution + vapor at T = 107°C, p = 690 mm Hg (Ref. 24)

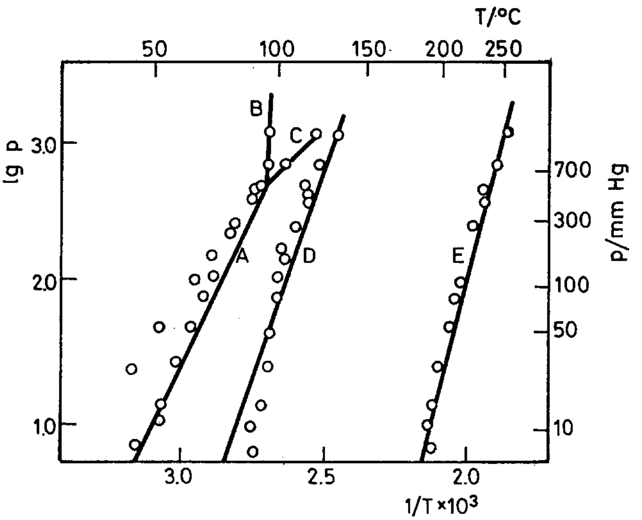

Fig. 6 Relationship between the water-vapor pressure P and the peak DTA temperature for the dehydration of $CuSO_4 \cdot 5H_2O$

A. $CuSO_4 \cdot 5H_2O \rightleftarrows CuSO_4 \cdot 3H_2O$ + vapor

B. $CuSO_4 \cdot 5H_2O \rightleftarrows CuSO_4 \cdot 3H_2O$ + solution

C. Solution $\rightleftarrows CuSO_4 \cdot 3H_2O$ + solution

D. $CuSO_4 \cdot 3H_2O \rightleftarrows CuSO_4 \cdot H_2O$ + vapor

E. $CuSO_4 \cdot H_2O \rightleftarrows CuSO_4$ + vapor

Invariant point

$CuSO_4 \cdot 5H_2O + CuSO_4 \cdot 3H_2O$ + soln + vapor at $T = 96°C, p = 540$ mm Hg

Ref. [25]

The use of commercial equipment for this kind of study is limited because the thermal analysis unit must be capable of being isolated to operate from vacuum to high pressures of product gas.

It must not be thought that investigations of this kind are only possible with thermal analysis techniques. If only one transition of the kind

$$A(s) \rightarrow B(s) + \text{Gas}$$

is involved there is hardly any advantage in employing a thermal analysis unit, one can easily arrange a manometer connected to the solid sample (A) held initially under vacuum and then plot the log of the equilibrium pressure against the reciprocal of the absolute temperature. There is some advantage in applying thermal analysis techniques such as DTA when the system shows multiple changes as in manganese oxides when the succession of oxide dissociations is:

$$MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$$

and there is also the possibility of solid phase transitions in each oxide system (for example Mn_2O_3 exists in at least two forms). Here the endothermic peaks due to the oxide (reversible) dissociations will all respond to the partial oxygen pressure and move to higher temperatures as the pressure of oxygen is increased while the solid-solid transitions will be invariant with respect to oxygen pressure. The availability of DTA response equipment located in pressure containers is a welcome addition to thermal analysis equipment but the increase in product gas pressure sends the DTA signal up to higher temperatures at present beyond the capabilities of the most normal commercial equipment. Nevertheless there are reports in the literature of data being collected by high pressure DTA techniques [26, 27].

Kinetic processes

In the study of solid-state kinetic processes the conventional method of study is to follow the isothermal decomposition of a material at a succession of temperatures, identify the reaction mechanism over the temperature range studied, and then determine the specific reaction rate at each temperature. One can then proceed to plot the Arrhenius parameters (the pre-exponential term A, and the Activation Energy E) from a plot of $\log k\ (T)$ *vs.* $1/(T)$ [where $k\ (T)$ is the specific reaction rate constant and T is the corresponding temperature of the isothermal experiment (in Kelvin)].

In the formulative years much attention was paid to the establishment of kinetic models and the consequent production of a mathematical relationship between the fraction decomposed (α) and the time of heat treatment [28]. Almost all these kinetic decomposition models were based upon the appearance of nuclei and the consequences of their subsequent growth through reaction interface advance. Since in many cases the nucleation process took place at the particle surface, subsequent growth reflected the geometry of a contracting area of interface often imposed by the original shape and surface of the decomposing particles [29]. Other studies mainly on materials of interest to ceramicists explored the additional process of diffusion of species away from or towards the controlling interface [30]. Certain specific mathematical relationships have become associated with particular models [31]. This is often a mistaken notion as the studies by Mampel [32], Erofeev [33] and Avrami [34] show quite clearly that the same model can give rise various mathematical relationships. However to demonstrate the point just, made Table 1 provides the form of the mathematical relationships for particular models.

Table 1 Mathematical models of reaction mechanisms

		$g(\alpha) = kt$	$f(\alpha) = 1/k\,(\mathrm{d}\alpha/\mathrm{d}t)$
1) Acceleratory α – time curves			
P1	Power law	$\alpha^{1/n}$	$n\,(\alpha)^{(n-1)/n}$
E1	Exponential law	$\ln \alpha$	α
2) Sigmoidal α – time 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 α – time 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	α^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	$[1/(1-\alpha)]^2$	$0.5(1-\alpha)^3$

Except in gasification processes the reaction interface is not the surface area. The point made above regarding the same kinetic model leading to different kinetic relationship can be demonstrated. In the simplest case the rate of decomposition per unit area of contact interface can be regarded as constant. The variation in rate of the overall reaction is then a consequence of variation in shape and size of the reaction interface area. Thus

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k\,R\,s\,(t)$$

where α 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, itself a function of time. The effect of particle shape can be judged by considering the decomposition of plate-like crystals. On the assumption that there is a constant rate per unit area and the contribution from the edges or sides are negligible then

$$\frac{d\alpha}{dt} = k \text{ or } \alpha = kt$$

This kind of zero order reaction is shown by clays [35] and silver mellitate [36]. In the case of carbon blacks however it is the edge atoms which react many times faster than the basal plane atoms in oxidation by air [37]. It can be shown that in this case as well the order is zero. Other kinds of zero order are based on different geometrical models e.g. dehydration of cobalt oxalate [38]. In the case of cylindrical shaped particles decomposing the normal contracting area 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 these cases as the particle size diminishes the model predicts first a zero order then a first order relationship followed by the contracting area or contracting volume equation. So we have different models giving the same equation and the same model gives perhaps two or three alternative expressions.

It seems probable that there is no such thing as a truly isothermal experiment. The exothermic or endothermic nature of the decomposition precludes this and in some experiments the resultant alteration in temperature of the experiment is such that it has to be taken into account. This would be one reason for the development of rising temperature methods. However the main reason is that it offers the lure of saving time in collecting kinetic data. Although much publicity has been given to the use of recognized thermal analysis techniques for this purpose almost any kinetic technique can be easily adapted to a rising temperature experiment. The main trouble is that the use of the integral kinetic equations poses problems because one is faced with the integration of the function

$$\int e^{-E/RT} dT$$

A further restriction on the use of rising temperature techniques has been the formal choice of the correct rate expression (Table 1) mechanism. The

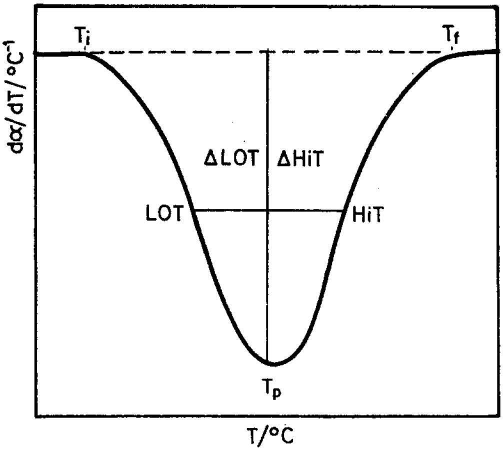

Fig. 7 DTG plot, T_i –onset temperature, T_f –final temperature, T_p –peak temperature *HiT* – *LOT* is the width of peak at half peak height. *ΔLOT* is T_p –*LOT*, and $\Delta HiT = HiT - T_p$ so that $\frac{\Delta HiT}{\Delta LOT}$ = assymetry factor

method selected in most commercial computer programs is to make an Arrhenius plot for each equation in turn and choose the best straight line. This is tedious and involves long computer programs. It is easier to inspect the differential plot of α-T data (see Fig. 7). Each rate equation gives a characteristic peak [39]. These can be judged by use of computer programs which will plot model α-T curve, where the mechanism, and both A and E are entered into the program. Extensive use of such data allows a preliminary identification of the kinetic expression [40]. In the $d\alpha/dT$ against T plot shown in Fig. 7, T_i represents the initial temperature or onset of the decomposition and T_f the final temperature, with T_p representing the peak temperature (rate maximum). If the vertical from T_p is drawn the width of the peak at half peak height can be drawn and the half peak temperature on the low temperature side designated as T_{LOT} and on the high temperature side as T_{HiT}. Now ΔHiT can be established and the asymmetry factor $\frac{\Delta HiT}{\Delta LOT}$ given. From these observations the facts regarding mechanism (referred to here by reference symbolized in Table 1), can be established, namely;

T_i and T_f sharp	Mechanism A2, A3, A4 (called here Group A)
T_i diffuse T_f sharp	Mechanism R2, R3, D1, D2, D3, D4 (called here Group B)

T_1 and T_f diffuse	Mechanism F1, F2, and F3 (called here Group C)

To proceed further we need data such as the value of α at the maximum rate (α max) and the 1/2 width (*HiT–LOT*).

Group A can be separated by noting the 1/2 width for A2 (14–320), A3 (12–22) and A4 (<10).

In Group B, the $\alpha_{\max}$ rate separated D1 (at $\alpha = 1$), D2 (at $\alpha = 0.790$–0.820), D3 and R3 together ($\alpha = 0.660 \sim 0.700$), D4 and R2 together ($\alpha = 0.720 \sim 0.760$). However the 1/2 width may separate D3 at 70–30, and R3 at 42–30 (there is some overlap here–see later). For the other two in Group B, D4 has a half width range of 38–80, and R2 a half width range of 24–34 which allows identification. In Group C the $\alpha_{\max}$ value allows easy identification of F1 (0.600–0.625), F2 (0.450–0.490) and F3 ($\approx$ 0.389). Any doubts as for D3 and R3 can be resolved by plotting the appropriate Arrhenius plot and noting the coefficient of determination (R^2). This approach is open to many modifications and allows many variations in use. The use of computers allows the easy development of the differential method of kinetic analysis and avoids the stumbling block caused by the difficulty of dealing with the integral term in the integral method. The details can be found in several publications, and is available as a computer program.

There is not space enough to deal with a further outlet of kinetic innovation–that of constant rate techniques innovated by Rouquerol [7]. This promises outstanding utilization in theory and practice. However ignored in many kinetic models is the simple fact that volume alteration in the solid reactant to solid product conversion can cause catastrophic alterations in particle size, which is reflected in measurements of surface area.

Surface texture and the active solid

The process of degradation on a solid state decomposition is to cause a strain to be set up within the solid system caused by stress, the applied force causing the strain. This stress is due to the alteration in volume (as evidenced by the different density of say a solid oxysalt and the product metal or oxide). The result is that the original particles may shatter during decomposition because the strain cannot be restrained in the solid structure beyond a certain value and often this is exceeded [41]. This is observed in practice as an increase in surface area during decomposition, the maximum surface area being attained at a value of α (the fraction decomposed) which does not correspond to complete decomposition. This should cause an abrupt alteration in the kinetic expression describing the decomposition [42]. There are studies in which this has been noted. Most kinetic studies ignore this effect of the fragmentation of particles. In the case of polymers where the existence of the reaction interface may be in doubt and in studies on decomposition above the Tamman temperature the materials are less rigid and this and the real possibility of diffusion processes occurring allows the product solid structure, to be formed with the dissipation of the strain. The alterations in the reaction interface has to be inferred from the kinetics. The process of activation can be followed from direct measurement of surface area. The effect is diminished by the ever present effect of sintering. It is a much more difficult task to relate the alterations in surface area with the kinetics. Nevertheless attempts have been made [43]. In summary let the surface area due to activation be denoted by S_a, then one can write,

$$S_a = k_1 \alpha$$

where α = fraction decomposed, k_1 is a constant.

In a typical case one may use a contracting sphere equation to describe the kinetics

$$1 - (1 - \alpha)^{1/2} = k_2t$$

or

$$\alpha = 1 - (1 - k_2t)^3$$

Substitute this into the equation for S_a gives:

$$S_a = k_1[1 - (1 - k_2t)^3] = k_1k_2t\,(3 - 3k_2t + k_2^2t^2)$$

This can be differentiated to give:

$$\frac{dS_a}{dt} = k_1k_2\,(3 - 6k_2t + 3k_2t^2) = 3k_1k_2\,(1 - k_2t)^2$$

The sintering process can be described by:

$$\frac{dS_s}{dt} = -k_4S$$

It is possible to apply this kind of treatment to alternative kinetic and sintering expressions [13, 14].

The overall rate of change of surface area is then,

$$\frac{ds}{dt} = 3k_1 k_2 (1 - k_2 t)^2 - k_4 S = A\,(1 - B\,t)^2 - C\,S$$

where A, B, and C are substituted for the various functions of k.

This can be rewritten as

$$\frac{dS}{dt} + C\,S = A\,(1 - B\,t)^2$$

After integration this gives;

$$S = A'[E - Ft + Gt^2] + \text{constant}$$

where A', E, F and G are substituted for various functions of k. Again there are various modifications of the above treatment depending on the alteration in surface area due to activation, or by sintering, or the kinetic expression. In the case of gasification reactions, such as:

$$C + O_2 \rightarrow CO_2 \text{ and } CO$$

the reaction interface may often be identified with the surface area [44].

Comments

It would seem that future developments in solid state decomposition should take note that activity resides at surfaces, the reaction interface and/or the surface area of the solid particles. This has an effect on both the attainment of a true equilibrium and the kinetics. Not enough attention is paid to what the kinetic expression implies in terms of a model. All kinetic expressions found should be substantiated by data indicating the extent of surface available and the texture and nature of the surface. A final controversial point which is worth making is that the kinetics derived from the rising temperature techniques should not necessarily coincide with those determined by classical isothermal experiments.

It can hardly be expected that the nucleation process or the growth rate of the interface should always be identical with those that exist over the temperature range covered in the classical set of isothermal experiments. However please note the conditional words in the above statement!

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Zusammenfassung — Die Herstellung eines aktiven Feststoffes durch thermische Zersetzung einiger Präkursorsubstanzen, meistens eines Oxysalzes, ist nur der eine Weg zur Herstellung solcher Substanzen. Die Aktivität der Feststoffe besteht an ihrer Oberfläche, obwohl sich ein Teil der Oberfläche auch im Innern oder bei Zersetzungsprozessen an der Reaktionsgrenzfläche befinden kann. Die eigentümliche Eigenschaft einiger Feststoffphasen besteht darin, daß man, um sie richtig beschreiben zu können, die Vorgeschichte der Substanz berücksichtigen muß und es kann gezeigt werden, daß die Vorgeschichte einer Substanz hauptsächlich die der Veränderung der Oberfläche und der Feinstruktur ist. Diese Tatsache beeinflußt die Anwendung von Thermodynamik und Reaktionskinetik bei Prozessen mit Feststoffen. Dies ist besonders bei aktiven Feststoffen offensichtlich, bei denen an oder in der Nähe der Oberfläche verhältnismäßig mehr chemische Stoffe vorkommen als üblicherweise. Dies wird durch die Existenz von vielen oder mehreren aktiven Feststoffen in einer amorphen Phase und durch die mögliche Koexistenz verschiedenartiger Festphasen bezeugt. In vorliegendem Überblick wird die Nützlichkeit der Strukturbestimmung normaler Feststoffphasen sowie die Art der möglichen Anwendung der Thermoanalyse bei der Bestimmung thermodynamischer und kinetischer Parameter diskutiert.