806. *The Production of Active Solids by Thermal Decomposition. Part I. Introduction.*

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If a solid B is prepared by a thermal decomposition of a solid A from which a volatile product is released, then the curve of specific surface against the temperature of calcination (for a fixed time) may assume one of at least four different forms: it may show a maximum, a continuous fall, or a continuous rise, or be more or less flat. The manner in which first, the physical structure, and secondly, the sintering, of B determines which of these forms of curve is pursued, is discussed in some detail.

Many solids are produced in an " active " condition if they are prepared by thermal decomposition from a parent substance A from which a volatile product is released: Solid A $\longrightarrow$ Solid B + Gas. Examples are provided by lime-burning, by the preparation of plaster of Paris, of active alumina by the heating of gibbsite, or of active magnesia by the calcination of magnesium hydroxide. The "activity," although difficult to define precisely, reveals itself in such properties as an enhanced rate of reaction of the solid with liquid reagents or with gases, an increased rate of dissolution in solvents, a marked adsorptive capacity for gases and for solutes from solution, an appreciable heat of immersion in inert liquids, and an increase in the heat of dissolution in, *e.g.*, acid, over and above that calculated from the normal heat of formation (cf. Fricke, Festskrift J.A. Hedvall, 1948). In general, two main factors are responsible for the phenomenon, *viz.*, the presence of an extensive "internal" area S in the solid, so that it is essentially porous on the microscopic and molecular scale; and the existence of lattice strain, so that some or all of the atoms or ions of the solid are displaced somewhat from the positions they would occupy in the perfect lattice (cf. Wood, *Nature*, 1948, **162**, 898). (The term " strain " would include Frenkel or Schottky defects, and dislocations, as special cases.)

Now the area S may, in general, arise in various ways: in dehydrated zeolites, for example, it is due to the large volume of channels, of molecular size, left by the escaping gas in a frame-work of the remaining solid—channels which permit the entry of molecules of adsorbate or of attacking reagent. More often, however, the existence of a large area S is due to the disperse state of the solid: it exists as crystallites, or micelles, of small dimensions. (The non-committal term " micelle " is to be preferred to " crystallite " in the present connection, to avoid the implication in the latter term that the lattice is perfect.) It is readily shown, for example, that if 1 cm.^{3} of a solid of density ρ is broken up into equal cubelets of side l, then the surface per g. of material is given by $S = 6/\rho l$. For less ideal cases—irregular shapes and varying sizes of particle—the increase in area, though quantitatively differently related to the mean linear dimension, is still of the same order. The area thus produced may still be termed an *internal* area, for the micelles will adhere in places to form the microscopic grains visible to the naked eye.

A solid will thus be rendered more active if the micellar size is reduced; and this will result from thermal decomposition of the type mentioned above if each crystallite of A gives rise on the average to, say, N micelles of B, where N is greater than unity. In principle there are at least two different ways in which this could come about: (i) each crystallite of A could contain N nuclei, each one of which would be the starting point of a decomposition interface, so that N micelles of B would form; or (ii) each crystallite of A could decompose as a whole giving a micelle having the composition of B but with the pseudo-lattice of A, the atoms or ions of B retaining much the same positions as they held in A. This pseudo-lattice would of course be highly strained and would tend to recrystallise into the stable form, *viz.*, the normal lattice of B (though no doubt still in a somewhat strained condition). This recrystallisation would, again, spread outwards from nuclei of B, so that the net result would be that each crystallite of A would give rise to N micelles of B, with a corresponding increase in the specific area.

Simple calculations based on the Polanyi–Wigner expression (*Z. physikal. Chem.*, 1928,

139, 439) suggest that mechanism (ii) is in general the more likely. According to this expression the number of molecules leaving 1 cm.^{2} of decomposition interface per second is $z = n\nu e^{-E/RT}$, where n is the number of molecules present per cm.^{2} of interface, ν the frequency of vibration of the linkage about to be broken, and E the energy of activation of the decomposition. Taking typical values, $\nu = 10^{13}$ sec.$^{-1}$, $E = 25{,}000$ cal. mole^{-1}, $n = 0{\cdot}5 \times 10^{15}$ cm.$^{-2}$, $T = 600°$ K, one obtains $z = ca.\ 8 \times 10^{18}$, and the interface thus advances through approximately $8 \times 10^{18}/10^{15}$ or 8×10^3 molecular layers in a second (cf. Gregg and Razouk, *J.*, 1949, S 36). A crystallite 10^4 Å across—the largest likely to be encountered—would thus decompose completely in some *ca.* 0·3 sec., once its decomposition had started at all. Now it is unlikely that the reaction would start to spread from a second nucleus in the same crystallite within 0·3 sec. of its starting from the first; and this suggests that crystallites will decompose " as a whole," *i.e.*, to give only one micelle each, under the usual conditions for the preparation of an active solid. [The Polanyi–Wigner expression represents the rate of decomposition *in vacuo* where the gas molecules can escape readily from the interface; " in air " the net rate of decomposition, though less by several-fold, will not be reduced sufficiently to invalidate the argument (Britton, Gregg, and Winsor, unpublished).]

An interesting confirmation of the " recrystallisation " mechanism is given in a later Part, devoted to the preparation of magnesium oxide from the hydroxide. At 400° C a sample of the solid continued to increase markedly in specific surface area when the amount of overall decomposition was almost constant (and nearly complete); the new area could not therefore have been brought into being by the formation of more magnesia, but must have owed its origin to some alteration in that already formed (cf. Wilsdorf and Haul, *Nature*, 1951, **167**, 945; Britton, Gregg, and Winsor, *J. Appl. Chem.*, 1952, **2**, 700).

The rate of crystallisation of the pseudo-lattice will depend on the rate r of formation of nuclei, and r in turn will depend on the energy change involved in the conversion from the pseudo-lattice of A into the normal lattice of B. In view of the essentially irreversible nature of the process, it is inappropriate to speak of a *free*-energy change, but one may expect some such expression as $r = \kappa e^{-\mathcal{E}/kT}$ to hold, where κ is a constant, and $\mathcal{E}$ is an energy quantity per molecule which is related to the difference in energy contents of the two forms in question. A crude measure of $\mathcal{E}$ would be the difference Δv in specific volumes between the two forms; the greater the value of Δv the greater would be the state of strain of the pseudo-lattice vis-à-vis the normal form, *i.e.*, the greater $\mathcal{E}$. The constant κ would be a function of the entropy difference between the two forms and again would be expected to increase as Δv increases. Thus the rate of nucleation of the pseudo-lattice, and with it the average number N of micelles formed from each crystallite of starting material, should increase as Δv increases.

As soon as the conversion of phase A into phase B is complete, so that each micelle of B is in contact with one or more other micelles of B, a process of *micellar growth* can take place and it will result in an increase in the average size of the micelles and a decrease in their number—a process that may conveniently be termed *sintering* if it occurs at elevated temperatures and ageing if it occurs at or near room temperature.

From its very nature, sintering is a rate process involving an energy barrier, so that the extent of sintering is a function of both temperature and time—an increase either in temperature for a fixed time, or in time for a fixed temperature, leading to an increase in the extent of sintering. The effect of an increase in temperature may be *qualitative* and not merely *quantitative* : it may alter the mechanism, as well as the extent, of the sintering, whereas the effect of increasing the time at a constant temperature will in general be merely quantitative, *i.e.*, it will increase the extent of whatever process is already occurring at the temperature.

It is not yet possible to give a completely definite picture of the mechanism of sintering, in spite of much work, both theoretical and practical (for many references, see Roberts, *Metallurgia*, 1950, August, p. 1). But it does seem clear that for comparison of different substances the temperature (°K) at which the substance is sintered should be expressed as α, given by $\alpha = T/T_m$ (T_m is the melting point of the substance in degrees absolute) (cf. Tammann, *Z. anorg. Chem.*, 1928, **176**, 46; Hüttig, *Kolloid-Z.*, 1942, **98**, 6, 263; 1942,

99, 262; Desch, *Trans. Faraday Soc.*, 1928, **24**, 57); and Hüttig's view (*loc. cit.*) seems reasonable, that there are three types of process to be considered, *viz.*, (*a*) adhesion, (*b*) surface diffusion, and (*c*) lattice diffusion, coming into play in that order as temperature increases. The last will only be important above the Tammann temperature ($\alpha = 0{\cdot}5$), for then the ions of the solid can move through the bulk of the micelle and into the areas of contact of neighbouring micelles; it should thus be possible for micelles to change their shape, to lose cracks and surface irregularities, for one micelle to grow at the expense of another, and for the area of contact of neighbouring micelles to increase, all processes leading to a reduction in specific surface; at the same time lattice strain would diminish. *Surface* diffusion involves the movement of ions of the solid along the surface of the micelles, *i.e.*, the surface layer is mobile. The general result would again be to tend to fill in surface irregularities of a given micelle, and to fill up cracks between neighbouring micelles, thus cementing them together and increasing the average micellar size. The process is likely to become important at lower temperatures than for lattice diffusion, and Hüttig gives the range $\alpha = 0{\cdot}33$—$0{\cdot}45$. The energies of activation of both (*b*) and (*c*) are high, of the order of some tens of thousands of calories per mole for typical cases, being lower for surface than for lattice diffusion (cf. Smoluchowski, " Imperfections in Nearly Perfect Crystals," ed. W. Shockley, Chapman and Hall, 1952, p. 467; Roberts, *loc. cit.*).

The first process, adhesion, should be capable of occurrence even at room temperature. It is brought about by surface forces, *i.e.*, by the reduction in surface energy consequent on the loss of surface area where the two particles join. It occurs at those places where the surfaces of neighbouring micelles are within atomic distance of each other; but the regions immediately adjacent to the area of contact are still within each other's range of attraction, and the forces between them are equivalent to a shearing stress exerted on the two micelles near the region of contact (cf. Bangham, *Trans. Soc. Glass Techn.*, 1947, **31**, 264). The effect is to deform the micelles, and so to increase the areas over which adhesion occurs. The process will go on until it is halted by unfavourable geometry, when surface irregularities are such that areas adjacent to the area of contact and belonging to neighbouring particles are outside the range of each other's attractive forces. Since a rise in temperature reduces the rigidity of solids (cf. Partington, " Advanced Treatise on Physical Chemistry," Longmans, Green and Co., London, 1952, **3**, 249), adhesion will be promoted by a rise in temperature. Quantitative relations cannot be formulated at present—the number of factors involved is far too large—but it should be noted that since the micelles of an active solid are strained, their rigidity will be much less, and their deformability correspondingly *greater*, than that of the normal solid; and also that the micelles are *small* and relatively close to one another owing to their mode of formation, features which again favour adhesion.

It is clear, then, that no sooner has the active solid been produced by thermal decomposition than it will begin to sinter at an appreciable rate unless it is cooled. Consequently, if the heating is continued beyond the time at which conversion of phase A into phase B is complete, then sintering will occur and the activity will begin to fall. Thus if experiments are conducted in which samples of the parent substance are heated separately at a succession of temperatures T_1, T_2, T_3, etc., for a fixed time t (a " calcination series "), then the activity of the product will rise with rising temperature as the proportion of A decomposed into B increases. The sample for which decomposition is just complete in time t will have especially high activity. Samples prepared at higher temperatures will be increasingly sintered, for they are now being subjected to increasingly long times of sintering at increasingly high temperatures: the time required for complete conversion into B becomes progressively shorter so that there is an increasingly wide margin for sintering. The curve of activity against temperature of heating should thus ideally show a maximum at or near the temperature for which the decomposition is just complete in time t; but in practice it is impossible to avoid some degree of sintering, for those parts of B which are first produced (*e.g.*, on the outside of lumps) will begin to sinter whilst the later parts of A are as yet undecomposed. It may therefore happen that the most active product is one in which decomposition is not quite complete and in which this concurrent sintering has been minimised.

Examples of a maximum activity of the kind just described are provided by the thermal decomposition of calcium carbonate, of magnesium carbonate (Britton, Gregg, and Winsor, *J. Appl. Chem.*, 1952, **2**, 693; Staley and Greenfeld, *Ind. Eng. Chem.*, 1949, **41**, 520), and of dolomite (Britton, Gregg, Winsor, and Willing, *loc. cit.*, p. 698); with all these the maximum in the curve of activity against temperature is fairly sharp, as well as with magnesium oxide prepared from precipitated hydroxide (Gregg and Packer, unpublished work).

In the thermal decomposition of gibbsite (γ-aluminium hydroxide), however, the maximum is rather flat: the surface area calculated from, *e.g.*, the nitrogen isotherms falls off gradually over the wide range of temperature from 400° to 1000° C (Gregg and Sing, *J. Phys. Coll. Chem.*, 1951, **55**, 603). This is probably connected with the complex nature of the decomposition, which results in a further activation over this range of temperature and thereby partly counteracts the normal sintering process. The precise details of the decomposition process are not yet entirely clear, but there is no doubt that the initial steep rise in activity between 300° and 400° C corresponds to the loss of water from the gibbsite (Gregg and Sing, *ibid.*, 1952, **56**, 388), which results in a mixture of boehmite (γ-AlO·OH) and an anhydrous alumina, probably χ-alumina (Clark and Elliott, *J.*, 1953, **84**; cf. Stumpf, Russell, Newsome, and Tucker, *Ind. Eng. Chem.*, 1950, **42**, 1938). [It is possible (Day and Hill, *Nature*, 1952, **170**, 539) that the latter is the primary product and that the boehmite is formed as a secondary product by reaction between the χ-alumina and the water released from the gibbsite.] By a somewhat complex series of polymorphic changes the χ-alumina and the boehmite decompose over the range 400—1000° C to give ultimately α-alumina. These further conversions could, in the light of the views outlined above, produce further activation and so tend to counteract the tendency to sinter.

A similar explanation has been offered for the maxima at *ca.* 180° and *ca.* 300° C respectively in the curve of specific surface against temperature of calcination for heated gypsum (Gregg and Willing, *J.*, 1951, 2916). The first maximum is believed to be associated with the activating effect of the loss of $2H_2O$, yielding an anhydrous product (say Z) having, however, the same lattice as the hemihydrate, and the sintering of Z. [The product Z has zeolitic properties so that it can lose all its water yet retain the same lattice (Bunn, *J. Sci. Instr.*, 1941, **18**, 70).] The second maximum is postulated to correspond with the activating effect of the conversion of Z into the anhydrite lattice, and the sintering of the latter.

If the quantity $\mathcal{E}$ were small enough, the recrystallisation process could occur with only one nucleus per micelle, so that each micelle of A would be converted into one only of B and no appreciable increase in specific area would occur (apart from a possible small increase if the volatile product left " holes " large enough to admit molecules or ions of adsorbate). An extreme case of this would be where the volatile product is merely adsorbed on the solid so that no change of phase occurs in the solid when the product is lost, and no recrystallisation is necessary. In cases of this kind it would not be possible to activate the solid appreciably by heating it, and any heat treatment would tend to reduce the activity by sintering. An example is provided by ferric oxide hydrate (see following paper); if high activity is required in this substance, it must be obtained by precipitating it in a highly disperse state from solution, and then avoiding subsequent heating; even 150° is sufficient to bring about a significant reduction in specific surface. Silica gel offers a second example (cf. Milligan and Bachford, *J. Phys. Coll. Chem.*, 1947, **51**, 330; Shapiro and Kolthoff, *J. Amer. Chem. Soc.*, 1950, **72**, 776).

A third type of behaviour occurs when the pseudo-lattice of A constitutes a stable framework so that it does not tend to recrystallise. The examples *par excellence* are the zeolites, which can lose and regain their " zeolitic " water without any modification of the aluminosilicate framework. The channels corresponding to the lost water are capable of adsorbing gases provided their molecules are small enough (see, *e.g.*, Barrer, *Proc. Roy. Soc.*, 1938, **167**, *A*, 392, 406; *Trans. Faraday Soc.*, 1944, **40**, 195, 555). With kaolinite (see Part III, *J.*, 1953, 3951) the water is all constitutional, *i.e.*, it is present as OH groups, and is not lost until a temperature of 400° or so is reached; the process is accordingly much more drastic than the loss of water from zeolites; consequently, it is not surprising that some collapse of the structure occurs. However, the area as measured by nitrogen sorption is only very slightly affected, indicating that the holes are too small to admit the gas, also that the grains do not break up into smaller grains or micelles; as might be expected, however, the holes *are* large enough to admit hydrogen ions, as is shown by the greatly enhanced rate of dissolution in acid, consequent on heating to 500°. It is interesting that the loss of area by sintering is quite small at all temperatures below 800° or so; this corresponds to the facts that the grains are relatively large (of the order of 10^4 Å or so in equivalent Stokes's diameter), and that they were originally discrete in contradistinction to the micelles of an ordinary active solid which by their mode of formation are in much more intimate contact. The specific surface of kaolinite is thus remarkably resistant to alteration by heat.

With vermiculite, a silicate mineral having a mica-like appearance, and some analogy to mica in structure, one meets a fourth type of behaviour on thermal decomposition. Water is progressively lost if the substance is heated to a succession of temperatures, and the surface area (measured by nitrogen sorption) likewise progressively increases. A large proportion of the water is probably present in this compound as molecules (cf. Barshad, *Amer. Min.*, 1949, **34**, 675) and when they escape the spaces left are large enough to accommodate molecules of a gas. If the material is " shock-heated " by sudden immersion in a furnace at 900°, the product is exfoliated vermiculite, which has a specific surface of some 10 $m.^2$ $g.^{-1}$ and is expanded some 20 times in a direction perpendicular to the cleavage plane; exfoliation is to be attributed to the mechanical action of the escaping gas, which is able to cleave the grain in a direction parallel to the cleavage plane, into a large number of plate-like micelles, loosely aggregated together. The process does not go as far as the complete separation into the individual aluminosilicate layers, however, for the specific area of the exfoliated material is only some one-fiftieth part of that which would correspond to the complete accessibility of both sides of every sheet.

This increase in area by the mechanical action of the escaping gas may occur in certain other systems also.

In the sintering of active solids a complicating factor is the presence of traces of the volatile product (say G) which are not driven off until temperatures some hundreds of degrees higher than the decomposition temperature are reached. Thus magnesia from pure magnesium hydroxide contains 0·3% of water after being heated to 700°, even though 98% of the " water " is lost at 400° (with 2 hours' heating). There is evidence that sometimes at least this persistent trace exists chemisorbed on the surface of the micelles, *e.g.*, as OH groups when $G = H_2O$ or as CO_3 groups when $G = CO_2$; when micellar surface is destroyed the chemisorbed layer is driven off from that portion of the surface. The chemisorbed layer is likely to be of particular importance in sintering mechanisms (*a*) and (*b*)

Foreign ions, whether introduced during the preparation of the starting substance or present as impurities in the starting materials, will introduce further complications. The effect is likely to be specific and may, in principle, either help or hinder the process of sintering, especially if the impurity is present on the surface of the micelles. If distributed throughout the body of the material, the foreign ions may exert some influence on the recrystallisation of the pseudo-lattice (notably through their effect on nucleus formation) but are not likely to influence sintering until the Tammann temperature is reached.

Conclusion.—When a solid B is produced from a parent solid A by a thermal decomposition which results in the release of a volatile product, there are at least four possible forms of the curve of specific area against temperature of calcination : (i) if B is initially formed as an unstable pseudo-lattice which rapidly recrystallises into the stable form, there will be a maximum in the curve; (ii) if B has the same lattice as A (*i.e.*, A is adsorbed or absorbed) the curve will show a continuous fall; (iii) if B has a fairly stable structure similar to that of A, the specific area will vary only slightly with the temperature of calcination; (iv) if molecular water is lost over a wide range of temperature from a framework or layer structure, the curve may show a continual rise over the corresponding range of temperature.

Detailed data illustrating these various kinds of behaviour will be presented in the subsequent Parts of this series.

UNIVERSITY COLLEGE, EXETER. [*Received, June 23rd,* 1953.]