324. *The Thermal Decomposition of Solids.*

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Solid reactions usually commence at nuclei which are formed on the corners, edges, and faces of the crystals. From these nuclei the reaction spreads into the surrounding material with a velocity of propagation which depends on the arrangement and orientation of the molecules in the space lattice. If there be any lack of symmetry, the speed may vary in different directions, as was found by Hume and Colvin for the loss of water from potassium hydrogen oxalate hemihydrate (*Proc. Roy. Soc.*, 1929, *A*, **125**, 635). In reversible changes, such as the decomposition of hydrates, the rate of propagation is retarded as the thickness of the decomposition product increases (Smith and Topley, *ibid.*, 1931, *A*, **134**, 224). Consequently, the rate of growth of a nucleus formed on the surface will be greatest in directions parallel to the surface. Thus the rate of growth even in isotropic material will not be the same in all directions. This complication will not arise in solid reactions which proceed irreversibly.

The simplest type of solid decomposition will therefore be one which occurs irreversibly in isotropic material, for in such a case the reaction would be expected to possess a uniform velocity in all directions, and provided that self-heating or -cooling be absent, the rate of reaction at any time will be proportional to the total area of the nuclei. In the initial stages of the reaction, before the nuclei begin to touch one another, the rate will be proportional to r^2, where r represents the root mean square of the radius of the nuclei, and hence, assuming a *linear rate* of propagation, proportional to t^2, where t represents the root mean square of the age of the nuclei. Observation of partly decomposed crystals shows that the nuclei are variable in size and increase in number with time, so that at any moment t will vary between 0 and some upper value. No direct measurements have been made of the rate of generation of nuclei in solid decomposition, and information which is obtained indirectly from measurements of the rate of reaction is not very conclusive. We know, however, that this rate must depend on the total number of potential nuclei and on their respective activation energies. The available places for nuclei formation diminish as the reaction proceeds, so that it would be expected that the rate of generation would decrease with time; although, if both the number of potential nuclei and the activation energy be large, it may happen that in favourable cases they will be formed at an approximately constant rate.

Assuming the limiting case where N_0 nuclei are produced in unit time, then the rate of reaction will be given by

$$dp/dt = k(1^2 + 2^2 + 3^2 \; . \; . \; . \; . \; . \; t^2) = \frac{k}{6}(2t^3 + 3t^2 + t)$$

Thus in the simplest type of change, the plot of log dp/dt against log t should give a curve, the tangents to which should approach $m = 3$ for large values of t. For the purposes of the following argument we shall consider the equation, $dp/dt = kt^m$, where m in the simplest case will vary with the time and attain its maximum value of 3 at infinity. If the speed of propagation varies in different directions, the values of m must be modified accordingly. In the extreme case for which the propagation is much more rapid in one direction than in any other, the rate of reaction becomes proportional to the time, and the maximum value of m becomes unity. Further, if N_0 decreases as the reaction proceeds, it becomes possible for m to be less than 1 and thus over the whole range of possibilities m should range between 0 and 3.

In the investigation of solids which decompose with liberation of heat, it has been shown that the above values of m may be very largely exceeded. For dehydrated crystals of barium azide (Harvey, *Trans. Faraday Soc.*, 1933, **29**, 653), m is approximately 10, and for mercury fulminate, as shown in the present paper, m may exceed 20. In such cases, therefore, it is clear that the assumptions made above are inadequate, because either (*a*) the rate of nucleus formation increases with time, which at present appears unlikely, or (*b*) in the early stages of the reaction, the propagation of the reaction from the nuclei is not uniform. Evidence in favour of (*b*) was obtained by Harvey (*loc. cit.*), who observed that the nuclei of metallic barium formed in crystals of barium azide were very irregular in shape. It thus appears that (*b*) is a probable cause of the deviations from the simple laws outlined above.*

In all the cases yet investigated, the acceleration of the reaction which occurs in the decomposition of solids obeys the equations,

$$(1)\ \log_e dp/dt = k_1 t + \text{const.}$$
$$(2)\ \log_e p = k_2 t + \text{const.}$$

in which k_1 and k_2 have the same numerical value. These equations hold for barium azide (Harvey, *loc. cit.*) and for lead azide, mercury fulminate, and lead styphnate (present communication). This behaviour is of interest in connection with the abnormal values of m given by the equation $dp/dt = kt^m$.

Equation (1) is that which applies to a reaction which follows a branching mechanism. Now it is known that the above decompositions do not follow a chain mechanism in the molecular sense, for interruption of the reaction for a time does not affect the reaction rate (Garner and Hailes, *Proc. Roy. Soc.*, 1933, *A*, **139**, 576; Farmer, J., 1922, **121**, 174). The

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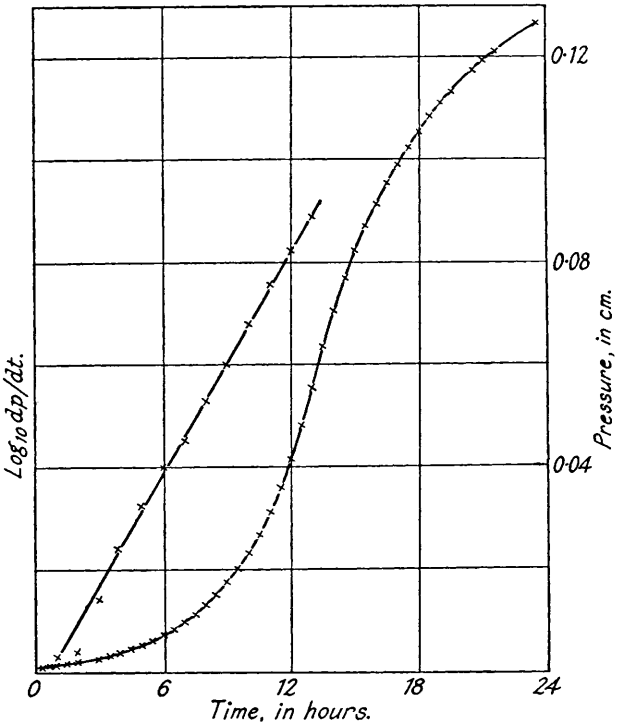
* It was shown in an earlier paper on mercury fulminate that self-heating of the crystal produces only second-order effects (Garner and Hailes, *Proc. Roy. Soc.*, 1933, *A*, **139**, 576), and therefore it follows that the anomaly cannot be due to this cause.

branching must therefore be concerned with the structure of the solid and be of such a nature as to be unaffected by cooling and subsequent reheating. It must also account for the non-uniform spread of the reaction throughout the crystal. A physical reason for non-uniform growth is to be found in lack of homogeneity of solids. Crystals possess a mosaic structure (Zwicky, *Proc. Nat. Acad. Sci.*, 1929, **15**, 253; Smekal, *Physikal. Z.*, 1925, **26**, 707; *Z. Physik*, 1927, **45**, 871), the components of the mosaic not possessing exactly the same alignment of the crystal axes. In the case of dehydrated solids, which are probably built up of a network of individual crystallites, the lack of continuity is particularly marked. If the progress of the reaction be checked at the boundaries forming the mosaic or at the surfaces of the individual crystallites, a non-uniform growth of the nuclei may be expected. In the extreme case, a reaction started by a nucleus may cease entirely when one crystallite has been consumed, in which case the reaction will follow a first-order law (Hume and Colvin, *Phil. Mag.*, 1929, **8**, 589). The reaction may, however, find suitable bridges whereby it can cross into a neighbouring crystallite. Provided the bridges be not too numerous, the propagation will partake of the nature of a chain mechanism (see later).



In the following discussion, experimental data, previously obtained, have been re-examined in order to throw light on these problems.

α-Lead Azide.—In an investigation into the thermal decomposition of lead azide (Garner and Gomm, J., 1931, 2123), crystals were heated in a hard vacuum, and the rate of liberation of nitrogen was measured. It was found that the decomposition commences on the surface and spreads inwards. On fracture, a partially decomposed crystal, 4 mg. in weight, shows a white core, the surfaces of which run parallel to the original crystalline faces. It was the object of this investigation to determine the critical increment of the reaction and in a few cases only was the reaction followed from the beginning to the end. In the results with single crystals, 2—4 mg. in weight, at 270°, the induction period was almost negligible and equations (1) and (2) could not be applied. For crystals of this size, the acceleration of the reaction rate is limited to the very early stages of the reaction. For smaller crystals, 0·025 cm. long and 0·0025 cm. wide, at 240°, pressure–time curves were obtained which show a definite induction period, during which equations (1) and (2) hold. A pressure–time curve for the smaller crystals is shown in the figure, together with the plot of $\log_{10} dp/dt$ against time. It will be observed from the figure that equation (1) holds up to the time of half decomposition, and in this respect, α-lead azide is similar to ground fulminate and lead styphnate. In Table I are given the coefficients k_1 and k_2, together with the values of n and m in the equations $dp/dt = kp^n$ and $dp/dt = kt^m$. The values of n verify equation (2). It will be seen that m lies between 1 and 3, which is in accord with the theory of uniform growth of the centres. The significance of this agreement can, however, only be understood when the results obtained with other solids are taken into account.

TABLE I.

k_1.	k_2.	n.	m.
0·35	0·34	0·91	1·14 (average)
0·21	0·19	0·97	1·38—2·67

Similar data were obtained for much smaller crystals of azide, but owing to the character of the induction period, the experimental error in the above constants was appreciably larger.

Mercury Fulminate.—Crystals of mercury fulminate go brown on heating and no reaction centres are visible under the microscope. The crystal is coloured throughout by the time it is one-fifth decomposed. The reaction is probably initiated along the internal surfaces separating the units of the mosaic structure (Garner and Hailes, *loc. cit.*). A very marked induction period is observed, after which an acceleration occurs which obeys equation (1). The rate of reaction during the period of acceleration, in a single crystal 2—4 mg. in weight, varies approximately as the tenth to the twentieth power of the time (Table II), which indicates a non-uniform growth of the reaction centres. Since equation (1) holds, it would appear that the non-uniform growth is due to a branching mechanism, which may be that of the transference of the reaction from one crystallite to another at certain points along their boundaries, although the explanation given previously (Garner and Hailes, *loc. cit.*) is not ruled out.

TABLE II.

Batch No.	Temp.	k_1.	k_2.	m.
I	100°	0·017	0·023	14·3
	105	0·032	0·028	13·5
	110	0·055	0·055	15·6
IV	100	0·022	0·025	14·9
	105	0·054	0·045	22·8
	109	0·076	0·074	22·3
	110	0·080	0·064	21·1
V	105	0·038	0·041	16·4
	108	0·061	0·071	18·1
II	105	0·023	0·030	11·2
IV. Crushed crystals	105	0·010	0·012	2·01
IV. Ground crystals	105	0·042	0·054	1·67
IV. Crushed crystals in hydrogen ...	105	0·012	0·014	4·29
IV. Ground crystals in hydrogen ...	105	0·035	0·024	1·33

* The plot of log dp/dt against t is slightly curved; the values of m given are average values.

Average values of k_1, k_2, and m are given in Table II; n in these experiments is approximately unity. It will be observed that k_1 and k_2 are practically identical. Where divergencies occur, these are in the main due to inaccuracies in k_2. These constants and m vary somewhat from one batch of crystals to another. Grinding and crushing the crystals do not markedly change the values of k_1 and k_2, the greatest effect being produced on crushing the crystal, the constants then being reduced to about one-quarter of their original value. m, on the other hand, is reduced from 14—20 to between 2 and 3, that is, to the limits expected for uniform spreading.

On grinding and crushing the crystals, there is a large increase in the rate of formation of nuclei (10^4 to 10^{10} times) and hence the reaction becomes measurable much earlier than in the case for a single crystal of the same weight. For a ground crystal, at 105°, the acceleration is evident within a few minutes, whereas for a whole crystal it becomes appreciable only after 350 minutes. Thus the value of m for crushed and ground crystals refers to a much earlier stage in the growth of the nuclei, that is, when the nuclei are very small. Large values of m are observed only when the nuclei have been growing for a long time. Therefore in the case of crystals of fulminate, m increases rapidly with t, in fact, much more rapidly than would be expected from the theory of uniform spreading.

The results obtained for fulminate are therefore consistent with the view that the centres of decomposition spread in a non-uniform manner.

Barium Azide.—Dehydrated crystals of BaN_6,H_2O were employed, so that there was a large internal surface on which centres of reaction could form. Consequently, nuclei of metallic barium were found both on the surface and in the interior of the crystals. These nuclei were irregular in shape. The initial stages of the reaction obey equations (1) and (2), and m is of the order 10 (Harvey, *loc. cit.*). The reaction occurs according to a branching mechanism and spreads from the nuclei in a non-uniform manner.

Lead Styphnate.—These were dehydrated crystals of $C_6H(NO_2)_3(OH)_2,PbO$ and hence possessed a large internal surface. No nuclei could be observed under the microscope, but it is very probable that reaction occurs throughout the mass as for barium azide. Values of k_1, k_2, and m are given in Table III. n is approximately unity.

The agreement between k_1 and k_2 is, on the whole, fairly good, but in some cases the slowness with which the water of crystallisation is removed from the salt renders these constants less accurate than is desirable. m is of the same order as that for crushed crystals of fulminate.

TABLE III.

Lead Styphnate.

Temp.	k_1.	k_2.	m.	Temp.	k_1.	k_2.	m.
225·0°	0·020	0·039	0·88	243·5°	0·237	0·278	3·15
231·5	0·083	0·094	2·38	246·0	0·290	0·253	1·65
232·5	0·076	0·087	2·95	246·5	0·223	0·198	2·62
235·0	0·124	0·117	—	248·0	0·352	0·347	3·00
238·0	0·216	0·184	—	250·0	0·439	0·347	4·43
241·5	0·242	0·246	2·44				

CONCLUSIONS.

The decomposition of the solids which have been investigated commences at nuclei which are formed either on the external or the internal surfaces of a crystal. It is suggested that the reaction spreads uniformly from these nuclei only within the individual grains composing the crystal, and that it is retarded at bounding surfaces. It spreads from grain to grain only at a few points on the boundaries, so that the outward growth from the centre is not uniform. Consequently, the rate of reaction in its early stages is governed by a branching mechanism, which can be formulated as follows. If N_0 be the number of nuclei formed per minute, and N be the number of crystallites attacked at a time t, then the rate at which new crystallites are attacked is given by

$$dN = (N_0 + kN)dt,$$

where k is the probability of the reaction passing from one grain to another. On integration is obtained

$$\log_e N_t = kt + N_0/k$$

and since dp/dt is proportional to N_t,

$$(1)\quad \log_e dp/dt = k_1t + \text{const.},$$

which is the equation which holds for the solid reactions studied.

The range over which equation (1) holds varies very much from one reaction to another. There are two principal causes operating in restricting its applicability. It must break down when the nuclei begin to touch one another, which cause is probably operating for small crystals of lead azide, for lead styphnate, and ground fulminate, where the equation holds up to the time of half decomposition. It should also break down when the nuclei have grown to a certain limiting size, for ultimately the nuclei will become approximately spherical in shape and the rate of reaction becomes proportional to the surface area. This is probably the cause of the breakdown in the cases of whole crystals of fulminate and barium azide where the equation holds only up to 1/10 to 1/5 of the total decomposition. From the results with fulminate (Garner and Hailes, *loc. cit.*, Fig. 5, p. 585) it is seen that the equation is obeyed at 105° for 450 minutes. By this time, the simple branching mechanism ceases to hold, on account of interference between the " chains." This stage is never reached for ground fulminate, where the number of nuclei is very large; the nuclei begin to touch before equation (1) ceases to apply to the branching mechanism.

The rate of reaction varies with the time to a power which lies between the limits 1 to 25. The value of this power varies with the substance studied and the size and age of the nuclei. It is at a maximum when the nuclei have reached a certain size.

It was observed previously that the final stages of the solid reactions obeyed the first-order law. According to the above hypothesis, towards the end of the reaction there will remain unchanged crystallites which have taken no part in the branching mechanism. Their decomposition ensues when new nuclei are formed on their surfaces. The probability of nuclear formation will be proportional to the surface area and, if the crystallites be of uniform size, proportional to their mass, which is the relationship which is found.

SUMMARY.

It is suggested that the nuclei formed in the decomposition of lead azide, barium azide, lead styphnate, and mercury fulminate do not increase in radius at a uniform rate. The non-uniform growth is ascribed to the occurrence of surfaces within the crystal boundaries, which check the spread of the reaction, causing the nuclei to grow according to a branching mechanism.

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