194. *The Thermal Decomposition of Silver Oxalate. Part II. Theoretical.*

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A MORE detailed analysis of the rate–time curves obtained during the decomposition of silver oxalate under various conditions (preceding paper) has now been made and theories are suggested as to the nature of the mechanisms which are believed to be taking part.

As the reaction is complex, it is not surprising that none of the simple equations suggested for such solid decompositions offers a complete explanation of the experimental results (see, *e.g.*, Lewis, *Z. physikal. Chem.*, 1905, **52**, 310; Centnerszwer and Bružs, *ibid.*, 1926, **119**, 405; Roginski and Schulz, *ibid.*, 1928, **138**, 21; Topley and Hume, *Proc. Roy. Soc.*, 1928, *A*, **120**, 211).

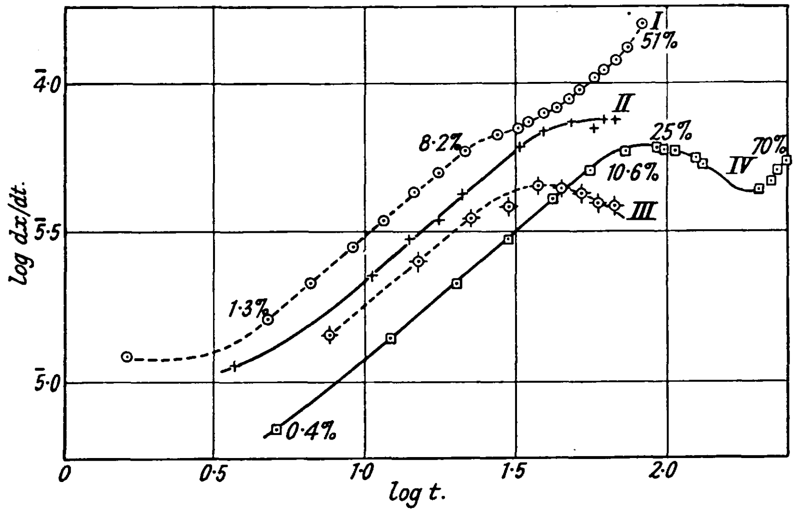
There appears to be no reason for departing from the hypothesis put forward by Macdonald and Hinshelwood (J., 1925, **127**, 2764), *viz.*, that the reaction is governed by the formation and growth, in the crystal, of nuclei of the reaction product. Quite apart from other considerations, this seems to be the only theory which is sufficiently adaptable to meet the necessary requirements. Since that theory was published, the spread of a reaction from small nuclei has been observed and photographed in several cases (Kohlschütter, *Kolloid-Z.*, 1927, **42**, 254; Coppock, Colvin, and Hume, *Trans. Faraday Soc.*, 1931, 27, 283; Garner and Southon, J., 1935, 1705). Topley and Hume (*loc. cit.*) were the first to deduce equations for this mechanism, taking two special cases: (i) where one nucleus was present on each crystal at the outset, and (ii) where the whole surface became rapidly covered with nuclei. Contributions on the same lines have been made by others, notably Garner and his co-workers (J., 1930, 47; 1931, 2123; 1933, 1393, 1398; 1934, 720; *Proc. Roy. Soc.*, 1933, *A*, **139**, 576). There seems to be little doubt that most non-explosive solid decompositions follow some modification of this mechanism, and are therefore essentially autocatalytic, proceeding at the interface between the original solid and the product of the reaction. Obviously, as the nuclei increase in size and number, so, in general, will the area of the interface increase, and with it the rate of reaction. When a certain fraction of the compound, which seldom greatly exceeds 50%, has decomposed, the growing nuclei interfere with one another, and the regions where decomposition first began become exhausted. The rate of the reaction will therefore pass through a maximum and finally fall to zero. It will be seen that the hypothesis gives a good qualitative description of the results reported in the previous paper.

A more detailed examination of the curves obtained in this and certain analogous decompositions, however, reveals a serious difficulty, *viz.*, that in many cases the decomposition follows an exponential law up to the maximum rate (with which portion of the curve alone this paper is concerned). Now, on the simplest hypothesis, which is that the linear rate of propagation of the reaction is constant and that the reaction spreads in all three dimensions so that the growing nucleus assumes a solid form, no such exponential equation can be deduced. The course actually followed is reminiscent of the familiar "branching chain" mechanism (see Semenoff, "Chain Reactions"), and Garner (*loc. cit.*) has investigated the possibility of the formation of linear chains of molecules, and of chains of crystallites, each of which decomposes rapidly compared with the time taken for the reaction to spread from one to another. In the present instance, it has been shown (Part I) that the reaction does not spread from one crystallite to another, and the cause of the exponential term must be sought in the decomposition of the individual crystallites. Let us examine, therefore, as simply as possible, the various ways in which a single crystallite may decompose, on the assumption that the number of nuclei on each is not very great. We may conveniently divide the possibilities into three groups, according to the "shape" which the nucleus assumes on growth.

The first is that in which the reaction tends to proceed in the form of linear chains, *i.e.*, each nucleus grows in one dimension only. There are here three possibilities. (*a*) The reaction proceeds solely from the n nuclei present initially. If K be the rate of linear advance of the reaction, the total rate of reaction will be constant ($= Kn$). This mechanism can only account for the decomposition of a very small fraction of the crystal, *viz.*, $n/$(the number of molecules on one crystal face). (*b*) Fresh nuclei may be formed spontaneously. In the simplest case these would be formed at a rate proportional to the area of the undecomposed oxalate, and at the outset of the reaction this would be virtually constant. The total rate of reaction would then be proportional to t, so long as the first chains to be formed were still active. This mechanism may be combined with (*a*) to give an equation of the type $dx/dt = Kn + K't$. (*c*) The chains may branch in the crystal. As we have seen, the reaction will then follow an exponential law.

In the second group, the reaction is to be considered as spreading in two dimensions along the planes of the crystal; *i.e.*, the nuclei grow in the form of thin plates. Such nuclei have recently been observed by Garner and Southon (*loc. cit.*). They may, within limits, be of any thickness, but we shall consider only the simplest case, *viz.*, that the layer has a depth of only two atoms of silver, this being the product of the decomposition of one molecule of oxalate. It is found that, if the reaction proceeds entirely from the nuclei originally present, the rate will be proportional to the circumference of the plates, *i.e.*, to the first power of t, and that this mechanism can account for the decomposition of a fraction of the whole equal to $n/$(the number of molecules on one crystal edge), *viz.*, the fraction of the total number of planes which possess nuclei. The spontaneous generation of nuclei will now give a rate of reaction which, in the simplest case, is proportional to the second power of t, and again, branching of the planes may take place, giving, as before, an exponential equation. It is to be expected that in the later stages of the reaction the rate will fall somewhat below the theoretical, on account of interference between the planes.

FIG. 1.



Curve I.—Spec. S, in Gelatin, 131°. *Curve II.—G, in vac.,* 131° (*nitrate excess*).
Curve III.—F, in air, 131°. *Curve IV.—B, exposed to light,* 110° (*in vac.*).

In the third group, the reaction spreads in three dimensions, though not necessarily at an equal rate along each. There are here only two possibilities: that the reaction proceeds from a fixed number of nuclei, or that the nuclei are generated spontaneously. This is the type of reaction considered by Topley and Hume (*loc. cit.*) and by Benton and Cunningham (*J. Amer. Chem. Soc.*, 1935, **57**, 2227). The reaction will be proportional to the second or third power of t according to whether fresh nuclei are formed or not, and again, the rate will tend to fall below the theoretical as the decomposition proceeds. It has already been noted that branching, and therefore an exponential type of equation, cannot occur in this case.

It is clear that the above considerations will be valid only for a time equal to that taken by a single nucleus to complete its decomposition.

The experimental results may be tested in the light of the foregoing discussion by plotting log dx/dt against log t (dx/dt being the observed rate of reaction). In every case except where branching occurs, a straight line should be obtained from which the constants of the equation

$$dx/dt = kt^m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

can be read off.

Process I.—It was shown in Part I that at least three different mechanisms are required to determine the complete decomposition. One of these, Process I, normally accounts for only about 3% of the reaction. This amount, however, can be increased by just those manipulations (grinding and exposure to light) which may be expected to lead to an increase in the number of nuclei. It can be isolated from Process II in a number of ways.

In Fig. 1, log dx/dt is plotted against log t for four experiments in which Process I predominates. In Curves I, II, and III, Process II has been suppressed by gelatin, by ionic adsorption, and by air, respectively, while in Curve IV, Process I has been greatly stimulated by exposing the sample to ultra-violet light. It will be seen that a good straight line is obtained over a fair range, and that the slope of the line is approximately equal to unity. Table I gives a complete list of the values of m found in all experiments in which Process I is expected to predominate. The values in parentheses indicate either that few observations were obtained over the significant portion of the curve or that the points do not fall very close to a straight line. Such values have been given half weight in the mean, which was found to be 1·05 ± 0·03. The closeness of this value to a whole number is doubtless partly accidental. As has been explained, one would expect the experimental value of m to fall somewhat below the theoretical value. On the other hand, in many of the experiments quoted, Process II has not been completely suppressed, and this would tend to raise the value again, thus counterbalancing the previous error. There seems little doubt, however, that the fundamental equation of Process I is

$$dx/dt = kt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

TABLE I.

Expt.	Method.	Temp.	m.	$10^8\,k_1$.	$10^8\,k_2$.	$10^4\,C$.
B 16	(p)	100°	(1·25)	0·25	4·45	0·845
B 6	(p)	110	(1·00)	5·75	57·5	3·40
B 9	(p)	110	(1·20)	1·91	30·3	2·08
B 10	(p)	110	(1·07)	4·57	53·8	3·04
B 8	(v), (i)	110	0·83	182	1230	22·7
R 1	(p)	110	(1·00)	3·6	36·0	2·69
F 8	(v)	110	(1·15)	3·47	49·0	2·69
G 5	(p)	110	(1·26)	0·71	12·9	1·36
G 6	(p)	110	(0·97)	3·55	33·1	2·66
G 3	(v)	110	1·32	0·72	15·1	1·40
G 4	(v)	110	1·30	0·83	16·5	1·45
B 11	(p)	120	1·34	15·9	348	5·32
B 12	(p)	120	1·10	31·6	400	7·94
B 14	(oil)	120	(1·31)	13·8	282	5·00
B 19	(p), (i)	120	1·07	93·3	1090	13·05
B 15	(p)	130	1·00	229	2290	21·41
F 1	(v)	131	1·32	219	4580	16·41
F 2	(air)	132	0·82	282	1860	29·11
G 2	(v)	131	0·79	363	2240	34·83
I 1	(v)	132	(1·00)	135	1350	16·48
S 1	(g)	131·2	0·84	444	3070	32·06
S 2	(g)	131·2	0·73	740	4080	57·28
H 1	(v)	131	(1·15)	490	6910	27·42
J 1	(v)	130	0·87	3·6	26·7	2·66

Mean value of m = 1·05 ± 0·035.

(p) in paraffin; (v) in a vacuum; (g) gelatin emulsion; (i) irradiated by ultra-violet light.

This conclusion seems to be in agreement with the experiments of Benton and Cunningham (*loc. cit.*), who, studying the effect of light on a specimen of silver oxalate prepared with a small excess of sodium oxalate, found that exposure to light increased the value of

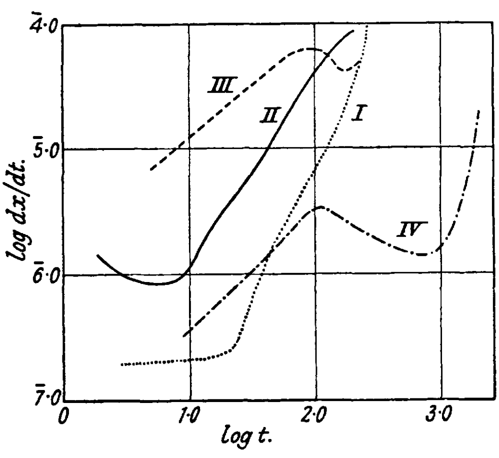
k and decreased that of m [equation (1)], values as low as 0·4 being obtained with prolonged exposure. Their results and those of the present author both seem to be more in accord with equation (2) than with their equation, in which m, in the ideal case, would have the value 2 (see also Fig. 2).

On the assumptions which have been made, equation (2) could result only from one of two mechanisms : a linear chain reaction with the spontaneous generation of fresh chains, or a reaction which spreads in two dimensions from a fixed number of nuclei. It has been clearly demonstrated, however, that Process I is dependent on the presence of nuclei at the start. It would seem, therefore, to consist in the growth of planes of silver atoms through the lattice of the crystal, each plane starting from a point on the surface. It has already been noted that such a mechanism can account for the decomposition of only a small fraction of the compound, a conclusion which is in complete accord with experiment.

If this theory is correct, the value of k should give a measure of the number of nuclei present at the outset, provided that the rate of forward propagation of the reaction through the crystal is always the same at any temperature. Thus if the nuclei predominate at the edges of the crystals, the length of each advancing line will be that of one-quarter of the circumference of a circle of radius Kt, and the total rate of reaction will be $\frac{1}{2}\pi nK^2t$, whence $k = \frac{1}{2}\pi nK^2$.

In Table I, cols. 5 and 6, are given the values of k_1 and k_2, the rates at 1 min. and at 10 mins. respectively, as read off the graph of log dx/dt against log t. Of these, k_2 (= $600k$, if t is expressed in seconds) is probably the more accurate measure of k, since it avoids the extrapolation necessary for the determination of k_1 (which thus reflects any error in m). It will be seen that k_2 exhibits a greater constancy than k_1, that for normal experiments k is always of the same order of magnitude, but that it is greatly increased by irradiation with ultra-violet light, and that the differences between specimens are of the same order as those between different samples of the same specimen. This supports the view that nucleation is rather easily influenced by accidental factors, but that it cannot be entirely eliminated by the normal methods of working. The abnormally low value of k for specimen J, which was precipitated in the presence of sulphuric acid, indicates a method by which specimens resistant to nucleation may be prepared.

FIG. 2.



Showing how grinding (Curve II) and exposure to light (Curve III) increase the value of k *and decrease that of* m *as compared with a normal specimen (Curve I). Curve IV, the decomposition under paraffin of a specimen worked entirely in the dark, shows that in this case* m *is decreased without any corresponding increase in* k.

The Energy of Activation of Process I.—The temperature coefficient of the primary reaction, and hence the energy of activation, may be determined in a number of ways. The most direct method is that of Topley and Hume (*loc. cit.*), in which the temperature is altered rapidly to a new value in the course of an experiment. The number of nuclei and the total interfacial area are the same immediately before and after the alteration, as is shown by the return of the rate of decomposition to the normal value on restoring the original temperature. The ratio of the rates at the two temperatures is thus the ratio of the rates of forward propagation of the reaction. The method is not particularly accurate unless the rate of reaction is constant over the time of the experiment, but it serves as a useful check on the other methods. A single determination between 130·5° and 136° gave a value of E = 38,500 cals., whereas the average of three determinations by Benton and Cunningham between 117° and 100° gives E = 25,400 cals. (These workers calculate a value of 8,500 cals. from the same data, but this seems to be due to a misunderstanding of the principle of the method.)

The energy of activation may also be calculated from the data in Table I, and by two methods, if it be assumed that the initial number of nuclei is independent of temperature. In the first method the rates are compared at such times that equal fractions of the oxalate (x) have decomposed, so that the total area of the advancing interface is the same in all cases. The required factor is obtained by integrating equation (1) :

$$x = kt^{(m+1)}/(m + 1) + \text{constant}.$$

The constant disappears if we assume that the true initial rate is vanishingly small, whence

$$t_x = [x(m + 1)/k]^{1/(m+1)}$$

and $$(dx/dt)_x = kt_x^{\,m} = [kx^m(m + 1)^m]^{1/(m+1)}$$

The values of $C = [k_1(m + 1)^m]^{1/(m+1)}$ are given in the last column of Table I. By taking all the values for normal experiments, and treating the variations as random errors, it is found that $E = 35{,}6000 \pm 1{,}610$ cals.

The second method is to put $k_2 = 300\pi n K^2$ in accordance with the theory outlined in the preceding section, whence $K \propto \sqrt{k_2}$. This is equivalent to assuming that the individual values of m are slightly in error, and should really equal unity. It gives $E = 32{,}700 \pm 1{,}160$ cals., which is probably the most accurate of the values, and its agreement with the other determinations is strong evidence in favour of the assumptions on which it is based. It is equivalent to a temperature coefficient of about 3·2 for 10°.

It is noteworthy that mercury fulminate, which decomposes at a comparable rate at the same temperature, has an energy of activation of 30,000 cals. (Garner and Hailes, *loc. cit.*).

Process II.—When we examine the decompositions in a vacuum of the specimens which are not retarded by ionic adsorption, and also the later portions of the experiments which are conducted under paraffin or in gelatin, we find that equation (2) no longer holds, but that the value of m increases with time up to a high figure. This is shown by the curve for specimen B (Curve I, Fig. 2), which is typical of many runs. The phenomenon is independent of temperature, and the curves at different temperatures can be derived from one another by altering the origin 0·5 logarithmic unit along both axes for each 10°, corresponding to a coefficient of 3·2. The shape of the upper portion of this curve suggests that the equation is now of an exponential type, *viz.*,

$$dx/dt = ae^{pt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The curve for the second acceleration in paraffin is approximately parallel to the corresponding portion of the decomposition in a vacuum (Curve IV, Fig. 2).

TABLE II.

		$p \times 10^4$.							
Specimen.	log [NO_3'].	96°.	100°.	106°.	110°.	117°.	120°.	131°.	Temp. coeff.
Am. (2)	—	—	—	—	—	—	—	71·9	—
O	−2·607	—	—	—	3·54	—	—	—	—
Q	−2·607	—	—	—	3·26	—	—	30·3	2·93
B	−2·041	—	1·07	—	2·82	—	6·35	27·4	2·75
P	−2·022	—	—	—	3·10	—	—	31·8	2·92
A	−1·744	—	—	1·22	2·15	—	—	21·6	2·97
C	−1·701	0·246	—	0·72	1·90	3·73	—	15·2	3·27
D	−1·699	—	—	—	2·22	—	—	—	—
E	−1·695	—	—	—	1·22	—	—	—	—
F	−1·041	—	—	—	1·88	—	—	13·3	2·54
S 1 (in gelatin)	—	—	—	—	—	—	—	2·6	—
B (in paraffin)	—	—	—	—	0·612	—	—	—	—

Mean 2·90 ± 0·23

Plots of log dx/dt against t show that, although the reaction is somewhat more complex than represented above, a sufficiently close approximation to a straight line is obtained over such a considerable period as to suggest that equation (3) represents a fundamental mechan-

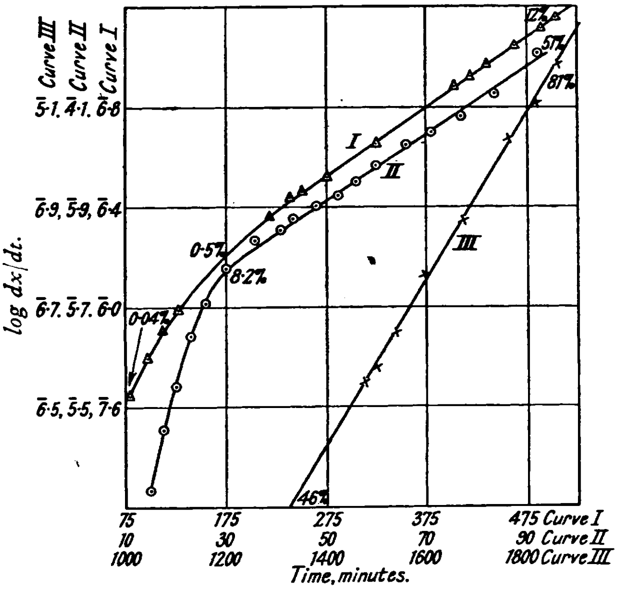
TABLE III.

Specimen.	$a \times 10^6$. 100°.	110°.	117°.	120°.	131°.	Temp. coeff.
Am (2)	—	—	—	—	16·4	—
O	—	1·89	—	—	—	—
Q	—	1·11	—	—	13·92	3·03
B	0·56	1·29	—	4·46	12·74	2·76
P	—	1·14	—	—	14·96	3·50
A	—	1·79	—	—	18·5	2·89
C	—	1·62	4·30	—	19·3	3·25
D	—	1·71	—	—	—	—
E	—	1·25	—	—	—	—
F	—	2·11	—	—	25·6	3·28
S 1 (in gelatin)	—	—	—	—	42·9	—
B (in paraffin)	—	0·149	—	—	—	—
						Mean 3·12 ± 0·24

ism of the reaction. The constants of this equation are given in Tables II and III, and examples of three experiments in Fig. 3.

This exponential equation indicates a mechanism quite different from the one discussed in the previous section. There seem to be but two possibilities—either that it is due to self-heating, the rate of evolution of heat being greater than the rate at which it can be conducted away, or that new nuclei are being formed at a rate which is a function of the rate of decomposition or of the amount of reaction which has already taken place. The first of these explanations is ruled out by the observation that the effect is independent of temperature, and by the fact that it appears in the decompositions in paraffin and in gelatin, where the heat generated can readily be conducted away (Fig. 3). It can be calculated, however, following the method of Garner and Hailes (*loc. cit.*), that self-heating may occur at the highest temperatures used, especially in the case of the more unstable specimens. This adequately explains an upward curvature in the plot of log dx/dt against t which is sometimes found in such cases, and care has been taken, in measuring the constants of Table II and III, to omit that portion of the curve where self-heating may be expected.

FIG. 3.



Curve I.—B 17, 100° *in a vacuum.*
Curve II.—S 1, 132° *in gelatin.*
Curve III.—B 6, 110° *in paraffin.*

The exponential character of this process seems, therefore, to be due to the formation of fresh nuclei, at a rate which is a function of the rate of decomposition. Now we have seen that the nuclei tend to grow in two dimensions, and that if such planes of reaction branch, the reaction will follow an exponential law. This is clearly the mechanism of Process II. We must therefore suppose that, at certain points on the decomposing planes, fresh planes of reaction start. That the points where branching occurs are confined to the surface of the crystal seems to be shown by the sensitiveness of Process II to external influences, such as the presence of air, of paraffin, and of adsorbed ions. Further, since the molecules in the front line of the advance will be "hotter" than those immediately behind them, branching is most likely to occur at the point where this advancing line cuts the surface of the crystal. The rate of formation of fresh planes (dN/dt) will thus be proportional to the number of planes (N) in an active state, or $N = ne^{pt}$, where n is the number of nuclei at the outset of the reaction and p is the number of times a single plane of reaction divides per second.

Now if N' be the number of active nuclei at time τ, then the number of *new* nuclei formed between τ and $(\tau + d\tau)$ will be $pN' . d\tau = pne^{p\tau} . d\tau$. At time t, these will have been growing for $(t - \tau)$ seconds, and the sum of the lengths of the active boundaries of these nuclei will be

$$dr = \tfrac{1}{2}\pi K(t - \tau)pne^{p\tau} . d\tau$$

Integrating for all values between $\tau = 0$ and $\tau = t$, we find

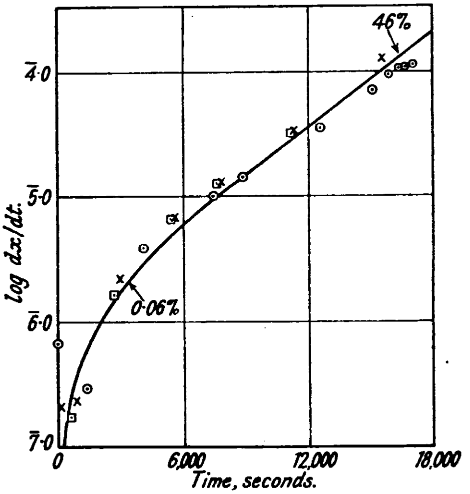
$$r = \tfrac{1}{2}\pi Kn[e^{pt} - (pt + 1)]/p$$

This gives the total interface due to nuclei formed since the beginning of the reaction. Adding to this the interfaces of the nuclei present at the outset ($\tfrac{1}{2}\pi Knt$) and multiplying by K, we find the measured rate of reaction

$$dx/dt = \tfrac{1}{2}\pi K^2n(e^{pt} - 1)/p \quad . \quad . \quad (4)$$

which is the required equation.

Fig. 4.



Showing three runs with specimen B in a vacuum at 110° compared with the theoretical equation. The line is drawn to the equation $dx/dt = 1{\cdot}29 \times 10^{-6}\, e^{0{\cdot}000107t}$.

□ *Expt.* B 3. × *Expt.* B 4. ○ *Expt.* B 5.

Attention should be directed to several points in connection with this equation. (i) It is based on the assumption that all planes of reaction product are actively growing at time t, and it will only hold good so long as the number of active planes is greatly in excess of those which have run their course. In practice, it holds well for the vacuum decomposition of specimens prepared with excess sodium oxalate, so long as these have not been greatly nucleated by artificial means. An example of the manner in which it can reproduce the experimental results is given in Fig. 4, in which the constants used are those found in Tables II and III, *i.e.*, the slope and intercept of the later portion of the curve. (ii) When the product pt is large, *i.e.*, in the later stages of the more strongly accelerating specimens, the equation approximates to equation (3). (iii) When pt is small, e^{pt} may be written $1 + pt$, and the equation reduces to equation (2), which, therefore, describes the decomposition of those preparations in which the rate of branching of the planes is small, as well as the early stages of all decompositions. (iv) The values of p (Table II) are roughly inversely proportional to the logarithm of the nitrate-ion concentration; *i.e.*, the rate of branching is dependent on the ionic condition of the surface. (v) The inverse proportionality which should exist between a (Table III) and p is largely obscured by the fact that, as can be seen from Table I, the values of n vary considerably from one sample to another. [a in equation (3) is equivalent to the term $\tfrac{1}{2}\pi K^2n/p$ of equation (4).] (vi) The temperature coefficient of p is not greater than that of a (and therefore than that of K). Now p is the rate of branching of the planes, and K is their linear rate of advance. The total number of divisions undergone by one plane in the course of its complete decomposition will therefore be proportional to p/K. Since this is almost independent of temperature, the extra energy required to start a fresh plane must be small, and division must take place whenever a suitable "bridge" is encountered.

These bridges may be permanent, and in the nature of surface discontinuities on the crystal. It seems more likely, however, that they consist of periodically recurring phase relationships between the atoms. It should be noted that the heat of reaction (29,150 cals.) is almost equal to the energy of activation. Reaction will take place if this heat be communicated to a neighbouring molecule at the moment when it is passing through its phase of minimum stability. The chance of branching taking place will therefore depend on the chance of such an energy transference taking place before the heat of reaction is dissipated in other directions. This, in turn, will depend on the presence, on the surface, of other molecules which may absorb the energy, such as nitrate ions and paraffin.

Process III.—Without some modification, the mechanism outlined above will not suffice to account for the results obtained under paraffin. First, it offers no explanation of the fall in velocity following the first maximum in the curve; and secondly, it is clear that as the total time of the reaction is much increased, it will no longer approximate to the time of decomposition of a single plane, so that the number of active planes will be only a small fraction of the total number of planes. These difficulties disappear if we assume that, in general, a plane may branch at any point along its edge. This is equivalent to assuming that nuclei may be formed spontaneously at the edges of the newly formed crystal blocks. As the reaction proceeds, these blocks become smaller, and the length of edge correspondingly greater. Thus the opportunity for the generation of fresh nuclei will increase with time. It must be supposed that this mechanism is active in the vacuum decompositions also, but that it is negligibly slow as compared with Process II. As explained above, the effect of paraffin is to remove the excess energy from the molecule in the front of the advancing plane, so that the leader behaves in no way differently from those behind.

In order to find the equation for this mechanism, it seems to be necessary to assume that the time of decomposition of a single plane is negligibly small compared with the total time of the reaction. Now, the first maximum in the curve is probably caused by the decomposition of the n nuclei present at the outset, and the maximum will correspond roughly with the time taken by a single plane to cross the crystal. For specimen B at 110°, this time is 138 mins., while the exponential portion of the second acceleration extends from 900 to 1800 mins. The assumption is therefore approximately correct.

If at time t the number of decomposed planes be N and if each of these gives rise to b new planes per second, then $dN/dt = bN$, and if w be the average number of molecules in one plane of the crystal, the total decomposition, x, is equal to wN, whence

$$dx/dt = w \,.\, dN/dt = WbN = bx$$

and

$$x = ce^{bt}$$

where c is the amount of reaction product at $t = 0$, which, if the original n planes decomposed instantaneously, would be wn. Differentiation gives

$$dx/dt = bwne^{bt} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

which is an equation of the type found experimentally.

Numerical Calculations.—We are now in a position to evaluate the various constants which have been referred to. The following data are for specimen B at 110°.

We have already assumed that the time of the first maximum in paraffin is approximately equal to the time taken for the reaction to cross the crystal. The average size of a crystal of specimen B is $(1{\cdot}7 \times 10^{-4})^3$ c.c. From this, one may calculate that there are 1×10^{11} molecules in the crystal, and that the length of the crystal edge contains $4{\cdot}64 \times 10^3$ molecules. The rate of forward propagation of the reaction is therefore $4{\cdot}64 \times 10^3$ molecules in 138 mins. or $K = 0{\cdot}56$ molecule/sec. Further, the amount of oxalate decomposed at this maximum is 2·68%. If we assume that each nucleus is responsible for the decomposition of a single layer equal to the cross section of the whole crystal, then

$$n = 0{\cdot}0268 \times 4{\cdot}64 \times 10^3 = 124 \text{ nuclei per crystal.}$$

The above value of K may now be checked by substituting for n in the expression $k = \frac{1}{2}\pi nK^2$. The average of the three relevant determinations of k_2 in Table I is $4{\cdot}7 \times 10^{-7}$, which is the rate, in fraction per sec., at $t = 600$ secs. Converting this into molecules per sec. at $t = 1$ sec., we find $\frac{1}{2}\pi nK^2 = 79$, and putting $n = 124$, we obtain $K = 0{\cdot}63$ mol./sec.

Again, a value for $\frac{1}{2}\pi nK^2$ may be obtained from the vacuum decomposition by multiplying *a* (Table III) by the corresponding figure for *p* (Table II). Taking the data for specimen *B*, and converting as before to molecules per sec., we find $K = 0{\cdot}434$ mol./sec.

The agreement between these three values seems to be as good as can be expected in view of the various simplifying assumptions made.

The other constants may be obtained as follows. The value of *p* is $2{\cdot}83 \times 10^{-4}$. This is the number of times the plane divides per second. As the plane takes 138×60 secs. to decompose, the number of divisions per plane is 2·34. The values for this specimen at other temperatures are: 100°, 1·73; 120°, 1·91; 130°, 2·84; average, 2·21.

The value of *b* is $6{\cdot}12 \times 10^{-5}$. This is the number of times per second that a new plane starts from one that has already run its course. Each plane therefore gives rise to a new one every 278 mins. As this is about the time taken by vacuum decomposition to reach its maximum rate, it is clear that we were justified in ignoring Process III when considering such experiments.

The value of *bnw* is $1{\cdot}49 \times 10^{-7}$ (fraction per second). With our previous value of $n = 124$, this gives $w = 1{\cdot}96 \times 10^{6}$ as the number of molecules in a single plane. The number calculated from the dimensions of the crystals is $21{\cdot}5 \times 10^{6}$, which indicates that the size of the plane diminishes somewhat as the reaction proceeds.

The general reasonableness of these figures,* and the extent of agreement in those cases where a constant can be calculated by two entirely independent methods, indicates that the figures are of the right order of magnitude, and offers very strong support for the theory on which they are based.

SUMMARY.

The rate–time curves obtained during the decomposition of silver oxalate under various conditions have been analysed. They show that the reaction starts from a fixed number of nuclei, which depends on the history of the sample. From these it spreads in two dimensions across the planes of the crystal in the form of thin plates. These planes of reaction may branch. In a vacuum they usually do so from the leading molecule on the edge of the plane, since this possesses considerable energy from the heat of reaction. When paraffin or certain other substances are adsorbed on the surface, however, this excess energy is removed. The reaction is thereby greatly retarded, and proceeds by the spontaneous generation of fresh planes at the edges of the spent reaction planes.

Calculations show that the rate of forward propagation of the reaction is about 0·5 molecule per second at 110°, and that the energy of activation is in the neighbourhood of 32,000 cals. Various other constants have been evaluated.

I thank the Carnegie Trust for the Universities of Scotland for a Teaching Fellowship, during the tenure of which much of the work described in this and the preceding paper was done.

THE UNIVERSITY, ST. ANDREWS. [*Received, March 30th*, 1936.]