193. *The Thermal Decomposition of Silver Oxalate. Part I. Experimental.*

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THE thermal decomposition of silver oxalate is of considerable interest because the course of the reaction can be profoundly modified by a variety of factors, each capable of being controlled so as to give reasonably reproducible results. It was pointed out by Macdonald and Hinshelwood (J., 1925, **127**, 2764) that specimens prepared with an excess of sodium oxalate decomposed much more quickly than those in which silver nitrate was in excess at precipitation; and that oxygen exerted a strong retarding influence. It has now been found that there are other modifying factors : that the dispersion of the precipitate in an oil or in molten wax slows down the reaction in a curious manner; that dispersing it in gelatin has a similar but less pronounced effect; and that mercury vapour produces acceleration. It was hoped that a close study of the decomposition under these different conditions would throw light on the mechanism of the reaction.

EXPERIMENTAL.

Preparation and Description of Specimens.—Fourteen specimens were prepared by precipitation from known concentrations of sodium oxalate and silver nitrate. The reagents were of analytical quality and were used without further purification. Precipitation was carried out with solutions of from $N/5$ to $N/500$, and one reagent was kept in excess the whole time except in one case, where an effort was made to keep the concentrations equivalent throughout. The specimens were washed from six to twelve times by decantation, filtered, and again washed. After drying in a vacuum desiccator, they were stored in the dark. During the preparation, light was excluded as far as was consistent with work in the open laboratory. The results obtained by this procedure were only approximately reproducible. Since the precipitate is of a semi-colloidal nature, it is probable that exact duplication of a specimen could not possibly be obtained unless the temperature, rate of stirring, and time of washing were controlled. Further, the preparations should be made and weighed out under photographic dark-room conditions.

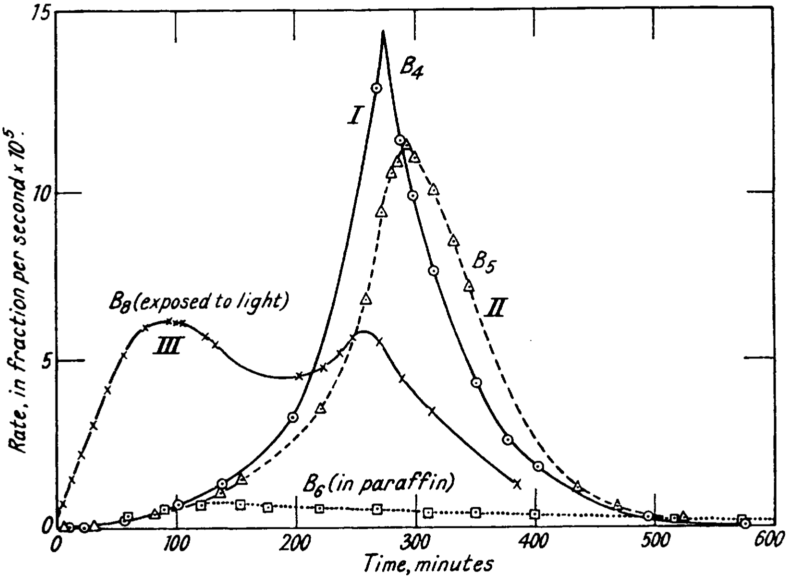
The substance prepared by the above method was microcrystalline, the average diameter of a single crystal being about 3×10^{-4} cm. The specimens with a considerable excess of either component had the smaller and more regularly sized crystals. (In all cases, however, some of the smallest crystals were lost in the process of filtration and washing.) Large crystals were also prepared, and by two methods : (1) 1 g. of oxalate was recrystallised from 45 l. of water by evaporation in a vacuum at 50° (slight decomposition had evidently taken place during manufacture, the crystals being somewhat discoloured); (2) an ammoniacal solution of the oxalate was evaporated, giving very imperfect crystals 1—3 mm. long, and affording a large proportion in irregular thin plates which floated on the mother-liquor until pushed under the surface. This flotation was an example of a phenomenon observed generally, *viz.*, that the substance resisted wetting by water.

The crystals obtained from the ammoniacal solution were examined by Dr. F. Walker, of the Geology Department, who reports that they are either monoclinic or triclinic, with an extinction angle ($Z\Lambda c$) of 16°, and a refractive index considerably greater than that of methylene iodide (1·72); and that there are two very well-defined cleavages at 83° to one another.

According to the I.C.T., the density of silver oxalate is 5·029, and its heat of decomposition 29,150 cals. per mol.

Measurements.—It is possible to measure either the quantity of carbon dioxide evolved or its rate of evolution. Both determinations may be required in the subsequent analysis, and since the process of graphical integration is much more accurate than that of graphical differentiation, the rate of decomposition was always measured directly. The method employed was a modification of that described in the earlier paper for decompositions in a vacuum, which gives directly the rate of reaction in arbitrary units. Briefly, the sample, usually weighing 0·01—0·02 g., was placed in a small bulb attached to a McLeod gauge and a vacuum train, and heated at constant temperature. Connection with the pumps was cut off periodically, and the rise of pressure in a measured short time (about 1 min.) was determined by the McLeod gauge. In order to start the reaction with the minimum time-lag, the bulb was pivoted on a ground-glass joint, so that it could be plunged into the previously adjusted oil thermostat. In the most rapid experiments, a differential manometer was substituted for the McLeod gauge, and the rate was measured by the time taken by the mercury to rise between two etched marks about 1 mm. apart. By this means, as many as four readings could sometimes be taken in one minute.

FIG. 1.



Decomposition of specimen B (excess oxalate) by three methods at 110°. *Curves I and II show the degree of reproducibility attained in experiments carried out (in a vacuum) under identical conditions.*

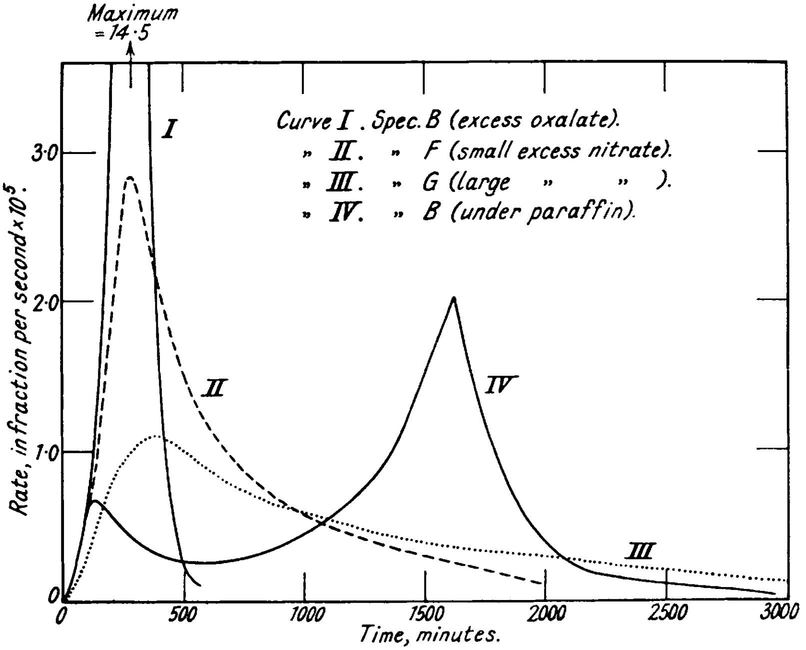
The rates are thus obtained in arbitrary units, which depend on the weight of the sample taken and the dimensions of the apparatus. They were converted into standard units by the following method. At the end of the experiment, the amount of any unchanged oxalate was estimated by attaching the sample to a micro-gas-burette and heating it strongly. The rate–time curve was then plotted, and integrated by square-counting, so that the area which corresponded to 100% decomposition could be determined. By dividing the observed rates by the area and multiplying by a constant factor, depending on the scale of the graph, the rates in units of *fraction per second* were found. This is the unit which is used throughout.

The general trend of nearly all the experiments is that which is typical of a large number of solid decompositions. The rate is very low at the outset, accelerates to a pronounced maximum, and finally falls off, frequently giving an approximately symmetrical curve. A striking feature, however, and one which appears to be not uncommon in reactions of this type, is the variable behaviour of different samples of the same specimen. Although in general each run was characteristic of the particular preparation used, it was found impossible to duplicate exactly any curve, and variations in the maximum rate of up to 20% were found. This is illustrated by Curves I and II (Fig. 1), which show two runs with specimen *B* under identical conditions, and these should be compared with Curves I, II, and III (Fig. 2), which show runs with three different preparations. (All curves drawn to the same scale enclose equal areas, representing 100% decomposition.)

In assessing the importance of these variations, it must be remembered that the decomposition is strongly autocatalytic, and that such a reaction is dependent on, and extremely sensitive to, traces of the reaction product that may be present at the outset. On the other hand, the differences which may be expected to exist between individual crystals cannot in this case affect the result, since approximately 10^8 micro-crystals were decomposed together in each run, and the chance factors associated with the different units must have averaged out. In attempts to trace the variations to some controllable factor, about 30 runs were made under different conditions, mostly with one specimen (*C*). The results of this investigation were mainly negative, and are summarised as follows.

(1) The earlier runs had been conducted at 131°, and it seemed possible that at this temperature self-heating might cause irregularities. Temperatures down to 86° were therefore employed, without any improvement being noticeable. Nevertheless, a temperature of 110° was thereafter employed normally. It has since been found that the self-heating effect enters into the decomposition of the more unstable specimens at 131°, but that it does not affect the early stage of the decomposition, which is the seat of the irregular behaviour.

FIG. 2.



Showing the retarding influence of silver nitrate (*Curves I, II, and III*) *and of paraffin* (*Curve IV*) (*Temp.*, 110°).

(2) It is known that air exerts a retarding influence, and it was therefore thought that variations in the hardness of the vacuum used might influence the reaction. This, and the possible effect of variations in the temperature of the thermostat, were therefore investigated by running the decompositions in pairs, a common vacuum system being used and the bulbs being immersed side by side in one thermostat.

(3) Adsorbed air and moisture were removed by 15 hours' evacuating at $< 10^{-5}$ mm., and comparative runs were made with long and with short evacuation.

(4) During the course of these experiments, it was observed that the presence of mercury in the reaction vessel (but not actually in contact with the salt) had a strong catalytic effect on the reaction, and a similar acceleration due to sulphur compounds has been reported by Sheppard and Vanselow (*J. Amer. Chem. Soc.*, **1930**, **52**, 3468). The possibility of accidental contamin-

ation by mercury vapour from the pumps and gauges, and of sulphur compounds from the gas used for sealing on the reaction vessel, was therefore investigated.

(5) It was found that strong exposure to ultra-violet light produced considerable acceleration (see p. 836). A specimen was therefore prepared, manipulated, and decomposed under photographic dark-room conditions.

It was clear that the variations were not due exclusively to any of the above factors, and little improvement resulted from the adoption of the precautions suggested by them.

(6) Lastly, it was thought that the decomposition might spread by infection from one crystal to the next (compare Pease and Taylor, *ibid.*, **1921**, **43**, 2179, on the reduction of copper oxide by hydrogen). This would have explained the irregular behaviour of the samples, and also the fact that, as will be shown in Part II, an exponential term appears in the analysis of the curves. It was tested by conducting the decomposition under molten paraffin wax (purified by boiling with alkali) or under oil (Cenco pump oil, No. 11032), and also by making a suspension of the oxalate in gelatin, after the manner of a photographic " emulsion." The decomposition in gelatin proved to be very similar to that in a vacuum, which effectively disposed of the hypothesis. The course of the decomposition under paraffin was, however, unexpected. The significance of the curves obtained, one of which is illustrated in Fig. 2, Curve IV, will be discussed later. At present it is sufficient to state that the experiments under wax or oil gave no higher degree of reproducibility than those in a vacuum.

It is probable that the cause of the discrepancies lies in the accidental production of nuclei prior to the beginning of the reaction. From the above experiments it would seem that these were mostly formed by mechanical damage to the sample during manipulation (it is known that quite light grinding causes marked acceleration), but that in some cases exposure to light was a contributory factor. This view is supported by the results obtained by other workers in the same field, who have, in general, found that reproducible results can only be obtained by previously treating the sample in a way which may be expected to lead to the formation of a constant number of nuclei. Another possible cause of variation, however, lies in the fact that the small portion of each sample in actual contact with the walls of the vessel attained the temperature of the bath much more rapidly than the bulk of the compound which, since the decompositions were carried out in a hard vacuum, were heated only by radiation.

A correction which takes account of this slow heating of the bulk of the sample has to be applied to the observed time and to the first few rate determinations. The necessary data were obtained from experiments in which a thermometer or a thermocouple was heated under the same conditions as the oxalate, and from the known temperature coefficient of the reaction. This correction had, of course, to be applied equally to all runs, and no account could be taken of variations in the size of the vessel, the thickness of its walls, the distribution of the solid, or the conducting effect of any gases liberated in the course of the reaction. An idea of the magnitude of the correction will be obtained from the fact that, at 131°, 7·5 mins. had to be subtracted from all times over 15 mins. In these cases, the maximum rate was reached in times varying between 22 mins. and 60 mins. from the start of the reaction, so that little reliance can be placed on observations made at this temperature, unless they are confirmed by those made at a lower temperature where the correction is relatively of much less importance. The results indicated that in some cases the correction applied was too large. That it is of the right order can be shown by a simple calculation based on the rate of heating of a blackened sphere by radiation.

When the decomposition was carried out in air or under a liquid, experiment showed that the necessary correction was negligible.

Results.

Effect of Ionic Concentration at Precipitation.—The method of preparation and some of the characteristics of the decomposition at 110° are given in the table. It will be seen that, in general, as the concentration of silver nitrate used is increased, so the maximum rate attained diminishes. It is clear that, of the ions normally present, it is the nitrate which is most effective in producing this result, for specimen *I*, though prepared with an excess of oxalate over silver, was rendered stable by the addition of a quantity of sodium nitrate. That the effect is not peculiar to the nitrate ion is clear from specimen *H*, in which silver sulphate was substituted for silver nitrate. The sulphate ion, indeed, seems to be more effective than the nitrate ion, and a specimen which was prepared in the presence of sulphuric acid (*J*) was extremely stable.

A study of the last three columns of the table, however, shows that the results are not at all simple. The decrease in the maximum rate which is associated with an increase in the nitrate-ion concentration is caused by two factors : (i) a general slowing down of the reaction, as indi-

TABLE.

Showing the method of preparation of the various specimens and the chief characteristics of their decomposition at 110°. (Results for specimens marked with an asterisk are calculated from experiments at about 131° by the use of a temperature coefficient of 3·0 for 10°.) In specimens *C*, *D*, and *E*, the two salts were added simultaneously to 100 c.c. of water. In all other cases the solutions were mixed in the order given. The first 12 specimens are arranged in order of increasing nitrate-ion concentration.

Spec.	Method of preparation.	Rate at max. $\times 10^5$.	Time at max. (mins.).	% at max.	Time at 90% (mins.).
O	2000 C.c. $N/5$-$Na_2C_2O_4$ + 25 c.c. $N/5$-$AgNO_3$	16·2	207	36·9	640
Q	2000 C.c. $N/20$-$Na_2C_2O_4$ + 25 c.c. $N/5$-$AgNO_3$	10·9	270	43·8	464
P	500 C.c. $N/20$-$Na_2C_2O_4$ + 25 c.c. $N/5$-$AgNO_3$	13·7	280	48·0	363
B	500 C.c. $N/5$-$Na_2C_2O_4$ + 600 c.c. $N/60$-$AgNO_3$	12·6	281	42·4	388
M	40 C.c. $N/20$-$Na_2C_2O_4$ + 20 c.c. $N/20$-$AgNO_3$ + 1 c.c. of 0·03% soluble fluorescein	5·08	230	38·0	570
A	500 C.c. $N/5$-$Na_2C_2O_4$ + 50 c.c. $N/5$-$AgNO_3$	6·85	319	42·6	550
C	203 C.c. $N/20$-$Na_2C_2O_4$ + 200 c.c. $N/20$-$AgNO_3$ + 100 c.c. H_2O	4·30	395	44·6	699
D	200 C.c. $N/20$-$Na_2C_2O_4$ + 200 c.c. $N/20$-$AgNO_3$ + 100 c.c. H_2O	3·88	379	43·7	735
E	203 C.c. $N/20$-$AgNO_3$ + 200 c.c. $N/20$-$Na_2C_2O_4$ + 100 c.c. H_2O	2·94	535	45·1	910
F	500 C.c. $N/5$-$AgNO_3$ + 600 c.c. $N/60$-$Na_2C_2O_4$	2·74	295	21·8	1500
G	500 C.c. $N/5$-$AgNO_3$ + 50 c.c. $N/5$-$Na_2C_2O_4$	1·16	375	15·5	4370
**I*	250 C.c. $N/20$-$Na_2C_2O_4$ + 50 c.c. $N/20$-$AgNO_3$ + 8·5 g. $NaNO_3$	0·56	562	5	(5600) [1]
**H*	500 C.c. $N/20$-Ag_2SO_4 + 50 c.c. $N/20$-$Na_2C_2O_4$	4·6	562	54	1820
****Am*** (1)	Recrystallised from ammonia	5·4	239	15·5	1025
****Am*** (2)	Recrystallised from ammonia	8·7	251	35·0	674
K	Recrystallised from water	1·56	360	13·8	—

[1] Approximate value, by extrapolation.

cated by the longer time elapsing before the maximum rate is reached; and (ii) the fact that this maximum is in some cases attained when a much smaller proportion of the substance has decomposed. In this connection, specimens *F*, *G*, and *I* are particularly instructive. The last column shows that with the exception of specimens *O* and *Q*, the time of 90% decomposition increases with the nitrate-ion concentration, *i.e.*, the tail of the curve is much extended. Some of these points are illustrated in Curves I, II, and III (Fig. 2).

The last three specimens in the table consist of large crystals. The figures show that the decomposition of these is similar to that of a precipitate prepared with a slight excess of silver nitrate.

Effect of Air.—Accurate measurements of the rate of reaction in the presence of air are not easy to carry out, since normally the carbon dioxide produced in the course of the reaction tends to displace the air in the neighbourhood of the crystals. A few experiments were, however, attempted, and these indicated that up to about 3% decomposition the reaction followed the same course as in a vacuum, but that thereafter, instead of continuing to accelerate, the rate decreased progressively.

Effect of Paraffin.—The result of decomposing the oxalate under molten paraffin wax is shown in Fig. 2, Curve IV. It will be seen that, as in air, the decomposition follows the same course as in a vacuum for a time equivalent to about 3% decomposition, and that the velocity then falls. Instead of continuing to fall, however, it rises again to a second and greater maximum. Irregular bumps were frequently observed around this second maximum, and to a less extent in the intermediate period of low velocity. The curve illustrated is for specimen *B*, precipitated with excess oxalate. The curve for specimen *G* (excess nitrate) under paraffin was similar, the only notable difference being that the first maximum represented only about one-third of the velocity found for *B*. It was not possible to differentiate between the second accelerations in the two cases.

Effect of Exposure to Light.—When specimen *B* was irradiated for 6 mins. by the light of a quartz mercury-vapour lamp, consuming 300 watts, and was subsequently decomposed under paraffin, the rate at the first maximum was doubled, but the curve was otherwise unaltered. Similarly, the specimen prepared and manipulated in the dark gave a smaller first maximum, though this may be due, in part at least, to the fact that the crystals of the precipitate were considerably smaller. Curve III, Fig. 1, exhibits the result of decomposing an irradiated sample of specimen *B* in a vacuum : the initial velocity has been greatly increased, and a curve with two maxima is obtained. The times of these two maxima make it evident that the first corresponds to the first maximum in paraffin, and the second to the normal maximum of a vacuum decomposition. A close examination of the curves obtained for the decomposition in a vacuum of the unexposed samples shows that there is always a slight hump present in the curve corresponding in time to the first maximum in paraffin, and that the effect of the action of light is to increase this very greatly. The size of the hump varies a good deal from one specimen to another, and in general increases with the age of the sample.

Microscopic Examination.—Crystals of the precipitate are too small for detailed examination even under the highest magnification, but it can be seen that at no time is there any great difference between one crystal and its neighbours. The decomposition, as indicated by a gradual darkening in colour, starts immediately in all particles. There is no evidence whatever of a spread of the reaction from one crystal to another. Examination of the large crystals shows that these darken through reddish-brown to opacity (5—10% decomposition), after which no change is observable, the final mass of silver being a pseudomorph of the original crystal of oxalate. The darkening appears to be quite uniform throughout the mass of the crystal, *i.e.*, it is proportional to the thickness of the crystal at any point. It clearly does not proceed on the surface, as does the decomposition of copper sulphate pentahydrate (Garner and Tanner, J., 1930, 47; Hume and Colvin, *Proc. Roy. Soc.*, *A*, **1931**, **132**, 548), nor does it spread from a few isolated nuclei as in potassium chlorate (Coppock, Colvin, and Hume, *Trans. Faraday Soc.*, **1931**, **27**, 283).

DISCUSSION.

It has previously been suggested (Macdonald and Hinshelwood, *loc. cit.*) that the decomposition is controlled by the formation and growth of nuclei of reaction product in the crystal. Benton and Cunningham (*J. Amer. Chem. Soc.*, 1935, **57**, 2227), who studied quantitatively the effect of light on the reaction, concluded that irradiation increases the number of nuclei present at the start. This conclusion is fully borne out by the experiments described above. The whole reaction is, however, somewhat more complex than these investigators realised, and changes in the shape of the curve follow upon alterations in the conditions in a manner which cannot be explained on the hypotheses which they put forward.

It will be clear from the foregoing description that there are several distinct modes of decomposition which can be more or less isolated from one another experimentally. It will be convenient to refer to such modes of decomposition as " processes." Their more obvious characteristics are summarised below.

The first, Process I, is best represented by the first maximum in paraffin. It normally accounts for not more than 5% of the reaction, but this amount can be greatly increased by exposure to light. The similarity of the first few per cent. of the decompositions in paraffin, in a vacuum, in air, and with various ionic concentrations at precipitation, shows that Process I is unaffected by any of these conditions. It is almost certain, therefore, that it consists in the decomposition of nuclei which are present at the outset of the reaction, and that each nucleus can account for the decomposition of only a small fraction of the crystal. The alternative explanation, that only a few of the crystals possess nuclei, is disproved by the microscopic examination of the partially decomposed substance.

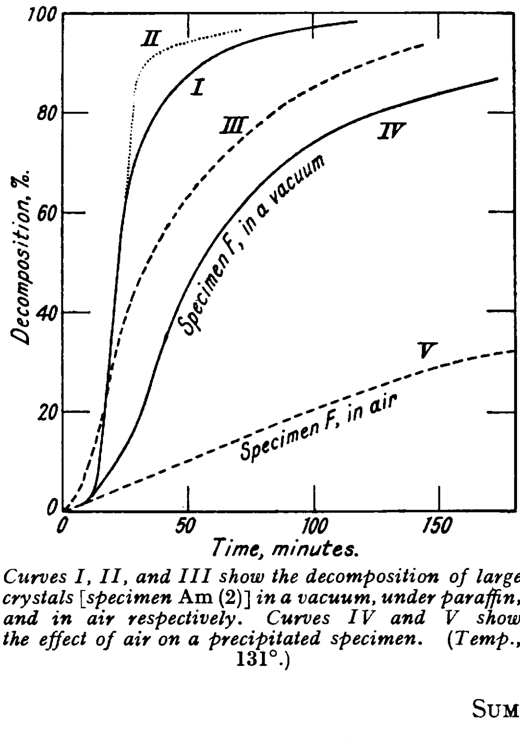
Process II is actively operative in the decomposition of the more unstable specimens in a vacuum. It is quite distinct from Process I, as is shown by the double maximum obtained when the sample has been irradiated, and by the fact that it may be reduced by increasing the concentration of nitrate ion and entirely eliminated by carrying out the reaction under paraffin or in air. Its sensitivity to the environment proves that it is essentially a surface reaction, and is thus connected with the formation of fresh nuclei.

The reaction which causes the second maximum in paraffin is Process III. This is apparently not so sensitive to environment as Process II, since it is not affected by the ionic condition of the surface. It is uncertain to what extent it is present in the decomposition of ion-retarded specimens in a vacuum, or in the decompositions in air.

The above processes are all of an accelerating type. It is probable that a fourth process is present, which controls the long period of decreasing velocity found in experiments in air, and with ion-retarded specimens; but it has not yet been possible to isolate this sufficiently from the other processes to enable any theory as to its nature to be put forward.

Finally, important evidence as to the nature of the reaction is obtained from the decomposition of large crystals. It has been seen that, when decomposed in a vacuum, these gave curves similar to those found for precipitated specimens. This indicates that the unit of decomposition is not the crystal as a whole, but the " crystallite " of which all large crystals are supposed to be made up (see Garner and Hailes, *Proc. Roy. Soc.*, *A*, 1933, **139**, 576). If we assume that the micro-crystals which comprise the precipitate consist of single crystallites, or contain, at most, a few, and that the large crystals contain many, then the only real difference between the two types will be that the external surfaces of the micro-crystals will become " internal surfaces " in the macro-crystals. Now when the large crystals are decomposed under paraffin, the course of the decomposition is found to be almost exactly the same as in a vacuum (Fig. 3, Curves I and II). The explanation is clear. Process II, which is the one affected by paraffin, is associated with the surfaces of the crystallites. In the case of a precipitate, these are the external surfaces, and are accessible to the paraffin; whereas in the case of large crystals, they are internal surfaces to which the paraffin is unable to penetrate, and whose decomposition is therefore unaffected by the medium in which the crystal is placed. Similarly, air, which also eliminates Process II, has little effect on the large crystals (Curve III, Fig. 3). In the latter case, however, the isolation of the inner surfaces is not so complete, and the reaction is retarded to a certain extent. It must be remembered that carbon dioxide is able to diffuse out of the crystal without disrupting it, and it is by no means unlikely that air is able to pass in by the same channels.

FIG. 3.



Curves I, II, and III show the decomposition of large crystals [*specimen* Am (2)] *in a vacuum, under paraffin, and in air respectively. Curves IV and V show the effect of air on a precipitated specimen.* (*Temp.*, 131°.)

The hypothesis that the crystallite is the unit of decomposition is in accord with the appearance of the large crystals when observed under the microscope.

SUMMARY.

A study of the decomposition of silver oxalate under a variety of conditions has proved that the reaction is complex. It has been found possible to isolate experimentally three independent mechanisms. Process I, accounting normally for about 3% of the reaction, is controlled by nuclei which are present at the outset, and whose number may be increased by various means. Process II, which normally accounts for the remainder of the reaction, is very sensitive to the conditions at the surfaces of the crystals (or, in the case of large crystals, of the component crystallites). When Process II is suppressed by conducting the decomposition under paraffin, Process III becomes prominent.

It has further been shown that the crystals of the precipitate or the crystallites of large crystals decompose as independent units unaffected by their neighbours.

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