CCLIV.—*The Homogeneous Decomposition of Ozone in the Presence of Oxygen and Other Gases.*

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It has been shown by H. E. Clarke and one of us (Trans., 1908, **93**, 1638) that the rate of decomposition of ozone on the surface of glass is so slow that even in moderately small globes the amount of ozone destroyed on the internal surface of the vessel may be neglected in comparison with that decomposed in the interior of

the gas. In other words, it has been demonstrated that the conversion of ozone into oxygen under suitable conditions may be assumed to be a homogeneous change without any appreciable error being made. It is the only slow chemical change in the gaseous state which has, as yet, been shown to satisfy the condition of homogeneity under realisable conditions.

Since the quantitative investigation of a chemical change entirely confined to matter in its least complex state might be expected to furnish results of exceptional theoretical significance, an attempt was made by Mr. H. E. Clarke and one of us to construct an apparatus with which the velocity of decomposition of ozone in the presence of oxygen and other gases might be measured; but before the apparatus had been sufficiently perfected to furnish satisfactory results, Mr. Clarke was unfortunately compelled to relinquish the work. The investigation has been continued by the authors of this communication with the aid of a slightly modified and improved form of the apparatus originally designed by Clarke and one of us. Before giving a detailed account of this apparatus, and the mode of conducting an experiment, it will be convenient to state the general conclusions that have been drawn from the results, and to indicate what we believe to be the theoretical significance of these conclusions.

The results demonstrate that:

(a) Oxygen, nitrogen, carbon dioxide, and possibly water vapour have no effect on the rate of decomposition of ozone, that is, the rate of decomposition of ozone in the presence of these gases is a function of the concentration of the ozone only.

(b) Nitrogen peroxide (Andrews) and chlorine accelerate in a marked degree the decomposition of the gas.

(c) If the order of the change can be represented exactly by an integral ordinal number, that number is the second.

In respect of their influence on the rate of decomposition of ozone, gases may therefore be separated into two classes—those which are without effect, and those which act as powerful catalysts. That a classification based on such a striking distinction should be possible lends strong support to the view that the catalytic action of the second class is chemical rather than physical in its nature, since a physical property is generally shared, in a greater or less degree, by all gases. Moreover, nitrogen peroxide and chlorine are substances of which the first is known to react with ozone, and the second is closely related to an element, namely, iodine, which has been shown to be oxidised by ozone.

The facts, so far as they have been made out, indicate that the mechanism of the decomposition of ozone in the absence of catalysts

is a simple process, consisting of the conversion of two molecules of ozone during a favourable collision into three molecules of oxygen. Such a view is in harmony with the fact that gases having no chemical action on ozone are without influence on its rate of decomposition (for the number of collisions between pairs of molecules of ozone is almost independent of the diluting gas), and also with the fact that the reaction is of the second order.

A result of exceptional interest is that which relates to the

FIG. 1.

influence of moisture. The discussion of this will be relegated to the experimental section of the paper.

EXPERIMENTAL.

The apparatus used for the preparation and collection of the ozonised oxygen is depicted in Fig. 1. The oxygen was prepared by heating potassium permanganate. Dust and carbon dioxide were removed from it by its being passed through a tube packed with glass wool and soda-lime. It was stored in a small gas-holder A, which contained concentrated sulphuric acid. The gas-holder was connected by narrow capillary tubing with a Brodie ozone generator B, made of thin glass, as recommended by Shenstone (*Trans.*, 1893, **63**, 938). The generator was immersed in dilute sulphuric acid, and its inner tube contained metallic mercury. It was connected by capillary tubing with a vessel C, containing concentrated sulphuric acid saturated with ozone. As the ozonised oxygen passed into this vessel, the displaced acid entered the

reservoir *D*. The receptacles *D* and *C* were connected by a wide tube *a*, in which a tap T_a was inserted, and also by a tube *b* of very fine bore.

When T_a was closed, the acid entered *D* very slowly, owing to the resistance offered to its motion by the capillary tube, and the rate at which the ozonised oxygen entered the receiver was correspondingly slow. The upper end of *D* was connected with a device by means of which the current of gas could be further regulated. The wide tube *E*, containing powdered potassium hydroxide, was ground into the mouth *d* of the receptacle *D*. *E* was in turn joined by rubber tubing to a flask *F*, containing water, which could be siphoned out drop by drop through the fine capillary tube *G*. By raising and lowering *G*, the rate at which the water siphoned over could be regulated, and the flow of gas through the ozone generator thereby controlled. The potassium hydroxide in *E* served to destroy traces of ozone which would otherwise have attacked the rubber tube. Before use, the apparatus was cleansed with a hot mixture of potassium chromate and concentrated sulphuric acid, and then with hot distilled water, and thoroughly dried.

All air was displaced from the apparatus before starting an experiment by a current of oxygen. Oxygen was collected in the gas-holder, and a volume of ozonised oxygen sufficient for one experiment was prepared from it. The tap T_b was then closed, and the oxygen remaining in the gas-holder *A* was allowed to escape. The gas in the receiver *C* was next transferred to the holder *A*, the taps T_a and T_b being left open. It was then again drawn slowly through the ozone generator into the receiver *C*, the coil being in action. The percentage of ozone was appreciably increased by the gas being submitted for a second time to the action of the silent discharge.

The section of the apparatus used to measure the rate of decomposition of the ozone (at 100°) is shown in Fig. 2.

The glass tubes, A_1 and A_2 , of about 100 c.c. capacity, in which the ozone was heated, communicated by capillary tubes, on the one side with the previously described section of the apparatus, and on the other with the left-hand limbs of the manometers m_1 and m_2 , which contained concentrated sulphuric acid. The right-hand limbs of the manometers were connected by capillary tubes and ground glass joints with two bottles, B_1 and B_2 , of about 2 litres capacity each. The corresponding parts of the apparatus were made as nearly alike as possible. The apparatus was connected with an injector pump at *P*, and was provided with a mercury manometer at *M*, as shown in the diagram. Taps T_1 , T_2 , and T_3 , and taps t_1 , t_2 , t_3 , t_4 , t_5 , t_6 , t_7 , t_8 , and t_9 , provided with mercury seals, were

inserted in the positions indicated in the figure. The pressure on the right-hand side of the manometers was kept constant by the bottles being immersed in a bath of water at a fixed temperature. The water in the bath was stirred by a current of air, and the temperature was controlled by a delicate electric thermoregulator.

During an experiment the tubes A_1 and A_2 were kept at 100° by means of a current of steam, which entered the jackets surrounding them from above. In a preliminary experiment, it was shown that the temperature of both of the tubes could be raised to that of the steam in the same time. Before the experiments

FIG. 2.

were started, ozonised oxygen was passed through the heated tubes for several hours.

Influence of Oxygen on the Rate of Decomposition of Ozone.

The object of the first series of experiments was to ascertain the effect, if any, of varying concentrations of oxygen on the rate of decomposition of the ozone. The method of conducting an experiment was as follows.

A quantity of ozonised oxygen sufficient for one experiment was collected in C , the ozone remaining in the generator and capillary tubes being subsequently driven out through the taps T_1 and T_3 by a stream of oxygen from the holder A .

With the taps t_1 , t_9 , and T_2 closed, and t_2 , t_3 , t_4 , t_5 , t_6 , t_7 , and t_8 open, the apparatus was exhausted as completely as possible by the injector pump. The taps t_5 , t_3 , and t_7 were then closed, and oxygen

admitted from the holder A through t_1 and t_9 until the volume between the taps t_1 and t_3 and between the taps t_9 and t_7 had been filled. The pump was again set in action, and the taps t_5 , t_3 , and t_7 cautiously opened. When the limit of exhaustion attainable with the injector pump had been reached, the process described above was repeated, the removal of traces of air from the tubes A_1 and A_2 being thereby ensured.

After the final exhaustion the taps t_5 , t_2 , and t_8 were closed. By cautiously opening t_1 and t_9 , ozonised oxygen was admitted to the tubes A_1 and A_2 from the receiver C , the pressure on both sides of the manometer being maintained the same by the simultaneous admission of air into the bottles B_1 and B_2 through the taps t_5 and T_2 . When the manometer M indicated a pressure of a little less than half an atmosphere, t_4 was closed. The ozone left in the capillary tubes on the left-hand side of the taps t_1 and t_9 was displaced by oxygen, and oxygen was then introduced into the tube A_2 by carefully opening the tap t_9 , air being at the same time admitted through t_5 . The taps t_6 and t_9 were closed when the manometer m indicated a pressure slightly less than an atmosphere.

The tube A_1 was thus filled with ozonised oxygen at the pressure of half an atmosphere, whilst A_2 contained the same amount of ozone, but approximately twice as much oxygen.

The tubes having been filled, the taps t_2 and t_8 were opened, and a rapid current of steam was passed through the steam jackets. After one and a-half minutes (when the contents of the tubes had attained the temperature of the steam), the taps t_2 and t_8 were closed. The differences of pressure registered by the manometers were noted at regular intervals. Curves were plotted, showing the relation between the increase of pressure in the tubes A_1 and A_2 and the time. It sometimes happened that the total amounts of ozone contained in A_1 and A_2 respectively (as indicated by the total change of pressure) were not exactly equal. In such cases a simple correction was applied in order that the results might be strictly comparable.

The changes of pressure in cm. of sulphuric acid are plotted against the times, and the four pairs of curves thus obtained are shown in Fig. 3. The circles correspond to the changes of pressure in the tube which contained ozonised oxygen at a pressure of half an atmosphere, and the crosses to changes of pressure in the other tube which contained the same amount of ozone per unit volume, but twice as much oxygen. The numbers attached to the curves indicate the order in which the experiments were performed.

These results point decisively to the conclusion that variation in

the pressure of the oxygen mixed with ozone is unattended by appreciable alteration in the velocity of decomposition of the latter gas at 100° . This conclusion does not appear to agree with the observations of previous investigators.

S. Jahn (*Zeitsch. anorg. Chem.*, 1906, **48**, 260) and Perman and

FIG. 3.

Greaves (*Proc. Roy. Soc.*, 1908, *A*, **80**, 353) assert that the rate of decomposition of ozone varies approximately inversely as the oxygen-pressure. If the reaction were reversible, this result might be expected; but Perman and Greaves and others have conclusively demonstrated that at 100° it may be regarded as irreversible.*

* Fischer and Braehmer (*Ber.*, 1906, **39**, 940), have recently shown that ozone is formed in small quantities from oxygen at temperatures above 1300° .

In order to explain his results, Jahn has suggested that the decomposition of ozone occurs in two stages, expressible by the equations:

the first stage being rapid and reversible, whilst the second is slow. These assumptions would require that the rate of decomposition of the ozone should be directly proportional to the square of the concentration of the ozone, and inversely proportional to the concentration of the oxygen. Jahn's experiments were carried out at 127° , at which temperature the reaction is bimolecular, according to Warburg (*Sitzungsber. K. Akad. Wiss. Berlin*, 1901, **48**, 1126).

Perman and Greaves, on the other hand, consider that Jahn's hypothesis is not justifiable, and that the alleged effect of the oxygen is due to variations in the gas film on the glass surface resulting from the changes in the oxygen-pressure. If, however, the decomposition occurs mainly in the body of the gas, as appears from the work of Clarke and one of us (*loc. cit.*), the suggestion must for that reason alone be discarded.

Influence of Aqueous Vapour on the Rate of Decomposition of Ozone.

A second series of experiments was performed in order to investigate the influence of water vapour on the rate of decomposition of the gas—a subject of considerable interest, both on account of the diversity of the results obtained by previous workers and of its bearing on the general problem of the catalytic effect of moisture on most simple chemical changes.

The experiments were carried out as described above, except that both tubes were filled with ozonised oxygen at a pressure of a little less than an atmosphere, and that the gas which entered the tube A_1 was saturated with water vapour by its being passed through a small wash-bottle containing distilled water. To prevent any moisture being carried over into A_2 , a tap was inserted on the left-hand side of the wash-bottle, which was shut off while A_2 was being filled.

The eight curves obtained by plotting the results of four experiments are shown in Fig. 4. In experiments IIIa and IVa, the moist gas was contained in the tube which held the dry gas in the two previous experiments. The crosses correspond to the changes of pressure of the moist gas, and the circles to the changes of pressure of the gas dried by concentrated sulphuric acid.

Andrews and Tait, and also Brodie, in their classical memoirs on

ozone, recommend the use of carefully dried oxygen for the preparation of ozone by the silent discharge.

Shenstone and Cundall (Trans., 1887, 51, 610) showed that carefully dried oxygen can be easily converted into ozone—a fact which was shortly afterwards confirmed by Baker (Trans., 1894, 65, 611), who stated that “ozone was formed as rapidly in oxygen dried with phosphorus pentoxide as it was in the same tube when the oxygen had been dried only by sulphuric acid.”

As a result of further investigations, Shenstone (Trans., 1897, 71, 471) drew the remarkable conclusion that all previous state-

FIG. 4.

ments on the subject were wrong. He observed that a high percentage of ozone is formed by the action of the silent discharge on oxygen saturated with water vapour, and that the ozone thus produced is remarkably stable. On partly drying the gas, the percentage of ozone produced was considerably reduced, and the gas was found to be singularly unstable. Oxygen which had been thoroughly dried was found to become ozonised exceedingly badly. Subsequent investigations have failed to confirm Shenstone's work, and Armstrong has suggested that his anomalous results may be due to the presence of oxides of nitrogen (formed by continuous action of

the discharge from traces of nitrogen contained in the oxygen), which, as Andrews has shown, immediately destroy ozone.

Thomson and Threlfall (*Proc. Roy. Soc.*, 1885, **40**, 340) assert that ozone is produced when an electric spark is passed through very carefully dried oxygen.

Warburg (*loc. cit.*) maintains that at 100° the dry gas is just as stable as the moist.

Warburg and Leithäuser (*Ann. Physik*, 1906, [iv], **20**, 751) have, moreover, shown that the formation of ozone both in oxygen and in air is retarded by the presence of moisture, the retardation being greater in oxygen than in air.

Fischer and Marx (*Ber.*, 1906, **29**, 3631), working with a Nernst filament, find that the first traces of moisture lessen the yield of ozone by catalytic action, whereas larger quantities of water vapour increase the yield of hydrogen peroxide at the expense of the ozone.

Perman and Greaves (*loc. cit.*) claim to have shown that water vapour accelerates the decomposition of ozone, and that the effect is roughly proportional to the amount of water vapour present. They consider that the effect is due to the deposition of moisture on the surface of the glass, which causes the ozone to be more rapidly condensed. They point out that their results do not agree with those of Shenstone.

Although in our experiments the ozone mixed with a considerable proportion of water vapour appears to decompose at a slightly greater rate than that which has been dried with sulphuric acid, the difference is so small that we are disposed to think that it ought to be attributed to the gradual removal of water vapour, adsorbed on the inner surface of the glass, at the higher temperature, or to some similar cause. We are, at least, justified in concluding that at 100° a large difference in the quantity of water vapour present with the ozone is not accompanied by any marked change in the velocity of decomposition. Our results agree with those of Warburg, whose experiments were also conducted at 100°.

Influence of Nitrogen, Carbon Dioxide, Carbon Monoxide, and Chlorine on the Rate of Decomposition of Ozone.

The negative character of the results obtained with the first three gases is sufficient proof that no appreciable quantity of impurity capable of destroying the ozone was contained in them. In each case concentrated sulphuric acid was used to dry the gas. The experiments were conducted as follows.

A tube containing soda-lime was introduced between the gas-holder and the ozone generator in order to remove any carbon dioxide from the oxygen. The tubes A_1 and A_2 were filled with

ozonised oxygen at a pressure of half an atmosphere in the manner previously described. Oxygen was then admitted to one tube until a pressure slightly less than an atmosphere was registered by the manometer. The gas of which the effect was being investigated was then introduced into the other tube through T_1 or T_3 until the pressure in both tubes was the same. The rates of decomposition of the ozone in the two tubes were compared. Several experiments were performed, the gas under investigation being introduced into A_1 and A_2 alternately.

FIG. 5.

In the case of nitrogen, no effect on the velocity of decomposition was observed, while the experiments with carbon dioxide and carbon monoxide demonstrate that the influence, if any, of these gases is small. Chlorine, on the other hand, was found to decompose ozone so rapidly that it was quite impossible to make any trustworthy measurement of the velocity of decomposition.

The six curves obtained by plotting the results of three experiments with nitrogen are shown in Fig. 5. In the experiments II and III, the nitrogen was contained in the tube which in the previous experiment held ozonised oxygen only. The crosses

correspond to changes of pressure in the gas which contained nitrogen, and the circles to the changes of pressure in the other tube.

The readings taken in the experiments with carbon dioxide I and carbon monoxide II are plotted in the curves shown in Fig. 6. The circles correspond to changes of pressure in the tube which contained the ozonised oxygen only.

FIG. 6.

Shenstone and Evans (*Trans.*, 1898, **73**, 246), while investigating the influence of the silent discharge on atmospheric air, were surprised to find that as much as 98 per cent. of the oxygen contained in the air could be converted into ozone, the maximum yield of ozone obtained from pure oxygen under the same conditions being only 13.6 per cent. A similar observation was made by Brodie (*Phil. Trans.*, 1874, **164**, 101) when he submitted carbon

dioxide to the action of the same agency; the carbon dioxide was decomposed into carbon monoxide and oxygen, 85 per cent. of the oxygen being in the form of ozone. It was conceivable that these interesting and peculiar phenomena might arise from inhibitive effects on the thermal decomposition of ozone of nitrogen and carbon dioxide respectively. The above experiments demonstrate that such an explanation is untenable, and that the phenomena in question must be due to some obscure influence of the nitrogen on the one hand, and the carbon dioxide or carbon monoxide on the other, on the energy of the discharge itself.

Observations on the Order of the Change.

In examining our results with a view to determining the order of the change, we have adopted a novel method. Instead of calculating the value of the constant for each observation on the assumption that the change is of a given order, we compare the amounts of ozone decomposed at given intervals of time with those calculated for changes of a specified order. This method of examining the results has the obvious advantage of enabling us to decide at a glance whether the departure of the experimental numbers from those calculated from any given set of assumptions as to the nature of the change lie within the limits of experimental error.

A curve of a given order is drawn through three points on the experimental curves, the points selected being the origin, and the points corresponding with the last observation, and an observation made when about half of the ozone was decomposed. The difference between the magnitudes of ordinates (amounts of ozone) of the experimental and calculated curve at different times are then tabulated. In the present case it was only necessary to compare the experimental curve with calculated curves drawn through it of the first and second order. It will be seen from the numbers given that the reaction is very nearly of the second order. Only the numbers obtained in those experiments in which large quantities of dry ozone were decomposed, and in which readings were taken for a considerable period of time are submitted to examination below.

Examination of the Measurements Made in Experiment IVa. (A_1 .)

Time.	Observed change of pressure.	Calculated change of pressure, 1st order.	Difference : $k_1=0.00648$.	Observed change of pressure.	Calculated change of pressure, 2nd order.	Difference : $k_2=0.00142$.
2	0.60	0.36	+0.24	0.60	0.48	+0.12
5	1.30	0.91	+0.39	1.30	1.16	+0.14
10	1.90	1.68	+0.22	1.90	2.12	-0.23
16	2.95	2.57	+0.38	2.95	3.11	-0.16
58	7.00	7.00	0	7.00	7.00	0
97	8.50	9.26	+0.71	8.50	8.65	+0.10
178	10.30	11.26	+0.96	10.30	10.07	-0.23
238	10.95	11.76	+0.81	10.95	10.93	-0.02
298	11.40	11.97	+0.57	11.40	11.34	-0.06
397	11.85	12.08	+0.23	11.85	11.78	-0.07
508	12.10	12.10	0	12.10	12.10	0
Sum of differences = +4.51				Sum of differences = -0.51		

The calculated curves are drawn through the origin, the point (58, 7.00), and the point (508, 12.10). If the difference between the ordinates of the calculated and experimental curves indicates that the order of the reaction is of a higher value than that corresponding with the calculated curve, a plus sign is attached to it, a minus sign having the reverse significance.

It will be evident on inspection of the above numbers that the reaction differs but slightly from one of the second order.

Examination of the Measurements made in Experiment IIIa. (A_1 .)

In this experiment the rate of change approximates still more closely to a reaction of the second order.

Time.	Observed change of pressure.	Calculated change of pressure, 1st order.	Difference : $k_1=0.00624$.	Observed change of pressure.	Calculated change of pressure, 2nd order.	Difference : $k_2=0.00141$.
1	0.25	0.17	+0.08	0.25	0.23	+0.02
3	0.75	0.50	+0.25	0.75	0.69	+0.06
6	1.55	0.95	+0.60	1.55	1.30	+0.25
9	1.95	1.44	+0.51	1.95	1.86	+0.09
12	2.40	1.88	+0.52	2.40	2.36	+0.04
18	3.15	2.69	+0.46	3.15	3.25	-0.10
24	3.85	3.26	+0.59	3.85	4.00	-0.15
30	4.50	4.15	+0.35	4.50	4.64	-0.14
51	6.10	6.16	-0.06	6.10	6.35	-0.25
60	6.85	6.85	0.00	6.85	6.85	0.00
75	7.50	7.82	+0.32	7.50	7.60	+0.10
105	8.60	9.24	+0.64	8.60	8.61	+0.01
129	9.15	10.00	+0.85	9.15	9.19	+0.04
156	9.75	10.60	+0.85	9.75	9.69	-0.06
276	11.00	11.63	+0.63	11.00	10.92	-0.08
381	11.40	11.81	+0.41	11.40	11.43	+0.03
489	11.80	11.85	+0.05	11.80	11.76	-0.04
531	11.85	11.85	0.00	11.85	11.85	0.00
Sum of differences = +7.06				Sum of differences = -0.18		

In the other experiments, in which the initial percentage of ozone was less, or the period during which observations were made shorter, the order of the change falls to a greater extent below the second. All the experiments are conclusive in demonstrating, however, that if the order of the change can be represented by an integral ordinal number, that number is the second.

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