

PHILOSOPHICAL TRANSACTIONS.

I. *On the Constitution and Properties of Ozone.* By THOMAS ANDREWS, M.D., F.R.S., M.R.I.A., Professor of Chemistry in Queen's College, Belfast.

Received May 16,—Read June 21, 1855.

AMONG the many interesting bodies which the researches of modern chemists have brought to light, few are more remarkable than the substance to which the name of ozone has been given, whether we consider its many singular and anomalous properties, or its intimate relations with the most important and widely-diffused element in nature. For the first recognition of ozone and description of its properties, we are indebted to the sagacity of SCHÖNBEIN, to whom the entire merit of the discovery unquestionably belongs. His earlier experiments were, however, chiefly directed to the elucidation of its properties, and of the conditions under which it is formed; but not being accompanied by quantitative determinations, they did not throw any clear light on its actual constitution. The subject has also attracted of late years the attention of several very distinguished physical and chemical inquirers, among whom I may particularly mention MARIGNAC, DE LA RIVE, BERZELIUS, WILLIAMSON, FREMY and BECQUEREL, and BAUMERT.

SCHÖNBEIN has shown that a body having a peculiar and highly characteristic odour and very similar properties is formed under the three following conditions:—

1. When electrical sparks are passed through atmospheric air.
2. When pure water, or water holding certain acids or salts in solution, is decomposed by the voltaic current, the new substance appearing, along with the oxygen gas, at the positive pole.
3. When certain bodies, and particularly phosphorus, are slowly oxidized at common temperatures in atmospheric air.

Two distinct questions here arise for consideration. Is the same substance produced under these different conditions, or has SCHÖNBEIN included under the name of ozone substances having different compositions, although agreeing in some of their

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properties? And next, what is the composition of ozone, or, if there be more ozones than one, how are they respectively constituted?

The experiments of WILLIAMSON* indicated the production of water, when ozone obtained by electrolysis was decomposed by being passed over heated copper, and BAUMERT† obtained similar results when he passed a stream of electrolytic oxygen through a tube containing anhydrous phosphoric acid, which was heated at one point to redness. These experiments were not, however, adapted to yield quantitative results, but they led to the general conclusion that this variety of ozone is an oxide of hydrogen containing more oxygen than water. But from another and very important experiment, to which I shall have occasion hereafter very fully to refer, BAUMERT has concluded that it is a teroxide of hydrogen, HO_3 .

On the other hand, the experiments of DE LA RIVE and of FREMY and BECQUEREL‡ have shown, that pure and dry oxygen gas may be converted by the electrical spark into ozone.

I am not aware of any experiments on ozone obtained by the action of phosphorus on atmospheric air, which throw any distinct light on its constitution. MARIIGNAC passed a stream of this ozonized air through a solution of iodide of potassium, till the whole of the iodide was converted into iodate of potassa, and concluded that ozone produced in this way must be either oxygen in a peculiar state, or a peroxide of hydrogen.

According to the results, therefore, of the most recent investigations, it would appear,—

That the substances comprehended under the name of ozone are not identical;

That the ozone obtained by the action of the electrical spark on oxygen gas is oxygen itself in an altered or allotropic state;

That the ozone obtained by the electrolytic decomposition of water is an oxide of hydrogen, having the formula HO_3 ; and

That the ozone obtained by the action of phosphorus on oxygen is either oxygen itself, or a compound of oxygen and hydrogen§.

The subject of ozone has at intervals engaged my attention during the last four or five years, and I was actually occupied with a series of experiments on the production of ozone by the electrical spark, when the appearance of FREMY and BECQUEREL's able researches induced me for the moment to lay aside the inquiry. The publication of BAUMERT's memoir led me subsequently to resume it, as his results were not in accordance with those which I had previously arrived at. But the method proposed by that physicist to determine whether ozone is an oxide of hydrogen, or oxygen in an allotropic condition, appeared to be so well suited to the purpose, that

* Memoirs of the Chemical Society, vol. ii. p. 395.

† POGGENDORFF'S Annalen, Band lxxxix. S. 39.

‡ Annales de Chimie, 3^{ème} série, xxxv. p. 62.

§ For a very complete account of all that is known on this subject, see the Article "Ozon" in the Handwörterbuch der Chemie, Band v. S. 835 (Braunschweig, 1853).

on resuming the inquiry, I considered it necessary in the first instance carefully to repeat his experiments. The results which I at first obtained were so far in accordance with those of BAUMERT, that they showed that the increase in weight of the apparatus was always more than the weight of the ozone, as deduced from its chemical action, but the relative proportion of these quantities was not in accordance with his results; nor, on repeating my own experiments, did they agree with one another. It was evident, therefore, that some disturbing cause existed which complicated the reaction, and, on further investigation, I not only found that such a cause did really exist, but succeeded in ascertaining its nature and the means of avoiding it. The experiments, on being now repeated, gave results very consistent with one another, and altogether at variance with the view that hydrogen is a constituent of ozone.

The apparatus which I employed was arranged as follows:—A is a vessel (Plate I. fig. 1) of about two litres capacity, containing a mixture of one measure of pure and strong sulphuric acid, and seven measures of distilled water. The cylinder B, which is filled with a similar solution, is closed below with a diaphragm of bladder, so as to prevent effectually any mixture of the gases evolved at the two poles. A platina wire, *pp*, traverses and is fused into a short glass tube, fitted by grinding into the tubulated neck *b*: this wire terminates below in a bunch of fine platina wires, which form the positive pole of a voltaic arrangement. The negative pole is a platina plate, *p'*, immersed in the liquid of the outer vessel. The vessel A was placed in a larger vessel containing cold water, to which ice was in some experiments added. This vessel has been omitted in the drawing for the sake of distinctness. CC'C'' is a continuous tube, united by fusion with the larger neck of B, and filled from C' to C'' with fragments of pumice, moistened with pure sulphuric acid. The length of the desiccating column was nearly one metre. D is a LIEBIG's apparatus, to the ends of which glass tubes were fused, which had previously been fitted by grinding, the one into the neck *c* of CC'C'', the other into a tube, which was in like manner fused to a second LIEBIG's apparatus, E. The connexions *c* and *e* were, therefore, formed by glass surfaces carefully ground. In my earlier experiments, these connexions were made by means of small and dry corks, which, on the whole, are more convenient than ground-glass joints, and are quite unobjectionable, as, when the surface is small and the cork dry, the amount of ozone destroyed by contact with the cork is wholly inappreciable. Caoutchouc connectors of any kind are altogether inadmissible; they are attacked with such energy by ozone, even when diluted with 1000 times its volume of other gases, that the tube becomes perforated in the course of a few minutes. The vessel D contained a solution of iodide of potassium, acidulated with a little hydrochloric acid, and the vessel E, concentrated sulphuric acid. The U-tube F, filled with pumice moistened with sulphuric acid, prevented any moisture from passing backwards into E. The oxygen evolved was collected in the graduated glass vessel G, inverted over water. The volume of the

oxygen gas was determined only for the purpose of ascertaining its relation to the ozone produced.

The mixture of oxygen and ozone, having been perfectly desiccated in its passage through the long tube *CC'C''*, enters the vessel *D*, where the ozone is decomposed, iodine being set free and caustic potassa formed, which latter, combining with the free hydrochloric acid, forms chloride of potassium. If a neutral solution of iodide of potassium is employed, the reaction is more complicated; for, while the greater part of the iodine is set free as before, and dissolves in the excess of iodide of potassium, iodate of potassa and caustic potassa are at the same time formed. Whether the solution be taken in an acid or neutral state, the final result is in this respect always the same, that the active oxygen enters into a chemical combination in the vessel *D*, and increases the weight of the liquid contained in that vessel.

The increase in weight of the vessels *D* and *E* will give the entire weight of the ozone, whether that body be allotropic oxygen, or an oxide of hydrogen. On the former supposition, the decomposition of the iodide of potassium will result in the substitution of oxygen for iodine, both remaining in *D*, while the sulphuric acid in *E* will retain the moisture which would otherwise be swept away by the current of dry gas; on the latter, ozone will become resolved into water and oxygen, both of which will be retained in the vessels *D* and *E*. Now by determining the amount of free iodine in the iodide of potassium solution at the end of the experiment, the amount of active oxygen by which it has been displaced may be easily calculated; and on comparing this with the increase in weight of the vessels *D* and *E*, it will at once be seen whether ozone be a peroxide of hydrogen yielding water in its decomposition.

Two experiments of this kind were performed by BAUMERT; in the first, the increase in weight of the apparatus amounted to 0·0133 grm., and the weight of the oxygen, as calculated from the iodine set free, to 0·0081 grm.; in the second, the same quantities were respectively 0·0149 grm. and 0·00989 grm. The iodide of potassium was employed in the state of a neutral solution, and the iodate of potassa was subsequently decomposed by the addition of a little hydrochloric acid.

It was from these results that BAUMERT inferred that the ozone which accompanies oxygen obtained by the electrolysis of water, is an oxide of hydrogen having the formula HO_3 ; and this conclusion, deduced from experiments which were devised with great skill and executed with care, has, in Germany at least, received very general assent.

Having, as already mentioned, found, on a repetition of these experiments, that a different expression resulted for the composition of ozone from every new trial, I instituted a diligent search into all the circumstances of the experiment, and at last succeeded in referring the irregularities to the presence of a small, but appreciable quantity of carbonic acid, which, unless very great precautions be taken, is always present in electrolytic oxygen. When baryta water was substituted for the solution of iodide of potassium in *D*, a precipitate of carbonate of baryta appeared in the

course of a few minutes. With caustic potassa in the same vessel, the increase in weight, for the same volume of oxygen gas, was considerably greater than with the solution of iodide of potassium, and at the end of the experiment it was found that carbonate of potassa had been formed. Now as a small quantity of free potassa is always produced during the action of ozone on a neutral solution of iodide of potassium, it appeared not improbable that this would seize upon a portion of the carbonic acid just referred to, and thus the augmentation in the weight of the apparatus would depend upon two distinct causes,—the ozone reaction, and the absorption of carbonic acid. To prevent the occurrence of the latter, it was only necessary to acidulate the solution of iodide of potassium, so as to prevent the formation of free potassa, or to boil for some time the liquid subjected to electrolysis. The acidulation of the solution alone was found to be sufficient to prevent the carbonic acid from being absorbed, for when this precaution was attended to, the results were the same, whether the electrolyte was boiled immediately before the commencement of the experiment or not. With this modification, the irregularities previously observed in different trials disappeared, and the simple and interesting result was obtained, that the increase in weight of the apparatus was exactly equal to the amount of oxygen deduced by calculation from the iodine set free.

I will now describe the chief precautions which I adopted to avoid, as far as possible, all sources of error in the following experiments, the delicacy of which will at once be apparent, if we consider that not more than 40 milligrammes of ozone are contained, under the most favourable circumstances, in 10 litres of electrolytic oxygen; and that it was necessary to have the arrangements so perfect, that this large quantity of gas (supposed to be free from ozone) should traverse the apparatus without producing any appreciable change in the united weight of the vessels D and E.

The solution of iodide of potassium employed in all the experiments had the same composition, although the quantity of ozone obtained in some cases was three times greater than in others. It consisted of 2 grms. of iodide of potassium dissolved in $22\frac{1}{2}$ grms. of a weak solution of hydrochloric acid, containing 2 per cent. of pure acid. As it is difficult to procure iodide of potassium entirely free from iodate of potassa, I always prepared, at the commencement of each experiment, two similar solutions, of which one was introduced into D, and the other preserved in a ground stoppered vial, till the experiment was finished. The amount of free iodine in both was determined at the same time, and the difference taken to represent the exact quantity of iodine due to the ozone reaction. The correction for the iodate of potassa in the original solution, when reduced, rarely represented more than 0.001 grm. oxygen, but quantities of this magnitude must not be neglected in these experiments.

Previous to weighing the vessels D and E, one litre of atmospheric air, deprived of carbonic acid and carefully desiccated, was passed through the apparatus. The object of this precaution was to bring every part of the apparatus into the same state

at the beginning of the experiment, in which it would be at the end. The same volume of dry air was passed through the apparatus at the conclusion of each experiment.

It is rarely necessary in chemical investigations to apply a correction to the direct indications of the balance for changes in the temperature and pressure of the atmosphere, during the interval between two successive weighings. By preserving the apartment at a pretty uniform temperature, the corrections for thermometric changes may be confined within very narrow limits, but the movements of the barometer are not under our control; and when, as in these experiments, a period of two and sometimes of three days elapsed between the first and second weighings, it occasionally happened that the change in the atmospheric pressure was considerable, and an appreciable error (amounting in some instances to nearly 0.002 grm.) would have occurred, if no correction had been applied*.

To ascertain how far the action of the apparatus might be relied on, one or two preliminary experiments were made, which gave very satisfactory results. The vessel D, containing pure water, E, sulphuric acid, and another LIEBIG'S condenser, also containing sulphuric acid, having been interposed between E and F, 3.5 litres of oxygen gas not containing ozone, followed by 1 litre of atmospheric air, were passed through the apparatus. The time occupied in the passage of the gas was about five hours. The vessel D lost 0.0311 grm., while E gained 0.0315 grm., the third vessel not sustaining any appreciable change of weight. If, therefore, D and E had been weighed together, the change of weight would have been only 0.0004 grm. In another experiment, in which a solution of strong caustic potassa was placed in D, the loss of D was 0.0175 grm., and the gain of E 0.0172 grm., the difference being less than one-third of a milligramme. Other experiments of the same kind, with different solutions in D, gave similar results. It is evident, therefore, that at the rate at which the gas traversed the apparatus, the whole of the moisture carried off from the liquid in D was retained by the sulphuric acid in E.

To determine whether a notable quantity of iodine would be carried over by the current of the gas from D to E, a solution of iodide of potassium containing a large

* This correction was calculated as follows:—To the volume in cubic centimetres of the solution of iodide of potassium in D and of sulphuric acid in E, was added the volume of the glass of which the vessels D and E were formed. From this was deducted the volume of the weights employed. Let V be the difference of the volumes so found in cubic centimetres; p and p' , the atmospheric pressures in English inches at the first and second weighings; t and t' , the corresponding temperatures in Centigrade degrees; x , the weight, in grammes, of a volume of air equal to V, measured under the pressure p , and at the temperature t ; x' , the weight of the same volume of air at p' and t' . Then, since 1 cub. cent. air, at 0°, and under a pressure of 29.92 inches, weighs 0.00129 grm.,

$$x' - x = V \left(\frac{1}{1 + 0.00367t'} \cdot \frac{p'}{29.92} - \frac{1}{1 + 0.00367t} \cdot \frac{p}{29.92} \right) \cdot 0.00129.$$

The value of $x' - x$ is to be added to, or subtracted from, the increase of weight, as found by direct experiment, according as it is a positive or negative quantity.

quantity of free iodine was introduced into D, and a solution of pure iodide of potassium into E. After passing 4 litres of air through the apparatus, E was found to contain 0.0015 gm. iodine. This is equivalent to one-tenth of a milligramme of oxygen, and, from the large excess of iodine in the first solution, must be a greater quantity than could have been carried over in any of the subsequent experiments, although in some of them larger volumes of gas were passed through the apparatus.

The free iodine was determined according to the very delicate method first, I believe, proposed by BUNSEN. A dilute solution of sulphurous acid was prepared, and its strength determined, immediately before analysing the liquid in D, by ascertaining how many measures of it were required to destroy a known weight of free iodine in a solution of iodide of potassium. A corresponding experiment was made with the solution in D, from which the quantity of free iodine in it was deduced by a very simple calculation.

I. 10.2 litres of electrolytic oxygen containing ozone were passed through the apparatus at the rate of about three-quarters of a litre per hour. At the first weighing, the barometer was 29.85 in. and the thermometer, 5°.9 C.; at the second weighing, the barometer was 29.98 in. and the thermometer, 5°3. The value of V (see preceding note) was 47 cub. cent. The gain in weight of the double apparatus D and E was 0.0375 gm., which gives, when corrected for atmospheric changes, for the true gain,

0.0379 gm.

The free iodine in the solution contained in D, was neutralized by 112.7 measures of a dilute solution of sulphurous acid. The other solution of iodide of potassium, which had been prepared at the same time as the first, and to which the same amount of acid had been added, required 0.8 measure of the same solution of sulphurous acid for neutralization. Hence the iodine eliminated by the action of the ozone was equivalent to 111.9 measures. Next, 0.5341 gm. pure iodine was added, together with 2 grms. of iodide of potassium, to a few drops of water, and when both were dissolved, the solution was diluted till it occupied exactly 100 cub. cent. From the mean of two experiments which closely agreed with one another, it appeared that 100 measures of the solution of sulphurous acid neutralized 95.96 cub. cent. of this solution, and hence 1 measure of the former corresponded to 0.00512 gm. iodine. From these data it follows, by an easy calculation, that the iodine disengaged by the ozone amounted to 0.609 gm., and the equivalent of oxygen to

0.0386 gm.

II. 2.72 litres of electrolytic oxygen were passed through the apparatus at the same rate as before. At first weighing, barometer 29.60 in., thermometer 5°8 C.; at second weighing, barometer 29.60 in., thermometer 6°0 C. Gain of weight of D and E 0.0107 gm., corrected,

0.0107 gm.

The free iodine in D, after deducting the iodine due to the small quantity of iodate

of potassa in the original solution, was neutralized by 30·23 measures of a solution of sulphurous acid, of which, as ascertained by direct experiment made at the time, 1 measure neutralized 0·00521 grm. free iodine. Hence the oxygen due to the displacement of iodine was

0·0100 grm.

III. 2·86 litres of the same gas as in the preceding experiments were passed through the apparatus. At first weighing, barometer 30·06 in., thermometer 6°·6 C.; at second weighing, barometer 30·20 in., thermometer 6°·1 C. Gain of weight of D and E 0·0152 grm., corrected,

0·0154 grm.

The free iodine in D, corrected as before, was neutralized by 41·52 measures of a solution of sulphurous acid, of which 1 measure neutralized 0·00525 grm. iodine; hence the weight of oxygen, as deduced from the weight of iodine set free, was

0·0138 grm.

IV. 6·45 litres of electrolytic oxygen were passed through the apparatus. At first weighing, barometer 29·96 in., thermometer 6°·8 C.; at second weighing, barometer 29·29 in., thermometer 7°·8 C. Gain of weight of D and E 0·0303 grm., corrected,

0·0288 grm.

The free iodine in D was neutralized by 100·4 measures of a solution of sulphurous acid, of which 1 measure neutralized 0·00441 grm. iodine; hence the weight of oxygen deduced in this way was

0·0281 grm.

V. 6·8 litres of electrolytic oxygen passed. At first weighing, barometer 30·53 in., thermometer 9°·8 C.; at second weighing, barometer 30·44 in., thermometer 10°·4 C. Gain of weight of D and E 0·0254, corrected,

0·0251 grm.

The free iodine in D neutralized 107·9 measures of a solution of sulphurous acid, of which 1 measure was equivalent to 0·00358 grm. iodine; hence the weight of oxygen deduced from the iodine set free was

0·0273 grm.

Collecting these results and adding them together, so as to obtain the mean of the whole, we have

Ozone deduced from the increase in weight of the apparatus.	Ozone deduced from the iodine liberated.
I. 0·0379 grm.	0·0386 grm.
II. 0·0107 grm.	0·0100 grm.
III. 0·0154 grm.	0·0138 grm.
IV. 0·0288 grm.	0·0281 grm.
V. 0·0251 grm.	0·0273 grm.
<hr/> 0·1179 grm.	<hr/> 0·1178 grm.

The agreement is complete, and proves unequivocally that water is not a product of the decomposition of ozone, which therefore does not contain hydrogen as a constituent. If its composition were HO_3 , the apparatus would have increased 0.1841 grm. in weight, instead of 0.1179 grm.

The amount of ozone formed in these experiments was tolerably uniform. For 1 litre of oxygen the following weights of ozone were obtained:—

I.	0.0038 grm.
II.	0.0037 grm.
III.	0.0046 grm.
IV.	0.0043 grm.
V.	0.0040 grm.
Mean . .	0.0041 grm.

In the arrangement above described, the oxygen gas derived from the electrolytic decomposition of water was therefore accompanied by about $\frac{1}{350}$ th of its weight of ozone.

In order to remove every possible doubt from these results, I fitted up an apparatus from every part of which organic substances were excluded. No diaphragm was used, and all the connexions were made, either by fusing the ends of the connecting tubes together, or by means of ground glass joints. The arrangement is represented in fig. 2. Two platina wires (fig. 3) were fused into the end of a glass tube, which was fitted by grinding to the tubulated neck *b* of the vessel A. The tube BB'B'' was connected at *a* with the vessel A by a ground joint, and with C by fusion. It contained pumice moistened with sulphuric acid. The vessel C was also filled with sulphuric acid, and was connected by a ground glass joint with the iodide of potassium vessel D. The vessel E contained, as before, sulphuric acid. In this experiment, both the hydrogen and the oxygen traversed the apparatus, the accuracy of which was thus exposed to a very severe test.

Twenty-two litres of the mixed gases were passed through the apparatus. The gain in weight of D and E was 0.0135 grm., the respective heights of the barometer at the first and second weighings having been 28.96 in. and 29.57 in., and the temperatures $11^{\circ}.1$ and $10^{\circ}.0$. The correction for change of pressure and temperature is therefore +0.0014 grm., and the true gain

0.0149 grm.

The free iodine in D, due to the action of the ozone, neutralized 62.65 measures of a solution of sulphurous acid, of which 1 measure corresponded to 0.00373 grm. iodine. The weight of ozone deduced from the iodine set free is therefore

0.0148 grm.

The identity of these results is very satisfactory, when it is considered that this small weight of ozone was separated from 22 litres, or nearly five gallon measures of

the mixed gases. The relative quantity of ozone to the amount of water decomposed is less than in the former experiments, arising perhaps partly from a single platina wire having been in this case employed as the positive pole. In this experiment, great care was taken to exclude both carbonic acid and nitrogen from the electrolyte.

My next object was to determine, by careful quantitative experiments, whether water is really formed, as WILLIAMSON and BAUMERT have stated, when ozone is decomposed by heat. For this purpose, the same general arrangement was employed as in the first series of these experiments; but the first LIEBIG'S apparatus D, instead of being filled with a solution of iodide of potassium, was now empty, and placed in the upper part of a metallic cylinder (fig. 4 HH), where it was raised to a temperature of about 400° C., by a current of heated air from a LESLIE'S burner. To the sulphuric acid apparatus E, was permanently attached and weighed along with it, a small U-tube G, containing anhydrous phosphoric acid, so as to secure the condensation of the last trace of aqueous vapour, if any were present. The oxygen gas was collected and measured as in the former experiments.

Two experiments were made. In the first, 6.8 litres of oxygen containing 0.027 grm. ozone were passed through the apparatus; in the second, 9.6 litres containing 0.038 grm. ozone. The compound sulphuric and phosphoric acid apparatus was found, all corrections having been made, to have increased, in the one case one-third, and in the other case one-half of a milligramme in weight. Such quantities can only be referred to the unavoidable errors of experiment. If ozone were a compound body having the constitution HO_3 , the apparatus would have gained in the first experiment 10, and in the second 14 milligrammes.

That ozone cannot contain nitrogen will appear from the following experiment. Two platina wires were hermetically sealed into the bottom of a small flask, into which water, containing a little sulphuric acid, was introduced and made to boil rapidly for some time. While the water was in a state of ebullition, the wires were connected with the poles of a voltaic arrangement, so as to disengage the mixed gases along with the vapour of water. So long as the ebullition continued, no ozone made its appearance; but on allowing the liquid gradually to cool, without arresting the current, its presence soon became manifest from its odour and action on iodide of potassium paper. The ebullition and the current of the mixed gases must have rendered the presence of nitrogen here impossible.

One question still remains to be answered. Does ozone, besides oxygen, contain any other constituent which is not absorbable by any of the reagents employed? Although the gas which escaped from the apparatus, after the separation of the ozone, appeared to be pure oxygen, yet it would be rash to assert that it might not have contained some unknown body amounting to $\frac{1}{1000}$ th of its weight, and having no very salient properties. This question appeared to me to admit of solution in another way. It will be seen, in a subsequent part of this paper, that there can be no doubt of the formation of ozone from pure and dry oxygen by the action of the electrical

spark, and nothing is easier than to convert the whole of a given volume of oxygen into ozone in presence of a solution of iodide of potassium. The next step in the inquiry was therefore to ascertain whether ozone derived from electrolysis, from the action of the electrical spark, and from the oxidation of phosphorus, exhibited a perfect identity in all its properties.

One of the most remarkable properties of ozone is its destruction by heat, or rather its conversion by heat into ordinary oxygen. To ascertain the temperature at which this change occurs, the vessel D, fig. 4, was placed in a bath of mercury, and the gas examined as it escaped, without previously passing it through the rest of the apparatus. On heating the mercurial bath, the amount of ozone, as determined by its action on iodide of potassium paper*, did not notably diminish till the temperature attained 230°C . It still continued, however, very intense till the thermometer rose to 235° . Between that point and 240° the ozone reactions entirely disappeared, when the ozone was in a very dilute state; but when more concentrated, slight traces of ozone could still be discovered, which no doubt would have also disappeared if the current of gas had been passed very slowly. Time is in fact an element in this action. Even at the temperature of 100°C . ozone is slowly destroyed. Two similar tubes were filled, at the same time, and by the same process, with ozone diluted as usual with oxygen, and afterwards hermetically sealed. One of these tubes was maintained for three hours in a vapour bath at 100°C ., the other was not exposed to heat. On examining both tubes at the end of the time, it was found that the ozone in the tube which had been exposed to heat was perceptibly less than in the other. I have no doubt that, even at the common temperature of the air, ozone preserved in an hermetically sealed glass tube would gradually change into common oxygen. I made an experiment of this kind two or three years ago, which resulted in the disappearance of the ozone, but I do not remember the source from which the ozone was derived, nor what precautions were taken to dry the gas.

On the other hand, ozone brought directly into contact with the vapour of water at the boiling-point is instantly destroyed.

To obtain a continuous stream of ozone from the action of the electrical spark, a current of pure oxygen gas, obtained from the decomposition of the chlorate of potassa, and purified and dried by passing through tubes containing hydrate of potassa and sulphuric acid, was exposed to a rapid succession of electrical sparks. To obtain a sufficient stream of electricity, an electrical machine, firmly screwed down to the floor of the apartment, was connected by a belt with a heavy cast-iron wheel, 40 inches in diameter, contained in a frame which was also firmly secured to the floor. By this arrangement, the machine could be worked for any length of time

* Bibulous paper which has been dipped into a solution of iodide of potassium of moderate strength and afterwards allowed to dry, but still retaining its hygrometric moisture, is the most convenient test of ozone. If it be exposed to a continuous current of dry air, it should be removed from time to time and its hygrometric moisture restored.

continuously, the plate performing about 360 revolutions per minute. It was of course necessary to apply very frequently a hand rubber covered with amalgam to the plate, and it required the cooperation of three persons to permit the work to be easily performed. On passing the gas through the apparatus at nearly the same rate as in the experiments already described, an abundant stream of ozone was obtained, which enabled me to institute a very exact comparison between its properties and those of ozone obtained by electrolysis.

When heated in the mercurial bath, ozone prepared in this way was rapidly destroyed at the temperature of 237°C ., which is the same temperature at which electrolytic ozone was also destroyed. The vapour of boiling water, in like manner, caused all the ozone reactions to disappear.

The action of water at common temperatures and of alkaline solutions upon ozone is very remarkable. It is commonly stated that caustic potassa absorbs ozone, but that pure water, and solutions of lime, baryta, and ammonia, have no action upon it. This statement is far from being accurate. Pure water does not absorb ozone, and a stream of air containing ozone may be passed for any length of time through water without producing any change in the properties of the water. I have also preserved ozone for several days in a stoppered vial containing a little distilled water, and although the vessel was agitated from time to time, the ozone did not disappear. On the other hand, pure water has the property of destroying a small quantity of ozone. If ozone, obtained by the electrolysis of water, or by the action of the electrical spark, or by means of phosphorus, be largely diluted with atmospheric air, it will entirely disappear, if an attempt be made to collect it in a jar inverted over water. The following experiment is more precise. A flask provided with a ground glass stopper, of the capacity of half a litre, was filled with equal volumes of water and atmospheric air and inverted in the pneumatic trough. The ozone in a single bubble of electrolytic oxygen, passed quietly through the water into this volume of air, could easily be detected; but on agitating the water briskly, even four or five bubbles were deprived of their ozone. The same gas, agitated with twice its volume of lime water, or one-third of its volume of baryta water, also ceased to exhibit the reactions of ozone. In like manner, the action of caustic potassa is also limited. A strong solution of that alkali in a LIEBIG'S apparatus deprived one litre of electrolytic oxygen of its ozone, after which the ozone passed freely through it. These phenomena are singular and characteristic, and are the same with ozone from whatever source it is derived.

Peroxide of manganese destroys ozone, affording an interesting example of what is commonly called catalytic action. The oxide of manganese does not increase in weight, nor is water formed. Ozone from the three sources gives the same results.

The odour of ozone, from whatever source derived, is the same. The same remark applies to its property of bleaching, without producing at first an acid reaction.

Iodide of potassium is decomposed with the formation of iodate of potassa, and

oxidable substances in solution, as the protosulphate of iron, are raised to a higher state of oxidation by all the varieties of ozone.

It would not be difficult to extend this comparison, but enough has been shown, I conceive, to establish the absolute identity in properties of ozone in whatever way it may be prepared. Any difference which, on a superficial examination, may appear to exist, will be found on further inquiry to arise from the ozone being in a more or less dilute state.

That ozone is formed by the action of the electrical spark on perfectly dry oxygen, is placed beyond all doubt by the following experiment. The curved tube *a*, fig. 5, having two platina wires, *pp'*, hermetically sealed into it, was inverted over mercury and carefully filled with pure oxygen, after which a little sulphuric acid was introduced into one end (*b*). The whole was allowed to remain for twenty-four hours, when the oxygen was considered to be perfectly dry. Electrical sparks were now passed for some time between the platina wires, after which a solution of iodide of potassium was introduced into the other end of the tube. It became immediately coloured from the formation of free iodine, and the colour continued slowly to increase as the ozone was gradually absorbed.

Again, a solution of iodide of potassium may be made to absorb the whole of the oxygen in a narrow tube, by the passage of electrical sparks. This experiment has been described by FREMY and BECQUEREL, and I have myself repeatedly verified its accuracy. With a thermometer tube 2 inches long, the whole of the oxygen may be made to disappear in the course of one minute. The solution becomes always red from the decomposition of the iodide of potassium.

We have already seen that neither hydrogen nor nitrogen can be constituents of ozone, whether it be obtained from electrolysis, or from the action of the electrical spark on oxygen; and further, that all the supposed varieties of ozone exhibit in all respects identical properties.

Connecting all these facts together, it clearly follows,—

That no gaseous compound having the composition HO_3 is formed during the electrolysis of water; and

That ozone, from whatever source derived, is one and the same body, having identical properties and the same constitution, and is not a compound body, but oxygen in an altered or allotropic condition.

