OZONE*

I.

TOWARDS the end of the last century, Van Marum, while experimenting with his powerful electrical machine, observed that oxygen gas through which electrical sparks had been passed acquired a peculiar odour and the property of attacking mercury. This subject attracted no further attention for upwards of half a century after the publication of Van Marum's observations.

The discovery of ozone was announced by Schönbein in a memoir which he presented in 1840 to the Academy of Munich. In this important communication he states that in the electrolysis of water, an odorous substance accompanies the oxygen evolved at the positive pole, that this substance may be preserved for a long time in well-closed vessels, and that its production is influenced by the nature of the metal which serves as the pole, by the chemical properties of the electrolytic fluid, and by the temperature of that fluid, as well as of the electrode. The same body he found to be produced by holding a strip of platinum or gold near the knob of the prime conductor of an electrical machine in good order. With great sagacity he recognised the identity of the peculiar odour which accompanies a flash of lightning with that of the new substance. In this memoir Schönbein supposes the odorous body, for which, in a note at

FIG. 2.

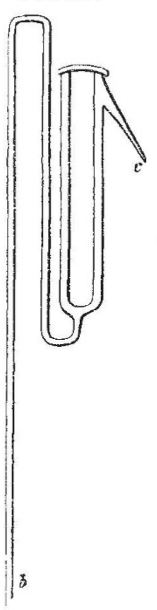
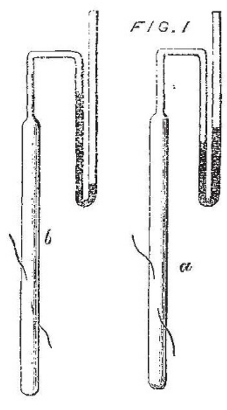


FIG. 1



the end, he proposes the name of ozone, to be a new electro-negative element belonging to the same class as chlorine and bromine; but in a paper published a little later he hints that ozone may be one of the constituents of nitrogen.

Schönbein soon afterwards discovered that ozone is formed when phosphorus oxidises slowly in moist air or oxygen.

In the following year, he returned to the consideration of the subject, and partly from his own observations, partly from experiments communicated to him by De la Rive and Marignac, he abandoned his former view of the nature of ozone, and concluded that it is an oxide of hydrogen different from the peroxide of hydrogen of Thénard.

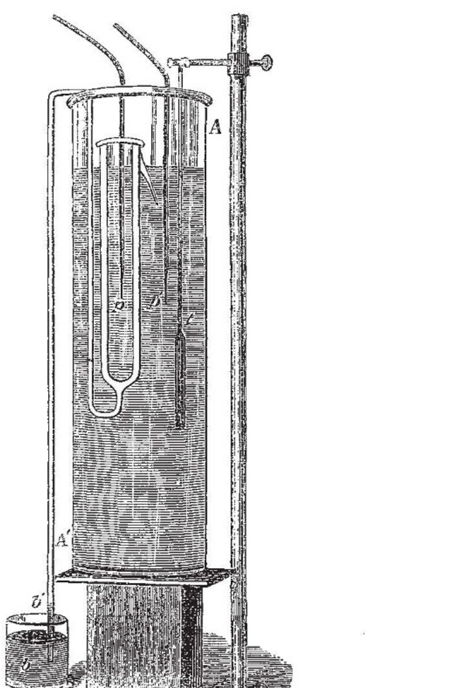
Many of the properties of ozone described by Schönbein were soon afterwards verified by Marignac, who found, as Schönbein had already stated, that it is only in the presence of moisture that air or oxygen when passed over phosphorus produces ozone, and that no ozone can be formed from air, even if moist, which has been deprived of its oxygen. He also confirmed the observations of Schönbein that the peculiar properties of ozone disappear when it is heated to a temperature between 300° C. and 400° C., and that it is not absorbed by water or sulphuric acid.

* An Address delivered before the Royal Society of Edinburgh on December 22, 1873, by Dr. Andrews, LL.D., F.R.S., Honorary Fellow of the Royal Society of Edinburgh.

In a subsequent investigation (1845) which Marignac conducted with De la Rive, the important fact was established that ozone is formed by the passage of electrical sparks through pure and dry oxygen gas. Frémy and Becquerel also showed that pure oxygen contained in a tube inverted over a solution of iodide of potassium is entirely absorbed by that liquid, if electrical sparks are passed for a sufficiently long time through the gas.

The last hypothesis of Schönbein, according to which ozone is an oxide of hydrogen, was manifestly inconsistent with the production of that body by the passage of electrical sparks through pure and dry oxygen. On the other hand, it received support from some experimental inquiries which appeared about this time, and particularly from an elaborate investigation which was conducted by Baumert in the laboratory of the University of Heidelberg, and published in *Poggendorff's Annalen* for 1853. Baumert maintained that water is always formed when dry ozone, prepared by electrolysis, is destroyed or decomposed by heat, and further endeavoured to establish its composition by determining the increase of weight of a solution of iodide of potassium when it is decomposed by ozone. He inferred, as the result of his researches, that two distinct bodies had been confounded

FIG. 3



under the name of ozone; (1) allotropic oxygen, formed by the passage of the electrical spark through oxygen; and (2) a teroxide of hydrogen, produced in the electrolysis of water. The experiments and conclusions of Baumert attracted a great deal of attention at the time they were published, and received very general assent.

Having repeated, soon after it was announced, the experiment of Baumert, in which ozone prepared by electrolysis was destroyed by heat, and having failed to obtain the slightest trace of water in numerous trials, I deemed it important to undertake a careful investigation of the subject, the results of which were communicated in 1853 to the Royal Society of London. By employing an acidulated solution of iodide of potassium, I found that its increase of weight, when decomposed by ozone, exactly agreed with the weight of the ozone calculated as allotropic oxygen from the iodine set free. The numbers deduced from five careful experiments were 0·1179 grammes for the increase in weight of the solution, and 0·1178 grammes for the calculated weight of the oxygen. As regards the supposed formation of water in the destruction of ozone by heat, it may be sufficient to mention the results of two experiments performed with great care, in one of which 6·8 litres of electrolytic oxygen containing

27 milligrammes of ozone, and in the other 9·6 litres of the same gas containing 38 milligrammes of ozone, were exposed to the action of heat, so as to destroy all ozone reactions, when not a trace of water was obtained; the increase in weight of the desiccating apparatus being in the first case only one-third, and in the second one-half, of a milligramme. If Baumert's experiments had been correct, 24 milligrammes of water should have been formed in these experiments. The general conclusions at which I arrived were: "that no *gaseous* compound, having the composition of a peroxide of hydrogen, 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.*" ("Phil. Transactions" for 1856, p. 13.)

The next step in the investigation of this singular body was the discovery that oxygen gas in changing into ozone diminishes in volume, or becomes condensed, recovering its original volume when the ozone is changed back into oxygen by the action of heat or otherwise. This relation between ordinary oxygen and ozone was first announced in 1860 by Prof. Tait and myself in a communication to the Royal Society of London. Oxygen gas in a dry and pure state was introduced into a tube sealed at one end and terminating at the other in a fine tube bent as shown in Fig. 1, and containing a short column of sulphuric acid. Two platinum wires were hermetically sealed into the sides of the wide tube, the distance of the ends within the tube being about 20 millimetres.

When an electrical discharge without visible sparks was passed between the extremities of the platinum wires, the sulphuric acid rose in the adjacent leg of the U-tube, and from the change of level the amount of the condensation, or diminution of volume, which the oxygen had undergone was easily calculated. The apparatus was then hermetically sealed and the reservoir heated to 270° C., so as to destroy the ozone. After allowing the reservoir to cool, the sealed end of the U-tube was opened, when the original volume of the gas was found to be restored. Strong electrical sparks were found to give scarcely one-fourth of the contraction which occurred with the silent discharge, and if sparks were passed through the gas when fully contracted by the silent discharge, the contraction was reduced to that which the spark would have produced in the original gas. In the same paper it was shown that no further diminution of volume occurred when the contracted gas was agitated with a solution of iodide of potassium so as to absorb the ozone. A similar result was obtained on agitating the contracted gas with iodine. The ozone reactions in all these cases disappeared, but without any change in the volume of the gas. With mercury and silver, not only was there no contraction, but expansion actually occurred, which was explained on the assumption that the oxide at first formed exercised a catalytic action on part of the ozone and restored it to the state of ordinary oxygen. Similar results were obtained with electrolytic ozone. Three years later these experiments on the condensation of oxygen in changing into ozone, and on the action of ozone upon a solution of iodide of potassium were repeated and confirmed by Von Babo and by Von Babo and Claus.

We did not attempt to give any absolute explanation of these singular facts; but discussed them under different aspects. We showed that on the allotropic view of the constitution of ozone its density must be enormously great; unless it was assumed that "when ozone comes into contact with such substances as iodine, or a solution of iodide of potassium, one portion of it, retaining the gaseous form, is changed back into common oxygen, while the remainder enters into combination, and that these are so related to one another that the expansion due to the former is exactly equal to the contraction arising from the latter." On this assumption, which however we did not consider probable, we remarked that "our experiments may be reconciled with the allotropic view, and an ordinary density, but still one greater than that of oxygen." A similar explanation of our experiments but connected with a peculiar view of the molecular constitution of oxygen was proposed in 1861 by Dr. Odling. "If we consider," he remarks, "ozone to be a compound of oxygen with oxygen and the contraction to be consequent upon their combination, then if one portion of this combined or concentrated oxygen were absorbed by the reagent, the other portion would be set free, and by its liberation might expand to the volume of the whole; thus, if we suppose three volumes of oxygen to be condensed by their mutual combination into two volumes, then on absorbing one-third of this combined oxygen by mercury, the remaining two-thirds would be set free and consequently expand to their normal bulk, or two volumes—

$$\overset{-}{O}\,\overset{+}{O}\,\overset{-}{O} + \overset{+}{Hg^2} = \overset{+}{Hg^2}\overset{-}{O} + \overset{+}{O}\,\overset{-}{O}."$$

Soret, experimenting in 1866 upon the mixture of oxygen and ozone obtained by electrolysis, made the important discovery, that if this mixture is brought into contact with oil of turpentine, or oil of cinnamon, a diminution of volume takes place, equal in amount to twice the augmentation of volume which the same mixture would sustain if the ozone were converted by heat into ordinary oxygen. In other words the volume of ozone, measured by its absorption by the essential oil, is twice as great as the difference between the volume of the same ozone and oxygen. Hence Soret concluded that the density of ozone is one and a half times that of oxygen gas.

The latest investigations on this subject are due to Meissner and Brodie. The former has fully confirmed my early experiments, according to which the increase in weight of an acid solution of iodide of potassium, when electrolytic ozone is passed through it, corresponds exactly to the weight of oxygen absorbed, as calculated from the liberated iodine. Meissner has also found, as I had long before stated, that when a neutral solution of iodide of potassium is employed, the results are variable and untrustworthy.

Brodie has examined the action of ozone on a variety of liquids, and has confirmed the results of Prof. Tait and myself that no diminution of volume occurs when ozone is removed from a mixture of ozone and oxygen by a solution of iodide of potassium. With other liquids he has obtained volumetric results which he considers to be definite and which differ from any previously observed. I am inclined to think that they are rather complex cases, involving the volumetrical changes already known in variable proportions. His experimental results, moreover, when examined in detail, do not appear to be sufficiently concordant to justify the sharp conclusions he has deduced from them.

Brodie has obtained for ozone prepared by the electrical discharge the same density (one and a half times that of oxygen) which Soret had previously obtained for ozone prepared by electrolysis. He considers a suggestion of Prof. Tait and myself, that oxygen may possibly be decomposed by the electrical discharge, not to be supported by the facts he has observed.

I will now give a brief statement of the methods of preparing ozone and of its leading properties.

Ozone may be obtained by the action of the electrical spark, or the glow or silent discharge on pure oxygen. With the silent discharge, as has been before stated, at least four times as large an amount of ozone is obtained as with the spark. As regards the actual amount of oxygen which, under the most favourable conditions can be converted into ozone, the highest recorded result was obtained in an experiment by Prof. Tait and myself, in which a contraction of one-twelfth of the original volume of the oxygen, or 8·3 per cent., occurred; but we were unable in other trials to produce again so great a diminution of volume. The greatest contraction attained in the experiments of Von Babo and Claus amounted to 5·74, and in those of Brodie to 6·52 per cent. The doubt which existed as to the accuracy of our solitary experiment I have lately been able to remove, and by a slight modification in the form of the apparatus I have succeeded in obtaining greater contractions than any hitherto recorded. In one of the first trials the diminution of volume amounted to more than 10 per cent., and there can be little doubt that with care even greater contractions than this may be attained.

As the method referred to enables the contraction of oxygen in changing into ozone to be exhibited as a class experiment, I will describe it in some detail. The excellent induction tube of Siemens, in which the electrical discharge from an induction coil acts upon air or oxygen, as it flows between two thin tubes of glass, whose surfaces are at a distance of a few millimetres from one another, has hitherto been employed to obtain a continuous stream of ozone in a more or less concentrated state. But this apparatus can easily be modified so as to show the contraction which takes place when oxygen is converted into ozone. Fig. 2 exhibits the modification I have given for this purpose to the ordinary form of Siemens' tube. At *c* it terminates in a capillary tube, the end of which is hermetically sealed, after a stream of pure and dry oxygen gas has been passed through the apparatus for a sufficient time to displace the air. In exact experiments the other end (*b*) is at the same time sealed and afterwards opened under sulphuric acid. For class purposes it will be found sufficient to immerse it quickly under the acid, contained in the beaker (*a*), as shown in Fig. 3, where the induction-tube is seen immersed to within 12 millimetres of its upper surface in water contained in an *insulated* cylindrical vessel (A A′). The inner cavity of the induction-tube is also filled with water to about the same level. By means of wires covered with caoutchouc, except at the lower ends (*p p*′), the discharge from an induction-coil, capable of giving 10 millimetre sparks in air, can be passed through the apparatus. The water in A A′ is maintained as steadily as possible at the temperature of the apartment, and any slight changes in the course of the experiment are noted by means of a delicate thermometer (*t*). The variations of the barometer are also carefully observed. In very exact experiments the surfaces of the induction-tube should be covered with tinfoil, and the cylindrical vessel filled with ice. Before commencing the observation, it will be found convenient, if the temperature has not already effected the adjustment, to expel a little oxygen from the induction-tube, so that the level of the acid may stand somewhere about *b*′. On passing the electrical discharge, the acid will at first be depressed a few millimetres, from the repulsive action of the particles of the electrified gas, but will afterwards steadily rise, and for some time with such rapidity that the ascent of the acid column can be easily followed by the eye. When the current is interrupted, a sudden rise of the acid column will occur equal to the depression which took place on first making connection with the induction coil, after which the new level of the acid may be read.

Another method of obtaining ozone is by the electrolysis of water and of certain acid and saline solutions. The most convenient liquid for this purpose is a mixture of one part of sulphuric acid with six or eight parts of water, and the lower the temperature at which the electrolyte is maintained during the process the greater is the amount of ozone. The simplest and most efficacious arrangement for obtaining ozone by this method is one I have used for many years and exhibited in my lectures. It consists

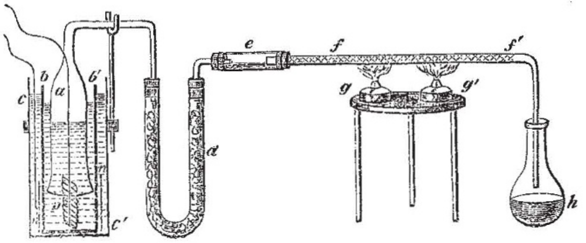


FIG. .

of a bell-jar (Fig. 4, *a*), or glass cylindrical vessel, open below, and contracted to a neck above, which is suspended in a round cell (*b b*′) of porous earthenware, leaving a clear space of two inches between its lower edge and the bottom of the porous cell. The whole is placed in a glass jar (*c c*′) of somewhat larger dimensions than the cell; a bundle of platinum wires (*p*) suspended below the bell-jar serves as the positive pole, and a broad ribbon of platinum (*n n*′) placed between the outer glass jar and the porous cell as the negative pole of a voltaic arrangement of three or four couples. A delivery tube hermetically united to the neck of the bell-jar conveys the mixture of oxygen and ozone disengaged at the positive pole to a sulphuric acid drying tube (*d*). From the desiccating tube the gas passes through the connecting tube (*e*) and thence to other tubes, for the purpose of illustrating the properties of ozone. Thus, in the figure, it is represented as traversing a tube of hard glass (*f f*′) covered with fine wire gauze, and terminating near the surface of mercury contained in the flask (*h*). So long as the gas is heated strongly as it passes through the tubes (*f f*′) by the spirit lamps (*g g*′), not the slightest change is produced upon the mercury; but when the lamps are removed, and the tube allowed to cool, the mercury is rapidly attacked. I ought, perhaps, to mention that all the junctions are made with dry and tightly fitting corks, care being taken that the ends of the connecting tubes project a little beyond the corks. With these precautions the loss of ozone, from its action on the corks, is altogether insignificant.

Ozone can also be obtained by the slow oxidation of phosphorus, and of certain ethers and essential oils in presence of moisture.

(*To be continued.*)

NOTES

ONE of the last and one of the best acts of the late Government was to grant a pension of 150*l.* a year on the Civil List to Prof. Sharpey. Dr. Sharpey has done as much as any living teacher for the advancement of physiological knowledge, while his personal worth has secured for him universal respect and esteem.

AT the last monthly meeting of the Russian Imperial Geographical Society M. Venioukoff, the secretary, before proceeding with the business of the evening, said the Society owed a duty which must first be fulfilled, and that was to render homage to the memory of Dr. Livingstone, the importance of whose discoveries and the perseverance of whose labours had placed him in the rank of the most remarkable travellers of all times and of all nations. His biography belonged to the annals of geographical science. M. Venioukoff then read a memoir of Livingstone, which concluded as follows:—"Let England, which may be proud of having given birth to Livingstone, and of having supported him in his labours, learn that among us the merit of her great men can be appreciated." The whole assembly, which was very large, then rose in order to pay a last tribute of respect to the memory of Dr. Livingstone.

THE University of St. Andrew's has conferred upon Mr. J. Gwyn Jeffreys, F.R.S., the honorary degree of LL.D.

WE would draw special attention to the programme, which has just been issued, of a new course of twelve lectures on Zoology, to be delivered during the ensuing spring, in the Zoological Gardens, Regent's Park; the Council of the Society having determined to appropriate the interest of a small bequest which they hold for scientific purposes—the Davis Fund—to the subject. Mr. P. L. Sclater, F.R.S., the Secretary to the Society, will deliver the Introductory Address on April 14; and he will follow it by four lectures *On the Geographical Distribution of Mammals.* After these Mr. A. H. Garrod, the Prosector to the Society, will give five lectures *On the General Classification of the Vertebrata*; and Dr. Carpenter, F.R.S., will conclude the course by giving two *On the Aquarium and its Inhabitants.* The lectures will be delivered on the Tuesdays and Fridays in April and May, at 5 o'clock in the afternoon; they will be free to Fellows of the Society and their friends, and to other visitors to the Gardens. The subjects will be treated in a manner which will make them of general interest, and it is to be hoped that ladies will avail themselves of the opportunity thus afforded, of obtaining information on this too much neglected branch of the great science of Biology.

MR. PHILIP BARNES, who died on Feb. 24, at the age of 82, was one of the oldest Fellows of the Linnean Society. He was a native of Norwich, and a cousin of the Sowerbys. Thirty-four years ago he founded the Royal Botanic Gardens in the Regent's Park, and was the oldest Fellow and father of the Society. A portrait of Mr. Barnes was in the last International Exhibition, and a bust in that of the year before. He was father of Robert Barnes, M.D., and of the late Philip Edward Barnes, the former known in the scientific world by his professional discoveries and writings, and the latter the author of a work on the Belgian Constitution.

THE death, from heart-disease, of Prof. J. F. Holton is announced as having taken place in Everett, Massachusetts, U.S., on the 25th of January. Prof. Holton was well known as a botanist, having devoted many years to the study of the science. He visited South America with special reference to prosecuting his researches in this direction, and studying the relation between the physical geography and the vegetation of the Andes. His somewhat extended sojourn in that country enabled him to collect materials for a work, which was published after his return by Harper and Brothers, and is frequently quoted by botanists.