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LVI.—*On the Electrolysis of Aqueous Solutions of Sulphuric Acid, with special Reference to the Forms of Oxygen obtained.*

By HERBERT MCLEOD.

DURING the discussion on Electrolysis at the meeting of the British Association at Aberdeen last year, Dr. Lodge remarked that it was well known that when Wollaston wires are used as electrodes in the decomposition of acidulated water, a considerable quantity of the oxygen is liberated in the form of ozone.

The following papers contain references to the production of ozone by this process:—

Shönbein (1840), *Ann. Phys. Chem.*, **50**, 616—635. "Beobachtungen über den bei der electrolysation des Wassers und dem Ausströmen der gewöhnlichen Electricität aus Spitzen sich entwickelnden Geruch." Five or six times diluted sulphuric acid [from 23·5 to 26·9 per cent. by weight] is best. Phosphoric acid and other solutions when electrolysed produce the same odour.

De Marignac (1845), *Compt. rend.*, **20**, 808—811. "Sur la production et la nature de l'ozone." The liquid used was water charged with sulphuric acid and kept cool. The size of the electrode, the strength of the solution, and the quantity of ozone produced are not stated.

Williamson (1845), *Mem. Chem. Soc.*, **2**, 395—398. "Some Experiments on Ozone." Liquid used consisted of 1 volume of sulphuric acid and 3 of water [38 per cent.]. No measurements of the quantity of ozone are given, as the experiments were made on the assumption that ozone was a peroxide of hydrogen.

H. Meidinger (1853), *Annalen*, **88**, 57—81. "Ueber voltametrische Messungen." The acid used had a density of 1·3. Small quantities of ozone were produced and large quantities of "peroxide of hydrogen."

Baumert (1853), *Ann. Phys. Chem.* **89**, 38—55, and *Phil. Mag.* [4], **6**, 51—63. "Ueber eine neue Oxydationsstufe des Wasserstoffs und ihr Verhältniss zum Ozon." Electrolytic oxygen obtained by electrolysis of dilute sulphuric acid with large positive plate and small negative electrode passed through solution of potassic iodide and afterwards through sulphuric acid, and the gain of weight of the absorption apparatus determined. In one experiment, an increase of 0·0133 in six days was obtained, and in another 0·0149 in eight days.

H. Meidinger (1854), *Chem. Soc. J.*, **7**, 251—255. "On the occurrence of Ozone and Peroxide of Hydrogen in the Electrolysis of Sulphuric Acid." The positive electrode used was 20 mm. long and

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$\frac{1}{2}$ mm. thick. The acid seems to have had a density of 1·4. 253 c.c. of hydrogen and 40 c.c. of oxygen were evolved in 19 minutes. When the oxygen was heated, no change of volume could be perceived, and when the gas was acted on by solution of potassic iodide there was a diminution of volume equal to $\frac{1}{300}$th. The acid that had been electrolysed decomposed potassic iodide and so was supposed to contain peroxide of hydrogen, but no determination of its quantity was made. He thinks that if the temperature were sufficiently lowered, pure ozone might be produced. The best acid to give hydrogen and oxygen in proper proportions has a density of 1·1, the negative electrode should be a wire and the positive a plate of not too small dimensions.

Andrews (1855), *Phil. Trans.*, 1856, 1—14. "On the Constitution and Properties of Ozone." The acid used was made by mixing 1 volume of sulphuric acid with 7 of water [20·81 per cent.]. The positive electrode was a bunch of fine wires, and the negative electrode a platinum plate; the liquid was cooled by ice and water. The electrolytic oxygen was passed through a solution of potassic iodide acidified with hydrochloric acid, at the rate of about 750 c.c. of gas per hour. The acid solution was found to give the same results as a neutral solution [a statement contested subsequently by Brodie]. After passing through the potassic iodide, the gas was conducted through drying tubes and the increase of weight determined. The quantity of iodine liberated was also determined volumetrically. Mean of five experiments gave 0·0041 gram of ozone for 1 litre of gas. If ozone is O_3, this number must be multiplied by 3, giving 0·0123 gram or 0·85 per cent. [He says, "Pure water does not absorb ozone."]

Tyndall (1862), *Phil. Trans.*, 1862, 84—86. In his second memoir—"On the Absorption and Radiaton of Heat by Gaseous Matter," used electrolytic oxygen. Small electrodes, less than one square inch in area, were employed, but the exact size is not stated. The quantity of ozone was not determined, but he says, "The quantities of ozone with which I have operated must be perfectly unmeasurable by ordinary means."

L. Soret (1863), *Arch. des Sciences*, **16**, 208—215; *Compt. rend.*, **56**, 390—393. "Sur la production de l'ozone par l'électrolyse et sur la nature de ce corps." The electrodes were very fine wires of platinum-iridium; when platinum is used, a black deposit is formed on the wires which destroys some of the ozone. The acid used contained 1 volume of sulphuric acid to 5 of water [26·9 per cent.]. At a temperature of 5° or 6°, oxygen containing 1 per cent. of ozone was produced (on the assumption that to one equivalent of iodine liberated from the potassic iodide corresponds one equivalent of ozone considered

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as an allotropic modification of oxygen). When the acid was cooled with ice and salt, 2 per cent. was formed. [As with Andrews' results, these numbers must be multiplied by 3, so that 3 and 6 per cent. were really obtained.]

Brodie (1864), *Chem. Soc. J.*, **17**, 293. In a paragraph at the end of his paper "On the Organic Peroxides theoretically considered," states that peroxide of hydrogen is not formed during electrolysis, and he thinks that the peroxide of sulphuric acid, H_2SO_5, is present.

C. Hoffmann (1867), *Ann. Phys. Chem.*, **132**, 607—618. "Einige Versuche über die bei der Elektrolyse des Wassers auftretenden Mengen von Ozon und Antozon." A negative wire used and a positive plate, but the dimensions are not given. Gases were not collected, but the relative oxidising action of the gas and the liquid was determined.

Berthelot (1878), *Compt. rend.*, **86**, 71—76, and *Ann. Chim. Phys.* [5], **14**, 354—361. Acid of density 1·4 was used; the positive electrode was of fine platinum wire, sealed into a glass tube. The size of the wire is not given. 910 c.c. = 1·250 grams of oxygen were collected and contained 6·6 mgrms. of ozone [0·528 per cent.]. Active oxygen in the liquid (not hydroxyl) was 44 mgrms. This Berthelot supposes to be present as persulphuric acid. The liquid effervesced. Phosphoric acid gave ozone, but no oxidising liquid. When sulphuric acid, H_2SO_4,H_2O, was used, a small quantity of peroxide of hydrogen was formed containing a quantity of active oxygen, only $\frac{1}{10}$th of that present as persulphuric acid. With the acid, $H_2SO_4,\frac{1}{2}H_2O$, only half this quantity of peroxide of hydrogen was produced.

Schöne (1873), *Ber.*, **6**, 1224—1229. "Ueber das Verhalten von Ozon und Wasser zu einander." The percentage of ozone by volume in the electrolytic oxygen varied between 3·29 and 8·63.

Carius (1874), *Annalen*, **174**, 1—30. "Verhalten das Ozons gegen Wasser und Stickstoff." The acid used was made by mixing 1 "part" of sulphuric acid with 5 of water, and the positive electrode consisted of a very thin platinum-iridium wire 15 mm. long. 100 c.c. of the oxygen contained quantities of ozone varying between 1·438 and 3·44 c.c.

Many of the papers just cited were consulted after the completion of the experiments described in this paper, and it will be seen that some of the results obtained have been anticipated by other experimenters.

As it appeared to be of interest to determine what quantity of ozone is generated during the electrolysis, a series of experiments was instituted in the hopes of throwing some light on the phenomena of the electrolysis of dilute sulphuric acid under various conditions.

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In the preliminary experiments, the hydrogen which was evolved from a pole of platinum foil was collected and measured, and the gas from the positive pole, which was of fine wire, was passed through a solution of potassic iodide mixed with hydrochloric acid. The quantity of ozone was calculated on the assumption that only hydrogen, oxygen, and ozone were produced during the electrolysis. Subsequently the oxygen was also collected, when it was at once seen that there was a great deficiency of oxygen, and on adding potassic iodide to the acid which had been electrolysed a considerable quantity of iodine was liberated. This was at the time supposed to be hydroxyl, and means were adopted to prevent its being carried by the oxygen into the potassic iodide used for absorbing the ozone. For this purpose a tube containing potassic dichromate was interpolated, but after it had been in use for some time it was noticed that the dichromate was entirely unaffected, and on testing the acid with potassic dichromate and ether it was found that the oxidising substance is not hydroxyl. Shortly after this observation, Mr. Madan called my attention to a paper by Brodie, on "Organic Peroxides theoretically considered" (*Chem. Soc. J.* (1864), **17,** 281—294), at the end of which is the statement that, during the electrolysis of dilute sulphuric acid, an oxidising substance is produced which does not give the reactions of peroxide of hydrogen, but which may be the hydrate of SO_4, or H_2SO_5. In all probability, the compound is Berthelot's persulphuric acid, the anhydride of which he obtained by the action of the electric effleuve on a mixture of sulphurous anhydride and oxygen. I have not yet examined this compound, but I may mention that during a visit to my laboratory, Mr. C. E. Groves found that after boiling the liquid, it produced perchromic acid when shaken with potassic dichromate and ether.

In the early experiments, an error was probably introduced in the determination of the quantity of ozone by the employment of an acid solution of potassic iodide. Brodie showed that a strong solution of hydriodic acid gives results much too high, and although my solution was dilute and, in fact, almost of the strength that Brodie found to give nearly correct results, yet it will be safer to reject all the numbers, although it involves the sacrifice of 27 experiments.

The apparatus with which all the recent experiments have been made is the following:—A U-tube (see Fig., p. 595), 16 mm. in diameter, has a bulb blown on one limb, and joined near the top of each limb is a tube to conduct away the gases. The ends of the U-tube are closed with corks. The positive electrode consists of a tube closed at the lower end into which the fine platinum wires are sealed; this tube is filled with mercury to make the electric contact, and it is necessary to boil the mercury in the tube to ensure contact with the fine wires.

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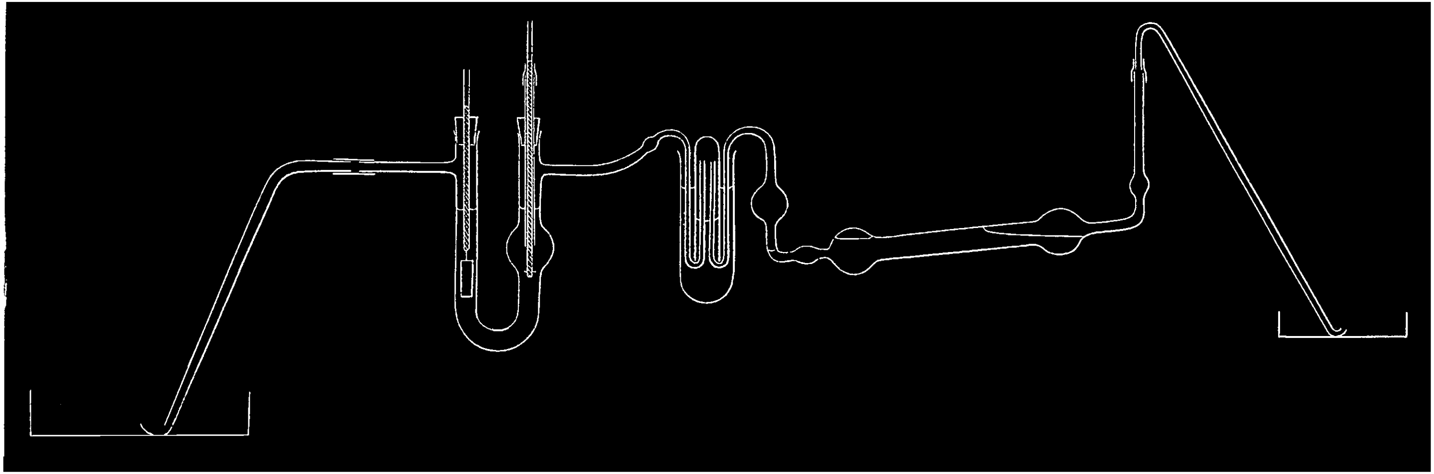

Apparatus used for the Electrolysis of Solutions of Sulphuric Acid. $\frac{1}{6}$ Real Size.

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This electrode passes through a slightly wider tube fitted to a cork well soaked in melted paraffin and fixed to the limb of the U-tube on which the bulb is blown, the fine wires being about the level of the bottom of the bulb. The negative electrode consists of a platinum plate welded to a platinum wire which is also fused into a glass tube containing mercury and fitted by a cork to the other limb of the U-tube. The hydrogen passes through the tubulure to a delivery-tube dipping into a pneumatic trough, and is collected in a graduated cylinder. During the electrolysis, the U-tube is placed in a beaker containing a mixture of ice and water which is kept stirred by blowing air bubbles into it through a thistle funnel as suggested many years ago by Harcourt and Esson; the air is supplied from a water-pump, and by this device the apparatus may be left with very little attention. The object of the bulb on the U-tube is to cause the cold convection currents to impinge on the positive electrode and prevent its rising in temperature. The ozonised oxygen passes through a narrow U-shaped tube to the absorption-tube containing solution of potassic iodide, this latter tube being also provided with a narrow U-tube; the free limbs of the U-tubes are covered by a closed piece of glass tube, and the whole stands in a wide test-tube containing water, thus forming a water joint which has been found more convenient than the paraffin joint used by Brodie. The absorption-tube is made of a piece of wide tube with a bulb at each end; it is placed in a slightly inclined position, and is similar to some of those employed in Brodie's experiments. To the further end of the absorption tube, a delivery-tube passing to a pneumatic trough is fixed by a caoutchouc joint, and the oxygen is collected in a 100 c.c. measure. The troughs are shallow tin vessels filled to the brim and of such a depth that the pressure is equal on the liquid in both limbs of the U-tube; as the water is displaced from the graduated measure it flows over the edges of the troughs and thus the pressure remains constant during the whole experiment. The absorption-tube contains about 30 c.c. of a solution of potassic iodide containing 0·75 gram of the salt.

When about 100 c.c. of oxygen have been collected, the electric contact is broken immediately after a bubble has passed through the absorption-tube, the delivery-tubes are removed from the troughs and a tube from an aspirator is connected to the oxygen delivery-tube. The test-tube of the water joint is lowered, the negative electrode removed and the greater part of the acid in the U-tube is withdrawn by means of a pipette. This liquid is saturated with ozone and usually effervesces. A slow stream of air is now drawn through the apparatus for about half-an-hour, so that all the ozone may be deposited in the potassic iodide solution. The apparatus is then dis-

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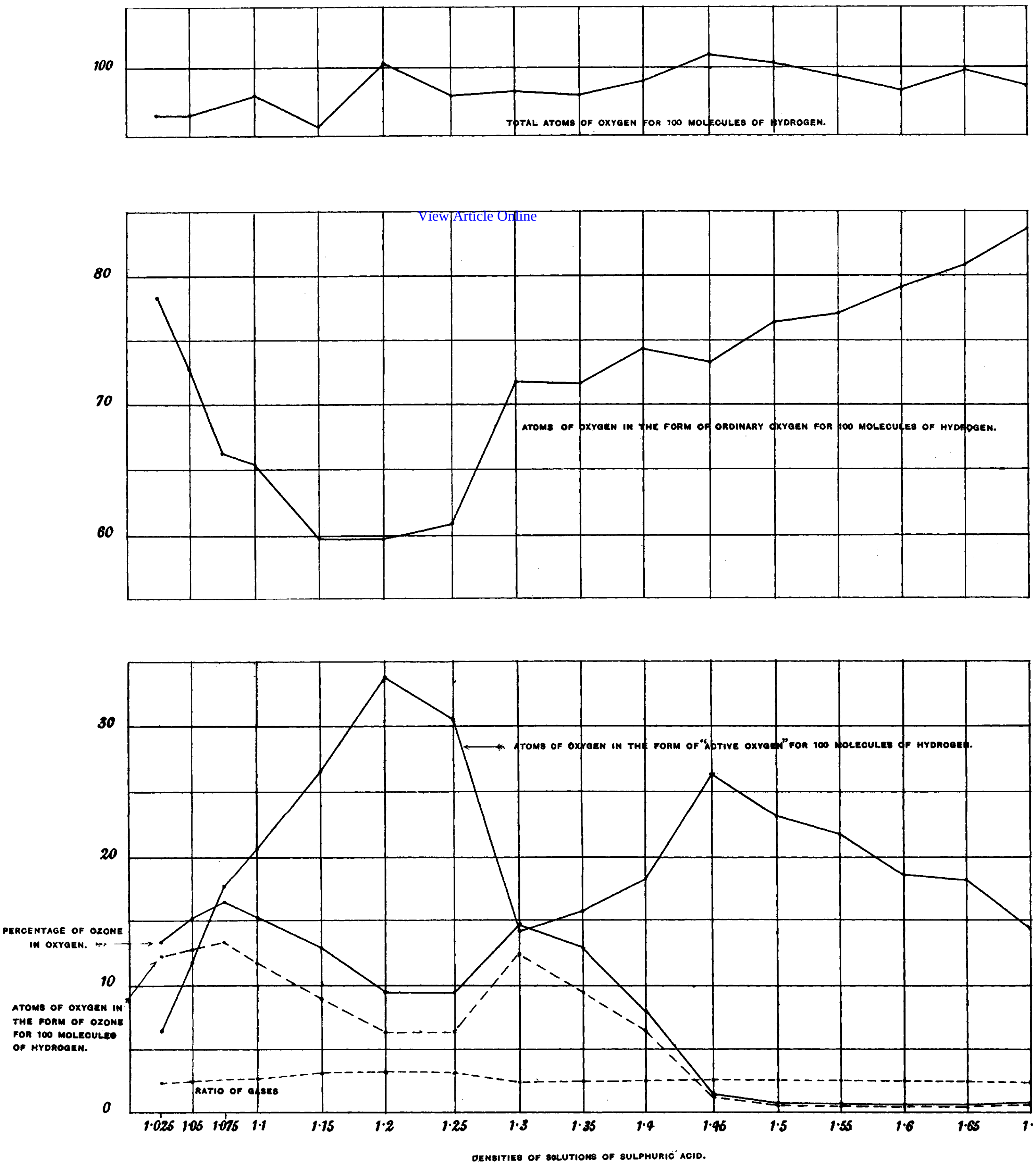
RESULTS OBTAINED WITH ELECTRODES MADE WITH WIRES ·045 MM. IN DIAMETER.



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RESULTS OBTAINED WITH ELECTRODES MADE WITH WOLLASTON WIRES ·027 MM. IN DIAMETER.

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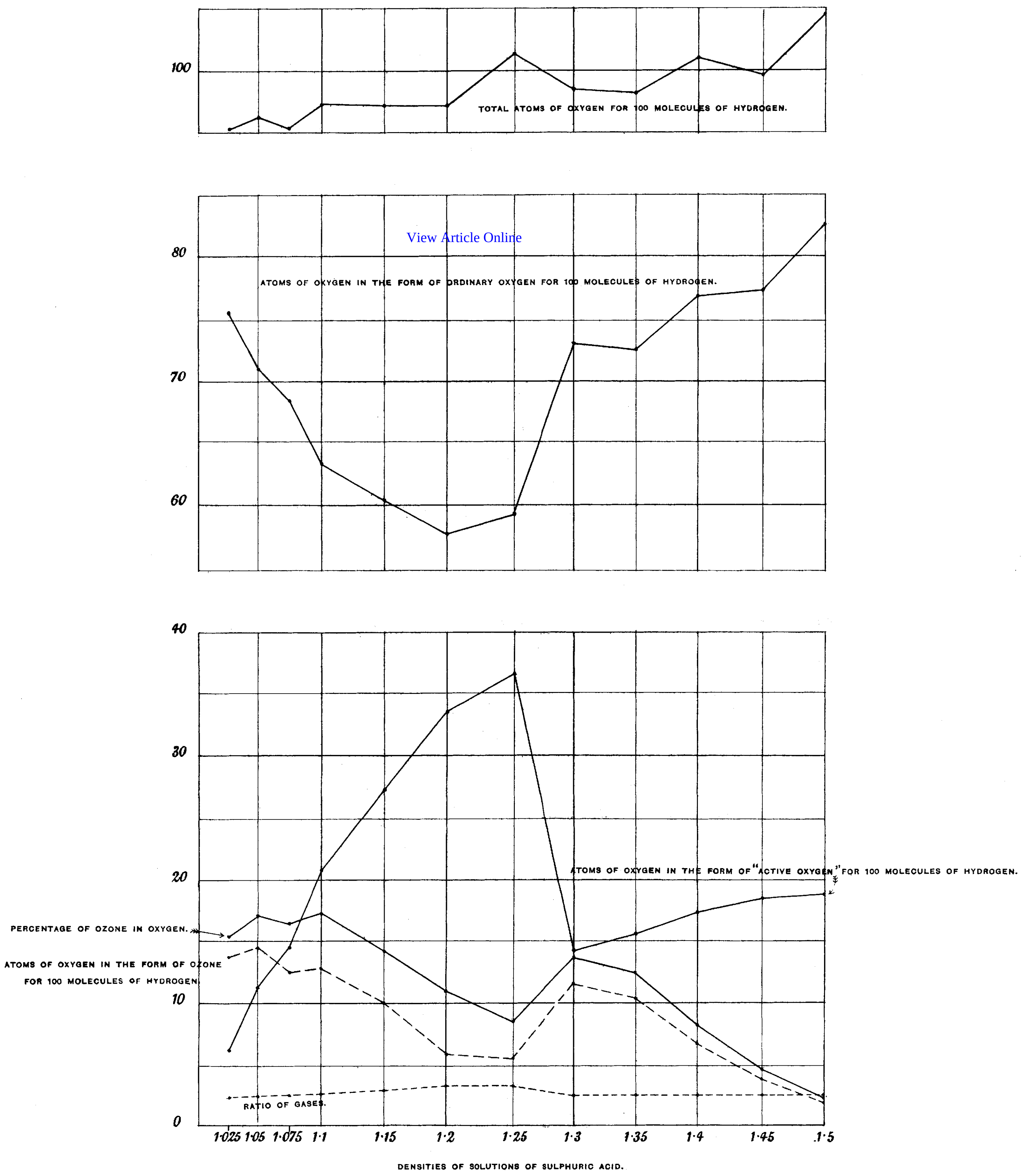

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mounted, the remaining acid poured from the U-tube and measured. The contents of the absorption-tube are washed into a flask and mixed with about one-fourth of its volume of dilute hydrochloric acid, when the brown colour of the liquid is much intensified. It is next decolorised by decinormal solution of sodic thiosulphate: the addition of starch is unnecessary, as the disappearance of the brown colour is quite sharply defined. The gases are measured by placing the cylinders in water so that the levels are equalised, the temperature and barometer being simultaneously read. To determine the quantity of oxygen which has formed the oxidising material produced in the acid, 10 c.c. of the liquid are placed in a flask, mixed with water and solution of potassic iodide, and kept in the dark until the following day, as the oxidising action is incomplete until after the lapse of some hours; it is then decolorised by decinormal solution of sodic thiosulphate. The oxidising substance not being identified, the quantities obtained are called "active oxygen," a name used by Berthelot.

The currents used for the electrolysis are measured by a tangent galvanometer, the values of the deflections of which are known. Latterly the wires of the positive electrode have been measured by a microscope micrometer before and after each experiment; and from the mean of the measurements, the area of the electrode is calculated, this combined with the current measured by the galvanometer gives the current density, that is, the intensity of the current at the surface of the positive electrode.

The solutions of sulphuric acid were made by diluting with distilled water some pure redistilled sulphuric acid supplied by Messrs. Hopkin and Williams. Their densities were taken by hydrometers at 15° C., and the quantities of acid they contained were determined by a standard solution of sodic hydrate. The following solutions were used:—

Density.	Percentage of SO_2Ho_2.	Molecules of OH_2 to 1 of SO_2Ho_2.	Density.	Percentage of SO_2Ho_2.	Molecules of OH_2 to 1 of SO_2Ho_2.
1·025	3·92	133·4	1·35	46·459	6·3
1·05	7·373	68·4	1·4	51·333	5·2
1·075	11·122	43·5	1·45	55·421	4·38
1·1	14·611	31·8	1·5	60·978	3·48
1·15	21·061	20·4	1·55	65·755	2·83
1·2	27·533	14·3	1·6	69·825	2·35
1·25	34·272	10·4	1·65	74·440	1·87
1·3	40·105	8·1	1·7	78·592	1·48

Various forms of electrode have been tried. In some of the preliminary experiments, pieces of Wollaston wire about 0·03 mm. in

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diameter were used. In others, some drawn wires about 0·045 mm. in diameter and flattened, were fused into the glass. One electrode was made with six wires, 0·047 mm. in diameter, the total length of the wires being 104 mm. A series of experiments was made with this electrode, the wires being shortened after each electrolysis, until the total length was only 6 mm. As the wires were shortened the quantity of ozone produced increased, the current being approximately the same in all cases, so that it appears that the formation of ozone depends on current density.

In the first set of experiments of which the results are given below, an electrode was used consisting of six wires, each about 1 mm. long and 0·045 mm. in diameter. Duplicate experiments were made, commencing with acid of density 1·025 and proceeding to that of 1·35. In the last experiment, the current was noticed to be very irregular, which was attributed to a bad contact in the battery, but after cleaning the binding screws there was no improvement, and the experiment was stopped. On examining the electrode it was found that the wires had been much attacked, three of them had almost disappeared, and the remainder were very much thinned. The negative electrode was blackened at its lower edge, which was thought at first to be due to the precipitation of lead from the sulphuric acid, but boiling nitric acid did not remove the stain: on heating the plate red hot, the black colour was at once destroyed and the metal became lustrous, so that the platinum dissolved from the positive electrode had been partially deposited on the negative. It was afterwards noticed that in determining the "active oxygen," in the acid that had been electrolysed, after the brown colour of the iodine had been discharged and before the liquid was quite decolorised, it assumed the pink colour of platinic iodide.

The next electrode was made with platinum wire containing 15 per cent. of iridium, this dissolved in the same manner in the acid of density 1·35.

As the electrodes with fine wires are somewhat troublesome to make, it was hoped that a thicker wire, but of such a length as to expose the same surface and thus maintain the same current density, would be equally efficacious. An electrode was therefore made with a piece of wire, 0·33 mm. in diameter and 0·6 mm. long, but this gave less ozone, although the "active oxygen" was increased.

The next electrode consisted of a fine platinum-iridium wire fed through a capillary tube, so that a fresh piece could be used for each experiment. The resistance of the wire, however, made the operation very slow and the electrode was abandoned.

A new electrode was then made with a single wire 6 mm. long, and placed vertically in the tube. This gave less ozone; but a similar

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electrode with the wire horizontal produced a larger quantity. This variation seems to be due to the heat generated in the wire by the current: when the wire is vertical, the evolved gas travels up the wire, and if this is heated some of the ozone will be destroyed; with the horizontal wire, however, the gas at once passes into the cold liquid and the ozone is preserved.

The next electrodes consisted of two wires projecting about 3 mm.; it appeared occasionally that one of the wires made a better contact with the mercury than the other, so afterwards a single wire was passed across the tube and projected about 3 mm. on each side. This form of electrode was used for the remaining acids, a new one being made for each pair of experiments.

Another series of experiments with acids of densities from 1·025 to 1·25, was made with an electrode of one Wollaston wire 0·027 mm. in diameter projecting on each side of the tube, having a total length of 5·3 mm. This was not much attacked by the acid, and I began to think that the previous destruction of the electrodes was due to the presence of a trace of chlorine in the distilled water, but when the acid of density 1·3 was used, the platinum was dissolved, and with the 1·35 acid the electrode had almost disappeared, when 53 c.c. of oxygen had been collected. New electrodes were then made for each experiment, but the series was not continued beyond the acid of density 1·5, as the results were so similar to those obtained with the thicker wires.

As electrolysis seems a convenient process for obtaining ozonised oxygen, it appeared to be worth while to endeavour to construct an apparatus which would yield it more rapidly than the one above described, which has never produced 100 c.c. in less than an hour, and has usually taken very much longer. Two things are essential, a high current density and the electrode being kept cool. The latter condition was fulfilled by blowing a hole on the side of a U-tube, and fusing on to it a small circular electrode made of platinum foil, and surrounding the edge of the platinum disc with arsenic glass or white enamel, which was recommended to me some years ago by Mr. Crookes. The enamel is very fusible, and as it adheres strongly to the platinum and fuses well into the glass, it retains the platinum firmly in its place. When the U-tube is placed in ice and water, the heat produced is rapidly conducted away through the plate of metal. The area of the electrode exposed inside the tube was about 1·9 mm. in diameter, and it was not found possible to obtain a high enough current density with the U-tube employed, for the resistance of the acid would not allow a sufficient quantity of electricity to pass. The result was that the percentage of ozone was only about half that obtained from the same acid with the fine wire electrodes. No doubt

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if a wider U-tube had been employed, the results would have been more favourable.

It may be well to give an example of the observations and calculations made in one experiment which will show all the data from which the results are obtained. I select the one giving the maximum quantity of ozone when the first electrode was used.

Jan. 12, 1886. Electrolysis of acid of density 1·075.

Electrode of six platinum wires 6 mm. long and 0·045 mm. diameter.

Area of electrode at sides $= 0{\cdot}045 \times \pi \times 6 = 0{\cdot}8482$ sq. mm.

„ „ ends $= 0{\cdot}045^2 \times \frac{\pi}{4} \times 6 = 0{\cdot}00954$ sq. mm.

Total area................ $= 0{\cdot}85774 =$ 0·0085774 sq. cm.

8 cells of Grove used.

Started	9.45,	galvanometer deflection	11°
	9.50	„ „	11·2°
	9.54	„ „	11·3
	10.0	„ „	11·4
	10.40	„ „	11·6
Stopped	11.7		

Mean deflection 11·3°; current = 0·4294 ampère.

Duration of experiment = 82 min.

Aspiration started at 11.12; stopped 11.38.

59·7 c.c. of acid in U-tube.

10·5 c.c. of acid mixed with potassic iodide solution.

Decolorised next morning; 7·0 c.c. of decinormal solution of sodic thiosulphate required (1 c.c. of solution = 0·000788 gram of oxygen).

$$7{\cdot}0 \times 0{\cdot}000788 = 0{\cdot}005516. \quad \frac{0{\cdot}005516 \times 59{\cdot}7}{10{\cdot}5} = 0{\cdot}031362$$ gram "active oxygen."

98·1 c.c. of oxygen were collected and measured at 9° C., and bar. 758·3 mm.

261 c.c. of hydrogen were collected and measured at 9°, and bar. 758·3 mm.

$$\begin{array}{r} 758{\cdot}3 \\ 8{\cdot}6 \\ \hline 749{\cdot}7 \end{array}$$ 8·6 pressure of aqueous vapour at 9°.

$$\frac{98{\cdot}1 \times 749{\cdot}7}{760 \times (1 + [0{\cdot}003665 \times 9])} = 93{\cdot}68$$ c.c. of oxygen at 0°, and 760 mm.

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$\frac{261 \times 749{\cdot}7}{760 \times (1 + [0{\cdot}003665 \times 9])} =$ 249·2 c.c. of hydrogen at 0°, and 760 mm.

0·09368 × 1·4336 = 0·13430 gram of oxygen.
0·2492 × 0·0896 = 0·022328 gram of hydrogen.

The liquid from the ozone absorption-tube required 10·05 c.c. of decinormal solution of sodic thiosulphate to decolorise it (1 c.c. = 0·002366 gram ozone).

10·05 × 0·002366 = 0·02378 gram ozone.

Of the ozone passing into the potassic iodide solution, $\frac{1}{3}$ of the oxygen is fixed, and $\frac{2}{3}$ passes on and is collected with the ordinary oxygen.

$$0{\cdot}02378 \times \frac{2}{3} = 0{\cdot}01585.$$

Total oxygen = 0·13430 gram.
0·01585

Ordinary oxygen = 0·11845 gram.

This ordinary oxygen was mixed with the ozone as it left the electrolysis apparatus.

Oxygen.............	0·11845
Ozone	0·02378
	0·14223

$\frac{0{\cdot}02378 \times 100}{0{\cdot}14223} =$ 16·719 per cent. ozone by weight.

In order to make the results of the different experiments comparable, the various products are reduced to molecules, and compared with 100 molecules of hydrogen which is the only constant.

$\frac{0{\cdot}022328}{2} =$ 0·011164 molecule of hydrogen.

$\frac{0{\cdot}11845}{16} =$ 0·007402 atoms of oxygen in the form of ordinary oxygen.

$\frac{0{\cdot}02378}{16} =$ 0·001485 ,, ,, ,, ozone.

$\frac{0{\cdot}031362}{16} =$ 0·001960 ,, ,, ,, "active oxygen."

$\frac{0{\cdot}011164}{0{\cdot}011164} \times 100 =$ 100 molecules of hydrogen.

$\frac{0{\cdot}007402}{0{\cdot}011164} \times 100 =$ 66·302 atoms of oxygen in the form of ordinary oxygen.

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$\frac{0·001485}{0·011164} \times 100 = 13·356$ atoms of oxygen in the form of ozone.

$\frac{0·001960}{0·011164} \times 100 = 17·556$,, ,, ,, "active oxygen."

The total number of atoms of oxygen for 100 molecules of hydrogen should obviously be 100.

$$\begin{array}{r} 66·302 \\ 13·356 \\ 17·556 \\ \hline 97·214 \end{array}$$

The total is usually a little less than 100 (occasionally a little above), this loss seems due to absorption of oxygen by the water in which it is collected.

The ratio of the gases is obtained by dividing the volume of hydrogen collected by the quantity of oxygen. The volume of the oxygen collected being equal to the volume of ordinary oxygen plus the volume of ozone—if our views of the constitution of ozone are correct.

$$\text{Ratio of gases} = \frac{249·2}{93·68} = 2·660.$$

$$\text{Quantity of hydrogen evolved per minute} = \frac{249·2}{82} = 3·039 \text{ c.c.}$$

1 ampère evolves 6·9549 c.c. of hydrogen per minute. The current used in the experiment was 0·4294 ampère—

$$0·4294 \times 6·9549 = 2·986 \text{ c.c. of hydrogen per minute.}$$

This number is a little less than that observed, doubtless from the mean deflection taken not being the exact one.

If we had taken 11·5° as the deflection of the galvanometer, the current would have been 0·4372 ampère, and—

$$0·4372 \times 6·9549 = 3·034 \text{ c.c. of hydrogen per minute,}$$

which is almost identical with the measured quantity, but the previous number is sufficiently accurate.

The current density is calculated by dividing the current by the area of the electrode in square centimetres:—

$$\frac{0·4294}{0·0085774} = 50·06 \text{ ampères per square centimetre.}$$

This example will render intelligible the following table of collected results. It has been considered advisable to give the method and numbers in detail, for at present it seems difficult to see what bearing they have on the phenomenon of electrolysis.

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Date.		Density of acid.	Molecules of hydrogen.	Atoms of oxygen in the form of			Sum of oxygen atoms.	Per cent. of ozone in oxygen.	Ratio of gases.	H evolved per min. c.c.	Current. Ampères.	H per min. calculated. c.c.	Density of current. Ampères per sq. cm.
				Ordinary oxygen.	Ozone.	"Active oxygen."							
Jan. 12	Electrode of six platinum wires about 1 mm. long and 0·045 mm. diameter......	1·025	100	79·348	12·345	6·130	97·823	13·461	2·283	1·833	0·2639	1·835	30·76
13		1·025	100	77·442	11·955	6·158	95·555	13·389	2·341	1·958	0·2829	1·967	32·98
12		1·05	100	72·864	13·053	11·020	96·937	15·184	2·452	3·085	0·4372	3·041	50·97
13		1·05	100	72·850	12·747	11·072	96·669	14·908	2·458	3·261	0·4883	3·396	56·93
11		1·075	100	66·356	13·266	18·076	97·698	16·668	2·659	2·650	0·3828	2·662	44·63
12		1·075	100	66·302	13·356	17·556	97·214	16·719	2·660	3·039	0·4294	2·986	50·06
13		1·1	100	63·688	12·003	20·794	96·385	15·873	2·728	3·163	0·4568	3·177	53·26
15		1·1	100	67·562	11·649	20·556	99·767	14·699	2·728	4·006	0·5678	3·949	66·2
15		1·15	100	59·920	8·955	25·858	94·733	13·016	3·034	3·143	0·4686	3·259	54·63
15		1·15	100	59·782	8·982	27·798	96·562	13·062	3·040	3·224	0·4647	3·232	54·18
18		1·2	100	60·408	6·279	34·334	101·021	9·421	3·097	3·300	0·4568	3·177	53·26
18		1·2	100	59·384	6·543	33·372	99·299	9·917	3·133	2·956	0·4294	2·986	50·06
18		1·25	100	60·692	6·288	31·486	98·466	9·413	3·081	2·916	0·4100	2·851	47·80
19		1·25	100	61·234	6·498	29·986	97·718	9·594	3·049	2·971	0·4216	2·932	49·15
19		1·3	100	71·562	12·243	14·320	98·125	14·608	2·508	3·273	0·4647	3·232	54·18
19		1·3	100	71·886	12·549	14·450	98·885	14·857	2·492	3·224	0·4529	3·150	52·8
20		1·35	100	76·258	9·393	15·486	101·137	10·965	2·423	2·975	0·4177	2·905	48·7
20		1·35	100	79·830	6·738	13·944	100·512	7·791	2·372	?	?	?	?

Electrode was found to have been dissolved. As the current densities are calculated on the assumption that the wire had a uniform diameter during all the experiments, the latter numbers must be much too low.

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Date.		Density of acid.	Molecules of hydrogen.	Atoms of oxygen in the form of			Sum of oxygen atoms.	Per cent. of ozone in oxygen.	Ratio of gases.	H evolved per min. c.c.	Current. Ampères.	H per min. calculated. c.c.	Density of current. Ampères per sq. cm.
				Ordinary oxygen.	Ozone.	"Active" oxygen."							
Jan. 25	New platinum iridium electrode. Six fine wires about 1 mm. long and 0·045 mm. diameter	1·1	100	67·368	10·779	19·522	97·669	13·789	2·682	3·043	0·4333	3·014	50·52
25		1·2	100	59·490	6·372	33·178	99·040	9·681	3·137	3·028	0·4255	2·959	49·61
25		1·3	100	70·342	12·345	14·682	97·369	14·944	2·545	3·045	0·4333	3·014	57·46
26		1·35	100	73·858	8·247	16·098	98·203	10·638	2·525	3·110	0·4490	3·123	59·55
26		1·35	100	74·390	7·821	16·038	98·249	9·519	2·513	3·025	0·4490?	3·123?	238·2?
27	Electrode of short thick wire 0·6 mm. long; 0·33 mm. diameter	1·35	100	63·378	2·649	31·822	97·849	4·026	3·070	3·005	0·4255	2·959	60·14
27		1·35	100	64·952	5·076	26·878	96·906	7·204	2·906	2·049	0·2928	2·036	43·47
29	Electrode of platinum iridium wire 6 mm. long. Fed through capillary tube	1·35	100	71·650	9·342	18·436	99·428	11·549	2·567	1·675	0·2411	1·677	32·83
*30		1·35	100	70·580	10·131	17·506	98·217	12·586	2·586	1·607	0·2259	1·571	30·7
30	New electrode platinum iridium wire 6 mm. long. 0·045 mm. diameter. Vertical	1·35	100	69·026	6·870	22·398	98·294	9·078	2·717	3·523	0·5001	3·478	66·32
Feb. 1		1·35	100	69·182	7·917	20·946	98·045	10·277	2·685	2·832	0·3906	2·717	67·49
1	New electrode like last, but wire horizontal	1·35	100	—	9·933	18·176	—	—	—	2·802	0·3867	2·689	51·9
1		1·35	100	71·586	9·282	18·820	99·688	11·494	2·571	2·747	0·3983	2·770	68·82
2	New electrode like last	1·35	100	71·076	10·983	17·374	99·433	13·394	2·570	2·606	0·3751	2·609	49·75
6	Electrode with two wires, each about 3 mm. long	1·35	100	70·490	10·932	15·668	97·080	13·423	2·572	3·079	0·4216	2·932	51·76
8		1·35	100	72·682	10·392	16·136	99·210	12·527	2·512	3·012	0·4372	3·041	60·84
9	Similar electrode	1·4	100	73·234	7·995	18·080	99·307	9·841	2·545	3·281	0·4725	3·286	60·65
9		1·4	100	74·992	5·214	18·706	98·912	6·527	2·547	2·202	0·3289	2·287	69·8

* Fresh end of wire.

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Date.		Density of acid.	Molecules of hydrogen.	Atoms of oxygen in the form of			Sum of oxygen atoms.	Per cent. of ozone in oxygen.	Ratio of gases.	H evolved per min. c.c.	Current. Ampères.	H per min. calculated. c.c.	Density of current. Ampères per sq. cm.
				Ordinary oxygen.	Ozone.	"Active oxygen."							
Feb. 10	Electrode with one wire projecting about 3 mm. on each side.	1·4	100	74·380	7·233	17·808	99·421	8·858	2·525	3·458	0·5239	3·644	75·66
10	Similar electrode	1·45	100	71·024	1·164	29·218	101·406	1·616	2·785	2·927	0·4372	3·041	52·81
12		1·45	100	75·286	1·116	24·182	100·584	1·463	2·630	2·334	0·3481	2·421	47·66
12	Similar electrode	1·5	100	76·438	0·717	24·280	101·435	0·930	2·600	1·779	0·2639	1·835	34·43
15		1·5	100	76·224	0·765	22·218	99·207	0·996	2·606	2·489	0·3020	2·100	42·02
15	Similar electrode	1·55	100	78·374	0·648	20·430	99·452	0·821	2·538	1·868	0·2677	1·862	34·57
16		1·55	100	75·736	0·558	23·264	99·558	0·734	2·627	1·877	0·2677	1·862	41·98
16	Similar electrode	1·6	100	79·144	0·543	19·192	98·879	0·681	2·515	1·286	0·1767	1·229	25·57
19		1·6	100	79·264	0·516	18·338	98·118	0·646	2·513	1·133	0·1616	1·124	26·72
Mar. 9	Similar electrode	1·65	100	81·076	0·528	18·220	99·824	0·646	2·457	1·035	0·1503	1·045	21·36
10	Same electrode	1·7	100	83·668	0·699	14·612	98·979	0·828	2·378	0·687	0·0938	0·652	14·22
12	Electrode of two Wollaston wires, total length about 5·3 mm., diam. 0·027 mm. .	1·025	100	75·406	13·713	6·066	95·185	15·404	2·365	1·472	0·2145	1·492	49·55
16	Same electrode	1·05	100	70·614	14·553	11·246	96·413	17·099	2·489	1·863	0·2715	1·888	66·69
17	Same electrode	1·075	100	68·306	12·489	14·512	95·307	16·573	2·585	2·184	0·3059	2·127	79·87
19	Same electrode	1·1	100	63·472	13·338	20·786	97·596	17·382	2·754	1·673	0·2411	1·677	65·82
April 5	Same electrode	1·1	100	73·572	12·846	17·782	104·200	16·527	2·719	2·201	0·3135	2·180	85·58
6	Same electrode	1·15	100	60·264	9·999	27·196	97·459	14·236	2·988	1·843	0·2677	1·862	76·55
6	Same electrode	1·2	100	57·902	5·961	32·450	97·413	10·948	3·192	1·304	0·2677	1·862	76·55
7	Same electrode	1·25	100	59·226	5·550	36·436	101·212	8·563	3·177	1·795	0·2639	1·835	79·25
May 21	Same electrode	1·3	100	72·862	11·610	14·182	98·654	13·774	2·482	1·928	0·2791	1·941	102·99*

* Electrode much attacked.

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Date.		Density of acid.	Molecules of hydrogen.	Atoms of oxygen in the form of			Sum of oxygen atoms.	Per cent. of ozone in oxygen.	Ratio of gases.	H evolved per min. c.c.	Current. Ampères.	H per min. calculated. c.c.	Density of current. Ampères per sq. cm.
				Ordinary oxygen.	Ozone.	"Active" oxygen.							
May 24	New electrode. Total length, 5·928; diam., 0·020 mm...	1·35	100	72·368	10·200	15·588	98·156	12·379	2·528	2·026	0·2982	2·074	153·95*
24	New electrode. Total length, 5·280; diam., 0·020 mm...	1·4	100	76·948	6·693	17·344	100·985	8·039	2·457	1·797	0·2906	2·021	146·5
25	New electrode. Total length, 6·582; diam., 0·016 mm...	1·45	100	77·332	3·816	18·552	99·700	4·714	2·504	1·605	0·2259	1·571	127·3
25	New electrode. Total length, 5·972; diam., 0·018 mm...	1·5	100	82·660	1·905	19·914	104·479	2·252	2·384	1·211	0·1691	1·176	35·7
27	Flat electrode about 1·9 mm. in diameter, fused on side of U-tube..............	1·1	100	81·446	6·372	10·870	98·688	7·275	2·334	2·994	0·4294	2·986	15·15
June 1		1·15	100	75·476	6·261	16·038	97·775	7·689	2·510	4·998	0·6982	4·856	24·62
8	Electrode with 10 short wires, 0·047 mm. diam. Total length, 6·788. Area, 0·01019 sq. cm.	1·1	100	65·254	11·253	20·340	96·847	14·710	2·748	3·334	0·4765	3·314	46·76

* Electrode dissolved.

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Various estimates of the solubility of ozone in water have been made, and one experiment has been carried out to endeavour to determine the coefficient. The result is so very different from some of those previously obtained, that it must be regarded as only preliminary, and other experiments must be made to confirm it.

The tube used for the absorption of the ozone in the above experiments was filled with water and connected to the electrolysis apparatus containing acid of density 1·075, and a current of electricity was then passed through the acid for 232 minutes, during which time 500 c.c. of hydrogen were evolved. From other experiments, the oxygen may be supposed to have contained about 16 per cent. by weight of ozone, or 11·27 per cent. by volume.

The water in the absorption-tube, which was at the temperature of 14° during the experiment, was mixed with potassic iodide and hydrochloric acid, and decolorised by the decinormal sodic thiosulphate. 0·9 c.c. were required equal to 0·002129 gram of ozone. The volume of the water in the tube was 32 c.c., so that 1 c.c. of water contained $\frac{0\cdot002129}{32} = 0\cdot00006653$ gram of ozone.

1 litre of ozone weighs 2·1504 grams, and

$$\frac{0\cdot00006653 \times 1000}{2\cdot1504} = 0\cdot03093 \text{ c.c. of ozone in 1 c.c. of water.}$$

The pressure of the ozone in the tube, calculated from the volume per cent. of ozone, was $\frac{1}{8\cdot875}$ of an atmosphere for $\frac{100}{11\cdot27} = 8\cdot875$, so that the coefficient of solubility of ozone from this single observation is $0\cdot03093 \times 8\cdot875 = 0\cdot2745$, which is nearly ten times that of ordinary oxygen, 0·02989.

The coefficient obtained by Schöne (*Ber.*, **6**, 1224—1229) was 0·366 at 18·2°. That obtained by Carius (*Annalen*, **174**, 30) was 0·834 at 1°.

When ozone is passed into a solution of potassic iodide, especially an acid solution, a dense white fume is produced. This is generally said to be hydric peroxide, but I had a suspicion that it at least contained iodic acid. An attempt to prove this was, however, a failure, owing to the omission of a precaution which was obvious when it was too late; however, since the paper was communicated to the Society I have had an opportunity of repeating the experiments in a more careful manner.

About 100 c.c. of ozonised oxygen, containing probably about 15 per cent. of ozone, were collected in a small flask. When the flask was filled, a solution of potassic iodide mixed with about one-third of its volume of dilute hydrochloric acid was introduced into the flask and

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agitated with the gas. After a minute or two some sodic hydrate solution was introduced into the flask to fix the free iodine (this was the precaution omitted in the previous experiment), and after agitation the flask was fitted with a cork carrying two tubes, and one of these was attached to a glass tube heated in the centre to the softening point. Between the flask and the hot part of the tube were placed a slip of paper coated with starch, and next a piece of paper with potassic iodide and starch. Beyond the hot portion were two similar papers. Air was slowly drawn through the flask into the tube by an aspirator. The first piece of starch-paper was entirely unaffected, the first piece of potassic iodide and starch-paper was rendered very slightly blue, from the presence of either a trace of ozone or of peroxide of hydrogen. The starch-paper beyond the hot part of the tube became intensely blue, from the iodine liberated by the decomposition of the iodic acid, subsequently the second piece of potassic iodide and starch-paper became equally blue from the action of the free iodine on the starch, for of course the high temperature of the glass would have destroyed ozone or hydroxyl if either had been present.

Note on the Action of Oxygen on Hydrochloric Acid under the Influence of Light.—In the foregoing experiments, it was noticed that when concentrated hydrochloric acid was added to potassic iodide, the liberation of a small quantity of iodine took place, whilst no such result followed the addition of dilute acid. The concentrated acid had been standing in the laboratory for some time in a bottle only partly filled.

It struck me that the reaction might be due to the evolution of a small quantity of chlorine from the oxidation of the hydrochloric acid, and it recalled an observation which I had made several times when preparing a lecture experiment to show the decomposition of water by chlorine. This experiment is done annually, usually in the winter months, by filling a flask with chlorine-water, inverting it in chlorine-water, and placing it in the field for several days; sometimes the solution is entirely decolorised, and at other times the colour remains light yellow even after long exposure. During last winter, two experiments were made, one with some chlorine solution that had been in the laboratory for some time, and the other with some freshly prepared chlorine-water. The first was entirely decolorised and the second was not. This seemed to show that when a certain quantity of hydrochloric acid has been formed, the decomposition of the water is arrested, or at least checked; and it seemed probable also that the process would be reversible, and that hydrochloric acid would be decomposed by oxygen.

To put this to the test six **V**-shaped tubes, closed at one end, were filled with the following liquids :—

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1. Saturated chlorine-water.
2. Chlorine-water mixed with an equal volume of distilled water.
3. Concentrated hydrochloric acid, density 1·153, saturated with chlorine.
4. Hydrochloric acid, density 1·1, saturated with chlorine.
5. Hydrochloric acid, density 1·03, saturated with chlorine.
6. Concentrated hydrochloric acid with oxygen in the closed limb.

These tubes were exposed to sunlight on May 5, and left in the field until the 18th. The sunshine was very brilliant on the 5th, 6th, and parts of the 7th, 8th, 9th, 10th, 15th, and 18th.

The dilute chlorine-water was soon decolorised, oxygen being evolved; the concentrated solution retained a colour for some days longer. No gas whatever was evolved from the hydrochloric acid solutions that were saturated with chlorine; and almost the whole of the oxygen was absorbed by the concentrated acid.

No free chlorine remained in what had been the chlorine-water, as it gave no coloration with potassic iodide.

When the hydrochloric acid which had absorbed the oxygen was tested in the same way, a brown coloration was produced.

I am not aware that this fact has been published, at any rate it is not generally known.*