VII. *On the Volumetric Relations of Ozone, and the Action of the Electrical Discharge on Oxygen and other Gases.* *By* THOMAS ANDREWS, *M.D.*, *F.R.S.*, *M.R.I.A.*, *Vice-President of Queen's College, Belfast*; *and* PETER G. TAIT, *M.A.*, *late Fellow of St. Peter's College, Cambridge, Professor of Mathematics in Queen's College, Belfast.*

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§ 1.

THE molecular changes produced by the electric current, or discharge, in certain compound bodies through which it is transmitted, furnish some of the most interesting examples of the action of a decomposing force that have been discovered in later times. The discharge of the Leyden jar, through fine wires or thin metallic leaves, exhibited long ago the heating power of the current, and the interesting experiments of the Dutch chemists afterwards showed that the disruptive discharge has the power of splitting up compound bodies into their constituent parts. The great invention of the pile of VOLTA, by furnishing an abundant supply of electricity of moderate tension, led subsequently to the important discovery of the polar decomposition of water and of other compound bodies. In the case of gases, it has been known, since the time of PRIESTLEY and CAVENDISH, that the spark discharge has the apparently antagonistic properties of causing decomposition in some cases and combination in others. Finally, in our own day, SCHÖNBEIN made the fine observation that a new substance (ozone), alike remarkable for the activity of its properties and for the facility with which it is destroyed, is formed by the action of the spark on pure oxygen gas, in the electrolysis of water, and in certain cases of slow oxidation.

Our object in the present communication is to continue the investigation, already begun by one of us*, of the properties of ozone, by subjecting it under varied conditions to a series of careful volumetric experiments. We hoped, in this way, to throw some new light on the relations of this singular body to oxygen, by determining whether any, and what, change of volume occurs in its formation. Our expectations in this respect have not been disappointed. We have ascertained that when oxygen changes into ozone, a great condensation takes place; so great indeed, that it is almost incompatible with the existence of ozone as an allotropic form of oxygen in the gaseous state. This investigation has naturally extended itself to an examination of the effects produced by the electrical discharge upon other gases, simple as well as compound; and although, from its great extent, this part of the inquiry has as yet been only partially entered into,

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* Philosophical Transactions, 1856, p. 1.

some of the results already obtained are of considerable interest, and will be referred to in the present communication.

Before proceeding further, we must draw attention to the difference of action which, in many cases, we have found to exist between the spark, or spark discharge, and the glow, or silent discharge. When the former terms are employed in this paper, they indicate a succession of brilliant sparks between two fine platinum wires, usually at the distance of 20 millims. (0·8 inch) from each other, and hermetically sealed into the tube containing the gas under observation. This form of discharge was obtained by connecting the free end of one of the platinum wires with an insulating stand, provided with a brass ball which was brought within a short distance of the prime conductor of an electrical machine in high order, while the free end of the other platinum wire was in connexion with the ground. The silent discharge presented no visible character except a faint glow, not visible by daylight, at each metallic point, and was obtained by connecting the first platinum wire, not with the insulator, but directly with the prime conductor. To avoid the mixture of the "brush" with the silent discharge, it was necessary to establish the connexion firmly both with the conductor and with the earth wire; and, in some cases, where a full effect was required, the machine had to be turned very slowly.

The electrical machine employed was a small plate one (18 inches in diameter), screwed down firmly to the floor of the apartment, opposite to an open fire. On the prolongation of the axis of the plate, a wheel, 6 inches in diameter, was fixed, from which a belt passed to an iron wheel, 40 inches in diameter, revolving in a wooden frame, which was also fastened to the floor. By this arrangement, the machine could be easily made to turn at the rate of 350 revolutions per minute. To maintain a regular and powerful stream of electricity at this rapid rate of motion, it was found necessary, in addition to the ordinary cushions, to hold with the hand against the plate a rubber covered with amalgam. When in ordinary working order, the machine gave above 600 sparks per minute, and in decomposing water produced in the same time 0·0002 cub. cent. of the mixed gases*.

The ordinary forms of eudiometrical apparatus were found to be wholly inapplicable to this inquiry. We failed in discovering, by their means, whether even a change of volume occurs, when ozone is produced from oxygen. To increase the difficulty, the experiments could not be carried on in presence of mercury or water, as the former is immediately attacked by ozone; and the latter not only destroys it rapidly by contact, but introduces a disturbing cause, in the form of aqueous vapour, exceeding in general the whole effect to be measured. In the apparatus now to be described these difficulties were overcome, and very minute changes of volume determined with certainty.

In Plate III. figs. 1 and 2, the vessel in which the oxygen was contained is represented of different forms. It consists of a cylindrical tube *ab*, having two fine platinum wires hermetically sealed in opposite sides, and terminating in a capillary tube *cde*, of the

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* Reports of the British Association for 1855, Trans. of Sect. p. 46.

form represented in the figure. The liquid in the limbs *d*, *e* is hydrated sulphuric acid (HO, SO_3), and it is by the changes in the level of this liquid that the alteration in the volume of the gas in *abc* is determined. In order to make the necessary corrections for changes of temperature and pressure, during the interval between two observations, a vessel filled with dry air, of the same form and size as that employed in the experiment, was read along with it; the reservoirs of both vessels being immersed in a large calorimeter, as shown in fig. 3. To the first of these vessels, we usually gave the name of *primary* vessel, and to the second that of *auxiliary* vessel. In order to correct for any slight difference in the size of the vessels, or in the diameters of the capillary tubes, simultaneous readings of both were made at different temperatures, and a coefficient thus determined, by means of which the indications of the two vessels could be afterwards accurately compared. When the reservoirs were large, the corrections so to be applied were frequently less than the errors of observation.

The extreme delicacy of this apparatus will be evident from the following considerations. If we take the case of a vessel with a large reservoir (fig. 1), the changes in volume of the contained gas, supposing the temperature to remain constant, will be nearly proportional to the changes of pressure indicated by a barometer filled with sulphuric acid. As the height of such a barometer, at the mean pressure of the atmosphere, would be about 5500 millims., an alteration of 1 millim. in the difference of levels of the acid in the siphon tube (*de*, fig. 1) would correspond to a change of volume of about $\frac{1}{5000}$th of the entire gas; but, as it was easy to read to 0·5 millim., or even to 0·25 millim., the apparatus in this form enabled us to estimate a change of volume not exceeding one-half, or even one-fourth of that quantity. With a smaller reservoir (fig. 2), the indications of the apparatus were, it is true, not quite so delicate, and a careful set of comparative readings with the auxiliary vessel was always required; but even here, a change of volume, amounting to not more than $\frac{1}{5000}$th of the whole, could be determined with certainty.

The absolute change of volume of the gas, corresponding to a given change in the levels of the acid in the siphon tube (corrected in the first instance by the aid of the auxiliary vessel), was estimated in two ways; first, by observing the change of level produced by raising or lowering the temperature of the water in the calorimeter through a small number of degrees; and secondly, by accurately determining, at the end of the experiment, the capacity of the reservoir and that of the capillary tube.

The form of apparatus now described can only be employed when the entire change of volume of the gas does not amount, in the course of the experiment, to more than about one-tenth of the whole. When large changes of volume occur, the free end of the siphon tube must be hermetically sealed, so as to include a certain quantity of air, from whose subsequent change of volume that of the gas in the reservoir can be readily calculated. This modification of the apparatus we have found to be very convenient in experiments upon the action of the spark and silent discharge on the compound gases.

§ 2.

The oxygen gas employed in the following experiments was prepared from fused chlorate of potash, and, to purify and dry it, was passed through two U-tubes; the first containing fragments of marble moistened with a strong solution of caustic potash, the second, fragments of glass moistened with sulphuric acid. The potash tube was sometimes suppressed. In order to remove every trace of nitrogen, the whole apparatus was placed in connexion with a good air-pump, and a vacuum produced to the extent of at least half an inch, while the gas was still being evolved from the fused chlorate (fig. 4). When the process of exhaustion was discontinued, the gas soon filled the apparatus, and was expelled through the mercury at the lower end of the long gauge. The operation of exhausting and refilling the vessel was performed three times in every experiment. Supposing the connexions of the apparatus to have been perfectly air-tight, the nitrogen remaining, after this triple exhaustion, could not have amounted to more than $\frac{1}{200,000}$th of the whole. This degree of accuracy was not, it is true, realized in practice, but the oxygen gas, prepared in this way, did not contain $\frac{1}{1000}$th of its volume of nitrogen. The connexion with the air-pump at *a* having been broken (the gas still continuing to pass freely over), the end of the tube was softened in a lamp and bent downwards at an obtuse angle, so as to allow it to dip into sulphuric acid contained in a small dish, as shown in fig. 5. The current of gas was now arrested, by removing gradually the lamps from the chlorate of potash, so as to allow the apparatus to cool slowly. When the acid had ascended a short way in *a c*, the vessel was sealed hermetically at *b*, and, after the acid had ascended to about the point *c*, the vessel was removed, and placed in the upright position represented in figs. 1 and 2. It was sometimes necessary to expel a bubble or two of gas, in order that the column of acid in the siphon tube might be in a convenient position when the vessel was placed in the calorimeter.

Previous to filling the vessels, they were always cleaned by means of boiling nitric acid, and subsequent washing with distilled water. They were afterwards carefully dried. To the success of several of the following experiments, this precaution was indispensable.

An auxiliary vessel having been filled in the same manner, either with air or with oxygen, the two vessels were placed in the calorimeter (fig. 3), and the difference of the levels of the acid in each carefully read. In our earlier experiments we generally used a cathetometer for this purpose, but latterly we found it more convenient and sufficiently accurate to apply to the limbs of the siphon tubes a scale divided into millimetres. From the rapidity indeed with which the readings were thus made, the results were found to be fully as trustworthy as those obtained with the cathetometer. When quantitative determinations were required, the temperature of the water in the calorimeter and the height of the barometer were carefully noted.

After the levels were read, the free ends of the siphon tubes in both vessels were hermetically sealed. The primary vessel was then removed from the calorimeter and placed in connexion with the electrical machine, to be exposed to the action either of the spark or silent discharge. When this operation was finished, the vessel was replaced in the calorimeter, the siphon tubes were opened, and the levels of the acid in the two vessels again read.

In order to examine the effects of heat, the reservoir of the vessel was placed in a sort of air-bath, formed by suspending a long copper cylinder above a LESLIE'S gas-burner, the siphon tube being outside the cylinder, fig. 6. In this way a temperature of 300° C., which was sufficient to destroy in a short time all the ozone reactions, was readily obtained. This temperature was estimated without difficulty, by observing the amount of compression of the air in the outer leg of the siphon tube. Our apparatus, with a slight modification, might, in fact, be employed as a thermometer for all temperatures below that at which glass begins to soften.

It will probably tend to perspicuity, if we state, before going further, some of the general results of our experiments on the action of the electrical discharge on pure oxygen.

I. *When the silent discharge is passed through pure and dry oxygen, a contraction takes place. This contraction proceeds, at first rapidly, but afterwards more slowly, till it attains a limit, which, in one of our experiments, amounted to* $\frac{1}{12}$*th of the original volume of the gas.*

II. *If a few electrical sparks be passed through the gas in this contracted state, it expands till it recovers about three-fourths of the contraction; but, however long the sparks are passed, the gas never recovers its original volume.*

III. *When electrical sparks are passed through pure and dry oxygen, it contracts, but to a much smaller extent than when acted on by the silent discharge. The oxygen is, in fact, brought to the same volume as when electrical sparks are passed through the same gas, previously contracted by the silent discharge.*

IV. *When oxygen, contracted either by the silent discharge or by sparks, is exposed for a short time to the temperature of* 270° *C., it is restored to its original volume, and, on opening the vessel, the ozone reactions are found to have disappeared.*

The following experiments, taken from a large number which gave similar results, will serve to illustrate the foregoing statements.

α. In a vessel, whose reservoir had a capacity of 5 cub. cent., sparks were passed for ten minutes, and produced a contraction of 5·9 millims., as measured by the change of levels of the acid in the siphon tube. By heating the vessel afterwards to 300° C., the levels were restored to within 0·1 millim. of their original position.

With the silent discharge in the same vessel, a contraction of 39·5 millims. (corresponding to about one-thirtieth of the volume of the gas) was obtained in ten minutes. Of this contraction heat restored 38·7 millims. This slight difference of 0·8 millim. is probably due to distortion of the vessel produced by heat.

Again, the silent discharge gave in ten minutes a contraction of 37·6 millims., of which sparks, subsequently passed for seven minutes, destroyed 29·7 millims., leaving 7·9 millims. undestroyed.

β. In another vessel, having a reservoir of the capacity of 0·8 cub. cent., active sparks gave, in fifteen minutes, 4 millims. of contraction. After fifteen minutes more of sparks there was no additional contraction.

The silent discharge was now passed for fifteen minutes, and increased the contraction to 20 millims.; in fifteen minutes more, the entire contraction was 31 millims. Four strong sparks reduced this to 22·5 millims., six or seven more to 16 millims., seven more to 11 millims., and sparks, continued for ten minutes, left 4 millims. of permanent contraction.

γ. In a third vessel, of about the same capacity as the last, sparks gave a final contraction of 7·5 millims.; while the silent discharge, pushed to its limit, increased the contraction to 90 millims., corresponding to about one-twelfth of the entire volume of the gas. This contraction was almost exactly destroyed by heat.

Before leaving this part of the subject, we should mention that, when a full contraction is obtained by means of the silent discharge, it will be found very slowly to diminish from day to day. We have not ascertained whether, at the end of a very long period of time, the original volume of the gas would be recovered. At 100° C., the contraction diminishes much more rapidly than at ordinary temperatures. Thus it appears that the state produced by the electrical discharge is not permanent, even at common temperatures, and that it becomes more unstable as the temperature rises, till at 270° C. it is rapidly destroyed.

§ 3.

We next proceeded to examine the volumetric changes which occur when oxygen, contracted by the electrical discharge, is brought into contact with other bodies.

The first body we tried was *mercury*, the physical changes produced on which by ozone are known to be very remarkable. When a capsule containing this metal is broken in a tube of oxygen gas through which the silent discharge has been passed, the mercury instantly loses its mobility, and, if gently shaken, covers the interior of the tube with a brilliant mirror. As the action continues, the mirrored surface breaks up, and the coating becomes converted into a blackish semipulverulent substance. Unless the tube be very violently shaken, the ozone reactions will not be entirely destroyed, until the mercury has been for some hours in contact with the gas.

To determine the volumetric changes, a thin capsule, filled with pure mercury and hermetically sealed, was placed in a vessel with a large reservoir of the usual form (fig. 1′), which was afterwards filled with dry oxygen. After the levels had been read, the silent discharge was passed until a considerable contraction was obtained. The corrections for changes of temperature and pressure were, as in other cases, furnished by an auxiliary vessel. The free end of the siphon tube having been sealed, the primary vessel was removed from the calorimeter, and the capsule broken by a sudden jerk. The breaking of the capsule, in this and other experiments, was greatly facilitated by introducing into the vessel a small piece of thick glass tube, which fell on the capsule when the vessel was shaken (fig. 1′, *k*).

Viewing ozone as an allotropic form of oxygen, in the gaseous state, we expected that when mercury came into contact with it, a contraction would take place, equal to the volume of the ozone which entered into combination with the metal. This anticipation has not been realized. After the rupture of the capsule, the vessel was immediately replaced in the calorimeter and the levels read. Not the slightest diminution of volume was observed in any one of a large number of experiments; on the contrary, an increase, corresponding to a change of 1 millim. in the levels, generally occurred. On allowing the vessels to remain in the calorimeter, and reading the position of the acid in the siphon tubes from time to time, the gas was found to expand steadily, but slowly, for some hours, till from two-thirds to five-sixths of the contraction produced by the discharge was recovered. If the vessel was opened at any time while this expansion was going on, the ozone reactions were always manifest; but, when the expansion was at an end, the ozone reactions had also ceased.

If the mercury, instead of being allowed tranquilly to act upon the gas, was violently agitated after breaking the capsule, a much smaller portion of the contraction was restored; in some cases not more than one-sixth.

Metallic *silver*, in the state both of leaf and of filings, gave similar results. The surface of the silver was partially blackened, about three-fourths of the original contraction was recovered, and the whole operation much more quickly terminated.

As the above reactions were evidently complex, the mercury and silver partly entering into combination with the gas, while the compounds formed appeared to exercise a catalytic action, we endeavoured to find an elementary body which would instantly destroy the ozone reactions, and at the same time be without action on dry oxygen. After some trials, we found that *iodine* possessed the required properties. We first ascertained that its vapour, although visible at common temperatures, has no appreciable tension. When a small capsule, containing pure and dry iodine, was broken in a vessel of the usual form filled with oxygen, the levels of the acid in the siphon tube were not altered. So slight also is the affinity of iodine for oxygen, that, on heating the reservoir so as to volatilize a considerable portion of the iodine, and afterwards allowing it to cool, the volume of the gas underwent no change. On the other hand, if ozone be present, the iodine is immediately attacked, a greyish-yellow compound is formed, and all ozone reactions are instantly destroyed.

The experiment already described with mercury was now repeated, substituting iodine for that metal. On breaking the capsule, the levels of the acid scarcely changed 1 millim., although the original contraction amounted to 50 millims. No subsequent expansion took place, and, on opening the vessel, the ozone reactions had entirely disappeared.

On the allotropic hypothesis, these experiments, and particularly the last, lead to the conclusion that ozone must have a density at least fifty times as great as that of oxygen. This conclusion is indeed unavoidable from the experiments just described, unless it is assumed that at the same moment that one portion of the ozone combines with the iodine, another portion changes back into oxygen, and that these quantities are so related to one another, that the expansion due to the one is exactly equal to the contraction arising from the other. Such a supposition can, however, not be considered probable.

§ 4.

In order to subject this remarkable property of ozone to a further examination, two additional series of experiments were undertaken, to a description of which we now proceed.

In the first series, a primary and an auxiliary vessel with large reservoirs were filled with pure and dry oxygen, small capsules hermetically sealed, and containing portions of the same solution of iodide of potassium, having been previously placed in each. The silent discharge was passed through the primary vessel so as to produce a considerable contraction, amounting in different experiments to from 40 millims. to 80 millims. The levels of the acid in the siphon tubes of both vessels having been carefully read while the vessels were in the calorimeter, the ends were sealed, and the vessels shaken so as to break the capsules in both. In the primary vessel, the iodide of potassium solution became instantly coloured dark brown from the iodine set free, while that in the auxiliary vessel did not change. On replacing the vessels in the calorimeter, and opening the ends of the siphon tubes, the change in the levels indicated a considerable expansion in both. In the auxiliary vessel, this expansion was due to the tension of the vapour of the solution of iodide of potassium alone; in the primary vessel, the expansion ought to have been less than this, on account of the absorption of ozone, if the volume of that body were capable of measurement.

In the following Table, which contains the results of five very careful experiments made in this way, the first column gives the amount of contraction produced by the silent discharge in the primary vessel, previous to the breaking of the capsules; the second, the temperature; the third and fourth, the respective expansions in the primary and auxiliary vessels; and the fifth, the differences of the numbers in the third and fourth columns:—

	mm.	°	mm.	mm.	mm.
I.	81·5	11·0 C.	68·5	70·0	−1·5
II.	62·2	13·5 C.	79·5	80·0	−0·5
III.	72·2	8·7 C.	50·7	52·0	−1·3
IV.	63·5	12·2 C.	71·5	73·0	−1·5
V.	45·5	16·2 C.	87·0	89·2	−2·2

The capacity of the vessels employed in these experiments was about 30 cub. cent., and the primary and its auxiliary were found, in each experiment, by careful comparative observations, to work accurately together. The solution of iodide of potassium was purposely employed of different strengths in the several experiments. In I. it contained $\frac{1}{400}$th part of iodide of potassium; in II. $\frac{1}{200}$th; in III. $\frac{1}{3}$rd; and in IV. and V. $\frac{1}{9}$th. In the two last the solution was slightly acidulated with hydrochloric acid, in the others it was neutral. The capsules contained each about 0·7 grm. of these solutions.

The agreement in the results of these experiments, made with solutions of iodide of potassium so widely differing, is very remarkable. We ought also to observe that direct experiments, performed with great care, showed that the iodine set free by the ozone in the primary vessel did not affect the tension of the vapour of the solution.

Taking the mean of the above numbers, the density of ozone, as compared with that of oxygen, must be expressed, on the allotropic hypothesis, by about the number 60; in other words, ozone must be a gas only about six times lighter than the metal lithium. If the small differences in the fifth column be due, wholly or in part, to accidental causes, which is far from improbable, a still higher number must, on the same hypothesis, be taken to express the density of ozone.

In the last series of experiments, the amount of iodine set free in the solution of iodide of potassium was determined by analysis, and the weight of oxygen deduced therefrom compared with the weight of oxygen, calculated from the volumetric change which had occurred in the formation of the ozone.

We shall describe these experiments with some detail, particularly as the methods employed will be found applicable to other cases of gas analysis, where small changes in a given volume of gas have to be estimated.

Before filling it with oxygen, a sealed capsule containing a solution of iodide of potassium was introduced into the primary vessel, while the auxiliary contained the dry gas only. The silent discharge was passed through the former, and the contraction carefully observed. The capsule was then broken, and the solution agitated in the primary vessel for a few seconds. The siphon tube was next cut off, and the liquid carefully washed out and analysed by means of a weak solution of sulphurous acid, the exact strength of which had been immediately before determined by observing the amount required to decolorize a solution containing a known weight of iodine.

In some of the experiments the solution of iodide of potassium was slightly acidulated, in the others it was neutral. In the latter case it was acidulated before being analysed. The results were the same, whether the solution was taken in the neutral or in the acid state. For, although oxygen gas acts upon an acid solution of iodide of potassium, the action requires time, and the contact in this case was only continued for a few seconds*.

The formula by which we calculated the results of these experiments may be thus investigated.

Let *f*, *g* (fig. 1) be the mean level of the acid in the legs of the siphon tube; *d*, *e* the levels at any time, *t* being the temperature, and Π the barometric pressure corrected for

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* BAUMERT has objected on this ground to some of the experiments in a former communication made by one of us to the Society. We have found that, in the circumstances in which those experiments were performed, about one-twentieth of the effect was due to this cause; but as the oxygen acting on the solution of iodide of potassium set free its equivalent of iodine, the equality of the numbers given in that paper could not be disturbed by this action. We have, since that time, by additional experiments, fully confirmed the statement that no water is produced in the destruction of electrolytic ozone by heat.

temperature. Let also $ge=fd=x$, and let H be the length of a tube similar to the siphon tube, and whose capacity is equal to that of the reservoir and of the siphon tube to f. Let a be the height of a barometer containing the liquid in the siphon tube, p the pressure of the gas in the vessel, and V the volume of the gas reduced to 0° C. and 760 millims.

Then, evidently,

$$p \propto \mathrm{V}\frac{1+\alpha t}{\mathrm{H}+x}.$$

But

$$p=\Pi\left(1+\frac{2x}{a}\right),$$

hence

$$\frac{\mathrm{V}(1+\alpha t)}{\Pi(\mathrm{H}+x)\left(1+\frac{2x}{a}\right)}$$

is a constant quantity. Taking the logarithmic differential, we have

$$0=\frac{\delta \mathrm{V}}{\mathrm{V}}+\frac{\alpha\delta t}{1+\alpha t}-\frac{\delta\Pi}{\Pi}-\frac{\delta x}{\mathrm{H}+x}-\frac{\frac{2\delta x}{a}-\frac{2x\delta a}{a^2}}{1+\frac{2x}{a}}.$$

Now $\frac{\delta a}{a}=\frac{\delta\Pi}{\Pi}$ is multiplied by $\frac{x}{a}$, a quantity rarely exceeding $\frac{1}{200}$. To this degree of approximation, then, at least,

$$\frac{\delta \mathrm{V}}{\mathrm{V}}+\frac{\alpha\delta t}{1+\alpha t}-\frac{\delta\Pi}{\Pi}=\delta x\left(\frac{2}{a}+\frac{1}{\mathrm{H}}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.)$$

If $\mathrm{V}_{,}$, $\mathrm{H}_{,}$, $x_{,}$ represent for the auxiliary vessel the quantities corresponding to V, H, x in the primary, we have, since $\delta\mathrm{V}_{,}=0$,

$$\frac{\alpha\delta t}{1+\alpha t}-\frac{\delta\Pi}{\Pi}=\delta x_{,}\left(\frac{2}{a}+\frac{1}{\mathrm{H}_{,}}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.)$$

If $\mathrm{H}_{,}=\mathrm{H}$, *i. e.* if the primary and auxiliary vessels be of similar dimensions, we have at once, from (1.) and (2.),

$$\frac{\delta \mathrm{V}}{\mathrm{V}}=(\delta x-\delta x_{,})\left(\frac{2}{a}+\frac{1}{\mathrm{H}}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

If the vessels be not similar, let

$$\delta x_{,}\left(\frac{2}{a}+\frac{1}{\mathrm{H}_{,}}\right)=\delta x_{,,}\left(\frac{2}{a}+\frac{1}{\mathrm{H}}\right),$$

then instead of (3.) we have

$$\frac{\delta \mathrm{V}}{\mathrm{V}}=(\delta x-\delta x_{,,})\left(\frac{2}{a}+\frac{1}{\mathrm{H}}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.)$$

Formula (3.) or (4.) gives the change of volume in the gas, as deduced from the observed change in the levels in the siphon tube.

For the estimation of the portion of the gas ($\delta_{,}\mathrm{V}$) taken up as ozone by the solution of iodide of potassium, let C be the capacity of the primary vessel to f in litres, s the number of measures of sulphurous acid required to decolorize the solution when washed out of the vessel, S the number required to decolorize 1 grm. of iodine. Then we have, evidently, as a sufficient approximation,

$$\frac{\delta_{,}V}{V}=\frac{\;\frac{Is}{15\cdot8S}\;}{\frac{1\cdot4367Cp}{(1+\alpha t)760}}.$$

If we suppose ozone to be allotropic oxygen, with a relative density $e:1$, then $\delta_{,}V$ of oxygen contracts to $\frac{\delta_{,}V}{e}$ on being changed into ozone. Hence, on this hypothesis,

$$\frac{\delta_{,}V}{\delta V}=\frac{e}{e-1}.$$

In order to verify this method, two similar vessels were filled with pure oxygen, one containing a capsule filled with a neutral solution of iodide of potassium, the other a capsule filled with an acidulated solution of the same salt, and of precisely the same strength. The neutral solution was also introduced into the siphon tubes of both vessels. After breaking the capsules, the levels were read, and the vessels set aside for some days; at the end of which time it was found that a portion of oxygen gas had been absorbed in the primary vessel which contained the acid solution, while no change had occurred in the other. The levels were now read again, and the solution in the primary vessel analysed.

The weight of the oxygen absorbed, as calculated by the foregoing formulæ from the volumetric change, was 0·0002188 grm., while its weight deduced from the analysis was 0·0002181 grm. The close agreement between these numbers shows that the method is susceptible of considerable accuracy.

The following Table contains the results of six experiments made in the manner above described. The primary and auxiliary vessels were carefully constructed of similar dimensions, and were found, on trial, to work accurately together, so that formula (3.) was directly applicable.

	I.	II.	III.	IV.	V.	VI.
	mm.	mm.	mm.	mm.	mm.	mm.
$2x_{,}$.	31·5	− 3·0	−18·5	−48·5	51·0	39·0
$2(x_{,}+\delta x_{,})$.	31·0	18·0	− 2·25	− 6·5	− 9·75	− 8·25
$2x$.	4·0	38·5	− 0·5	16·5	72·5	65·0
$2(x+\delta x)$.	−78·0	− 2·75	−55·25	− 5·0	−39·0	−27·5
C.	0·0338	0·0306	0·0288	0·0279	0·0269	0·0346
s.	9·1	5·4	5·7	5·1	4·5	4·5
	grm.	grm.	grm.	grm.	grm.	grm.
I.	0·0268	0·0684	0·0442	0·0674	0·0446	0·0621
S.	22·6	47·95	30·85	49·5	36·8	44·43
	mm.	mm.	mm.	mm.	mm.	mm.
Π.	777·0	772·5	763·0	751·0	747·2	751·0
t.	11°·0 C.	13°·45 C.	9°·1 C.	9°·8 C.	14°·0 C.	14°·7C.
$\frac{1}{H}$.	0·000025	0·000024	0·000025	0·000026	0·000027	0·000036
$\frac{\delta_{,}V}{\delta V}$.	0·932	0·938	0·947	0·927	0·952	0·933

On comparing these experiments with the foregoing, it will be observed that they do not give exactly the same result. Interpreted as they stand, they indicate a density for ozone, if we may use the expression, more than infinite, inasmuch as the quantity of oxygen deduced from the analysis is less than that corresponding to the contraction observed. But, although every precaution was taken to avoid all sources of uncertainty, it is not improbable that this difference between the amount of oxygen deduced from the contraction and from the analysis may arise from a slight defect in some of the data, particularly as it would only involve an error of the order of $\frac{1}{2000}$th of the entire gas.

Taking the mean result of the three series of experiments as they stand, it gives, on the allotropic hypothesis, almost exactly an infinite density for ozone.

§ 5.

The commonly received statement, that the whole of a given volume of dry oxygen gas can be converted into ozone by the passage of electrical sparks, is erroneous. In repeated trials, with tubes of different forms and sizes, we found that not more than one-twelfth of the oxygen could, under the most favourable circumstances, be converted into ozone, even by the silent discharge, and a much smaller proportion by the action of sparks. But if the ozone is removed as fast as it is produced, the conversion may be carried on indefinitely. An apparatus was constructed of the form shown in fig. 7. At *a*, *b* two fine platinum wires were hermetically sealed into the glass; at *c* there was a solution of iodide of potassium, and *de* was filled with fragments of fused chloride of calcium which allowed the ozone to pass freely, but arrested the vapour of the solution; so that while the discharge always took place in pure and dry oxygen, the ozone was gradually absorbed. The volumetric change was measured by the readings of the sulphuric acid in the siphon tube *fg* sealed at *g*. The experiment was continued till five-twelfths of the oxygen (whose entire volume was about 12 cub. cent.) was absorbed, and the action was still going on. It was not considered necessary to persevere further, as the labour of turning the machine was very great. To produce the effect just mentioned, the discharge from the machine in excellent order had to be passed through the tube for twenty-four hours.

When the electrical discharge is passed through rarefied oxygen, the phenomena are apparently the same as with the gas at the common pressure of the atmosphere. We filled a vessel with oxygen and exhausted it till the pressure was equal to 1 inch of mercury, in the hope that in this rarefied state a larger portion of the oxygen might be converted into ozone than under greater pressures, but this did not prove to be the case. We intend on a future occasion to pursue this part of the inquiry, and to examine particularly the effects of the electrical discharge on oxygen in different states of rarefaction and condensation.

Ozone, obtained by electrolysis, gave results nearly similar to those already described. As the volume of the oxygen gas from which the ozone was derived could not, in the case of electrolytic ozone, be observed directly, it was estimated indirectly by placing three vessels in line and passing the same stream of electrolytic oxygen through them all. By heating the first and last vessels to 300° C., and observing the expansion produced in each, it was easy to calculate the expansion which would have occurred in the middle vessel, if it had been exposed to similar treatment. This expansion was assumed to be equal to the contraction which occurs when ozone is produced from oxygen by means of the electrical discharge. Finally, the actual amount of ozone in the middle vessel was determined by introducing a solution of iodide of potassium, and ascertaining by analysis the amount of iodine set free. The individual experiments with electrolytic ozone did not agree so well with one another as those performed with ozone prepared by the discharge. This arose partly from the very small quantity of ozone in electrolytic oxygen, but chiefly from the irregularity in that quantity at different times, even when the current was passing very steadily, which made it difficult to ascertain with certainty the expansion due to the ozone in the middle vessel. Our earlier results, indeed, gave a measurable volume for ozone, and as a first approximation we obtained the number 4 as expressing its density*. But, by multiplying our experiments, and taking all possible precautions to ensure accuracy, we found that electrolytic ozone, like that produced by the discharge, has no appreciable volume.

Ozone is not condensed at common pressures by the cold produced by a mixture of solid carbonic acid and ether. A stream of electrolytic oxygen, passed very slowly, first through a U-tube surrounded by snow and salt, and next through a spiral tube immersed in the carbonic acid and ether bath (−76° C.), underwent no change. The ozone reactions, as the gas issued from the tube, after exposure to this low temperature, were as strong as before it entered the bath.

§ 6.

Hydrogen, prepared with care by the action of dilute sulphuric acid recently boiled on zinc, and purified by passing through three U-tubes containing corrosive sublimate in solution, hydrate of potash, and sulphuric acid, respectively, and finally, in order to remove the last trace of oxygen, through a tube filled with metallic copper heated to redness, was found not to be altered in volume, either by the sparks or by the silent discharge. It appears to be a much better conductor of electricity than oxygen.

With *Nitrogen*, prepared in the usual way by depriving atmospheric air of its oxygen by means of heated copper, the results were also negative.

Among the compound gases, *Carbonic Acid* is rapidly decomposed by the spark, slowly by the silent discharge; in both cases expansion takes place.

Cyanogen is at once decomposed by the spark with deposition of carbon (?); but presents so great a resistance to the passage of electricity, that the action of the silent discharge could not be ascertained with certainty.

Protoxide of Nitrogen is readily attacked by the spark, with the formation of hyponitric acid, whose characteristic red colour is distinctly seen. The primary result of the

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* Proceedings of the Royal Society, vol. viii. p. 498, and vol. ix. p. 606.

spark action is expansion, but on allowing the gas to stand, it gradually contracts, in consequence of the absorption of the hyponitric acid gas by the sulphuric acid in the siphon tube. It is impossible to determine the precise amount of the first expansion, as a certain amount of absorption occurs at the same time; but, in one imperfect trial, the ratio between the expansion and the subsequent contraction was nearly that of 1 : 2. This corresponds to the conversion of 8 vols. of protoxide of nitrogen into 4 vols. of hyponitric acid gas and 6 vols. of nitrogen. The silent discharge appears to produce the same result as the spark, but as the action is slower, the absorption interferes with any attempt to determine accurately the primary expansion.

Deutoxide of Nitrogen presents the interesting example of a compound gas, which, under the influence both of the spark and silent discharge, undergoes, like oxygen, a diminution of volume. This is independent of the subsequent absorption of the hyponitric acid formed. This gas is remarkable for the facility with which it is decomposed by both forms of discharge. The passage of sparks for two minutes, through a tube containing about 5 cub. cent., produced a contraction of the gas to nine-tenths of its original volume, followed after some time by a contraction not quite double of the former, from the absorption of the hyponitric acid gas. On continuing to pass sparks till the decomposition was finished, and waiting till the hyponitric acid gas was completely absorbed, the residue amounted to a little more than one-fourth of the original gas. This residue consisted of a mixture of 11 vols. nitrogen and 1 vol. oxygen. It is evident that the final result is a little complicated, but there can be little doubt that the action of the spark is to convert 8 vols. of deutoxide of nitrogen into 4 vols. of hyponitric acid gas, and 2 vols. of nitrogen. This decomposition may be due to the immediate action of the discharge; or the deutoxide of nitrogen may, in the first instance, be resolved into equal volumes of nitrogen and oxygen, the latter combining as it is formed with undecomposed deutoxide.

Carbonic Oxide has given results of great interest, the investigation of which has already occupied a considerable time, although it is not yet completed. The principal facts have, however, been already ascertained, and as they present some remarkable analogies to those already described in the case of oxygen, we shall briefly allude to them here, reserving the complete investigation for a future communication.

The carbonic oxide was prepared by heating oxalic acid with an excess of sulphuric acid, and absorbing the carbonic acid by means of a strong solution of hydrate of potash. The gas, as it escaped from the end of the apparatus, did not produce the slightest turbidity in lime or baryta water, and was completely absorbed by an ammoniacal solution of the subchloride of copper.

On exposing this gas to the action of the silent discharge, a steady contraction took place, and the surface of the positive platina wire became covered with a continuous deposit of a bronze colour. After some time, a trace, but only a trace, of the same deposit appeared at the point of the negative wire. If, after a contraction of 50 millims. or 60 millims. of the siphon tube had been obtained, a few electrical sparks were passed through the gas, the greater part of the contraction was, as in the case of oxygen, destroyed. Heat acted in the same direction, but did not restore the gas altogether to its original volume.

On continuing to pass the silent discharge, the gas continued to contract, and the deposit to increase on the positive wire. Portions of the same deposit were also scattered about the sides of the tube, being probably thrown off from the same wire. The experiment was in some cases continued till the gas had contracted to about one-third of its original volume. To effect this contraction, the machine had to be worked for sixty hours. The residual gas consisted of carbonic acid, oxygen, and undecomposed carbonic oxide. A similar deposit was obtained when the discharge took place between gold instead of platinum wires. This deposit appeared to be soluble in water. Its quantity was so small that direct analysis was altogether impossible. Its composition may, however, be determined by fixing with precision the ratio of the volumes of the carbonic acid and oxygen produced. We have succeeded in devising a method by which this analysis may be effected even with less than 0·5 cub. cent. of the mixed gases, but this part of the investigation is still unfinished.

Atmospheric Air is the only gaseous mixture which we have exposed to the action of the silent discharge. Like pure oxygen, it undergoes a diminution of volume; but the operation is more quickly terminated and the contraction is less than with that gas alone. If, after the passage of the discharge, the vessel be set aside for some hours, the contraction will be found to augment; and if the gaseous mixture be now again exposed to the action of the discharge, a further contraction will take place. On the other hand, heat destroys a portion only of the contraction at first produced. All these facts are easily explained from the simultaneous formation of ozone and one of the higher oxides of nitrogen, and the marked influence of the latter, when formed, in arresting the formation of the former. To the same cause we have succeeded in referring an apparently anomalous state of oxygen, produced by passing a stream of strong electrical sparks, for some minutes, through that gas containing a trace of nitrogen. The oxygen becomes by this treatment incapable of contracting or of changing into ozone under the action of the silent discharge, and only recovers its usual condition by exposure to heat or by standing for some hours. If the nitrogen amounts to not more than $\frac{1}{500}$th of the entire volume, this condition cannot be produced more than two or three times. At first we supposed it to be a new (passive) state of oxygen, but we have now no hesitation in referring it to the presence of a trace of hyponitric acid gas produced by the electrical sparks.

§ 7.

It is perhaps premature to attempt a positive explanation of the facts now described regarding ozone. The foregoing investigation into its volumetric relations has, for the moment, rather increased than diminished the difficulty of determining the true nature of that body. To reconcile the experimental results with the view that ozone is oxygen in an allotropic form, it is necessary to assume that its density immensely exceeds that of any known gas or vapour; being, as we have seen, according to the first and second series of experiments (§§ 3 and 4), from fifty to sixty times that of oxygen, and according to the third series (§ 4) absolutely infinite. Even the former results would make it only six times less dense than the metal lithium, and would place it rather in the class of solid or liquid bodies than of gaseous. The question may then be fairly proposed,—Can this singular body, at common temperatures, be actually a solid or liquid substance, whose particles, in an extremely fine state of subdivision, are suspended in the oxygen with which it is always mixed? This question will scarcely, we think, admit of an affirmative answer. Not only does ozone, mixed as usual with oxygen, pass through several U-tubes containing fragments of pumice moistened with sulphuric acid, but it exhibits its characteristic reactions when left for many hours in tubes of this kind. Besides, there is not the slightest cloud visible in a tube filled with oxygen, even when one-twelfth of the gas has been converted into ozone, nor does any deposit appear after long standing.

Ozone may be formed under conditions which exclude the possibility of its containing, as a constituent, any element except oxygen, or the elements of oxygen, if that body should hereafter be shown to be compound. As has been before stated, our experiments may be reconciled with the allotropic view and an ordinary density, but still one greater than that of oxygen, if we assume that when ozone comes into contact with such substances as iodine, or solutions 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. We do not, however, consider this supposition to be by any means probable, nor can it be easily reconciled with the results (§ 3) obtained when mercury acts on ozone.

If we consider the conditions under which ozone is formed, we shall find them to be different from those which produce allotropic modifications in other cases. Such elements, for example, as phosphorus or sulphur, are modified by the action of heat, and not by the electrical discharge. It is true, at the same time, that the destruction of ozone, or, on the allotropic view, its reconversion into oxygen, by exposure to a temperature of 270° C., is apparently analogous to that action of heat whereby common phosphorus is converted into the red variety.

Without rejecting the allotropic constitution of ozone, although the results of our volumetric experiments are certainly difficult to reconcile with it, it may not be uninstructive to consider whether the facts already known admit of a different explanation. As ozone is formed from pure and dry oxygen by the electrical discharge, if it is not an allotropic form of oxygen, the latter must be either a mechanical mixture of two or more gases, or it must be a compound gas. It is perhaps scarcely necessary to consider the former hypothesis, according to which, oxygen, in its ordinary state, would be a mechanical mixture, as atmospheric air is a mixture of nitrogen and oxygen. The contraction, which occurs when the electrical discharge is passed through oxygen, is at first sight indeed favourable to such a supposition, inasmuch as the combination of gases is usually accompanied either by a diminution, or no change of volume. But we have not been able to discover, in its other reactions, any facts which countenance this otherwise improbable view of the constitution of oxygen gas.

Finally, it remains to be considered, whether in the formation of ozone, oxygen does not undergo a more profound molecular change than is involved in an allotropic modification, whether, in short, this supposed element may not be actually decomposed. If, for the moment, we confine our attention to the phenomena which present themselves when the electrical discharge is passed through oxygen, this attractive hypothesis will be found to furnish a simple and plausible explanation of them all. It will be observed, at once, that the conditions under which ozone is formed from oxygen by the electrical discharge, are precisely those under which other gases, known to be compound, are decomposed. The electrical current is one of very high intensity, and therefore very favourable to decomposition: when passed in the form of the silent discharge, a large contraction takes place in the volume of the gas, which is partially destroyed by a few electrical sparks, and wholly by heat. With nitrogen and hydrogen no similar effects are observed, the volume of these gases being quite unaffected by either form of discharge.

The behaviour of carbonic oxide, when exposed to the action of the silent and spark discharge, corresponds remarkably to that of oxygen; the latter form of discharge, while producing itself only a limited contraction in carbonic oxide, destroying a part of the contraction produced by the former. Again, when deutoxide of nitrogen is exposed to the action of the same agents, an immediate contraction takes place without any solid or liquid product being formed, showing that in certain cases of gaseous decompositions, the resulting gases occupy a smaller volume than the original compound.

If we assume that oxygen is resolved by the electrical discharge into a new compound (ozone), containing the same constituents as the oxygen itself, but in a different proportion, and into one of the constituents themselves, in the same manner as carbonic acid is resolved into carbonic oxide and oxygen, or nitric oxide into hyponitric acid and nitrogen, the results of our experiments will admit of an easy explanation. One of the simplest suppositions we can make for this purpose is, that two volumes of oxygen consist of one volume of U and one volume of V, united without condensation (U and V being the supposed constituents of oxygen), and that one volume of ozone consists of two volumes of U and one volume of V; and further, that by the action of heat, iodine, &c., ozone is resolved into U and oxygen.

The appearance of ozone at the positive pole in the electrolysis of water, and its formation by the agency of so active a body as ordinary phosphorus, do not seem unfavourable to its being the result of decomposition. But the same observation will not apply to its production by the action of acids on such bodies as the peroxide of barium. We certainly should not have expected to see a body derived from the decomposition of oxygen produced under the latter circumstances, and, although the facts connected with its production in these cases have not been studied with precision, yet there appears to be no doubt that ozone is actually formed.

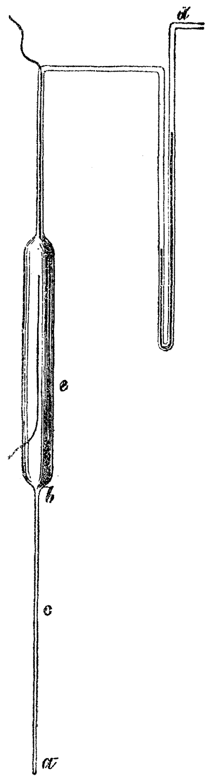
We must in conclusion add, that the few attempts we have made to isolate either of the supposed constituents of oxygen have failed.

We are still continuing to prosecute this inquiry, and hope on a future occasion to lay before the Society the results of further experiments which are now in progress.

Note, added July 12, 1860.

It having been suggested that a certain amount of the contraction produced by the passage of the electrical discharge through tubes containing oxygen might arise from the action on that gas of the platinum wires, or of finely divided platinum, which, as in Mr. GASSIOT'S experiment, might be thrown off by the action of the discharge, we have made the following experiment, in order to ascertain whether such an action could have occurred in the conditions under which we operated. Before describing the experiment, it may be proper to state, that in the passage of the discharge of the electrical machine, there is no visible separation of metallic platinum, as in that of the discharge from the induction coil, nor other evidence of the wires being acted on; on the contrary, both the wires and tube retain their original appearance after having been frequently exposed to the alternate action of the discharge and of heat.

A vessel, of the form represented in the annexed figure, was filled with pure and dry oxygen. It differs from the tubes usually employed only by having the lower end of the reservoir drawn out into a capillary tube *a b*. The platinum wires were inserted as usual, and an auxiliary vessel of the same size and form was filled with dry air. After determining the comparative range of the two vessels, their reservoirs were exposed, in the apparatus before described, to a temperature of 300° C., in order to bring them as exactly as possible into the same condition. When they had cooled, the levels of the acid in the siphon tubes were again read, and the silent discharge was afterwards passed through the primary vessel till a contraction of twenty-seven millims. was obtained in its siphon tube. The extremity of the capillary tube of the reservoir was next cut off at *a*, and the end of the siphon tube *d*, which had the form represented in the figure, was dipped under sulphuric acid. The open end at *a* was now connected with an apparatus, which supplied a slow stream of carefully dried air, and this was allowed to pass till the ozone and oxygen originally contained in the tube were entirely displaced by the dry air. It is obvious that by this arrangement the ozone was removed, while the platinum wires and the inner surface of the tube were left in precisely the same state as after the passage of the discharge. The tube was next sealed off at *c*, by the



application of the point of a fine blowpipe flame, the current having been arrested, so as to leave the usual column of sulphuric acid in the siphon tube. In sealing it, care was taken not to allow the air in *e* to become heated. The vessel was again placed, along with the auxiliary, in the calorimeter, and the levels read. The ends of the siphon tubes having been first sealed, the reservoirs were exposed to 300° C. An expansion should have taken place in the primary vessel, if the platinum had retained oxygen capable of being disengaged at 300° C.; but this was not found to be the case. The change of level in its sulphuric acid siphon (corrected by the auxiliary) did not amount to 0·2 millim., a degree of accuracy rarely attainable in these experiments.

Fig: 1

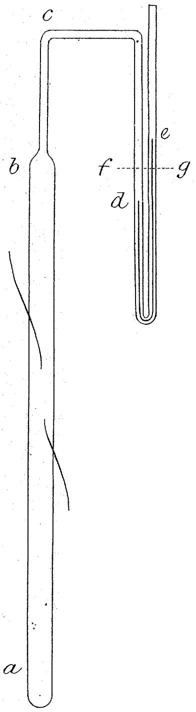


Fig: 1′

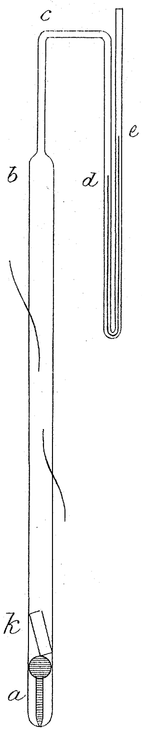


Fig: 2.

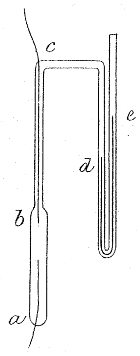


Fig: 3.

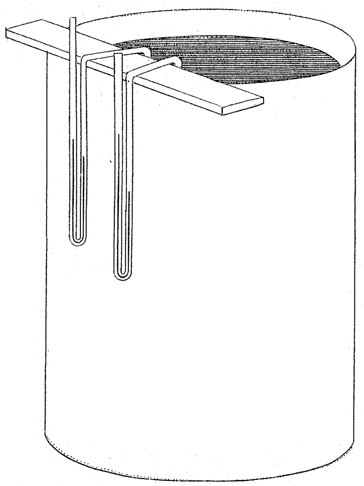


Fig: 5.

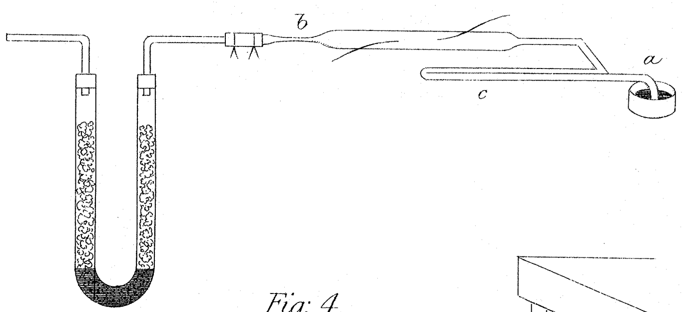


Fig: 4.

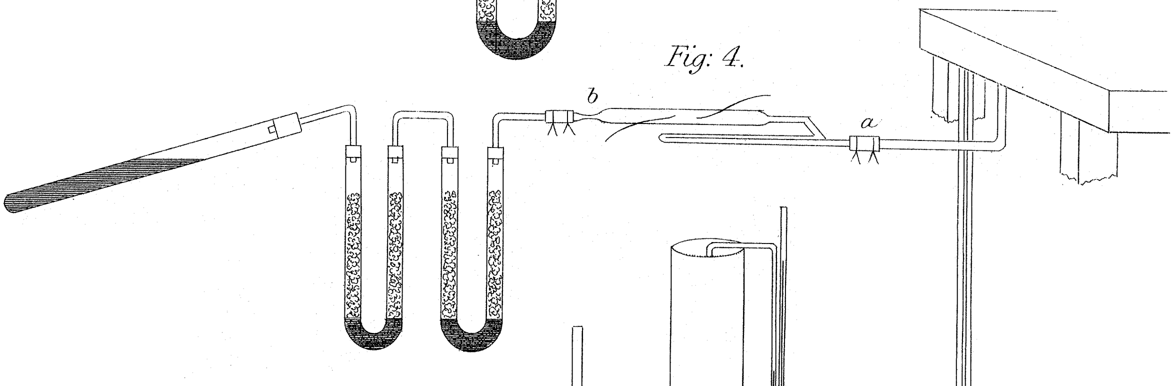


Fig: 7.

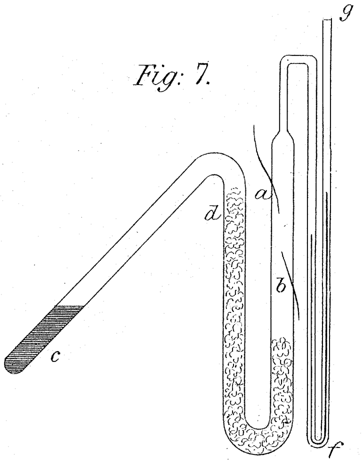
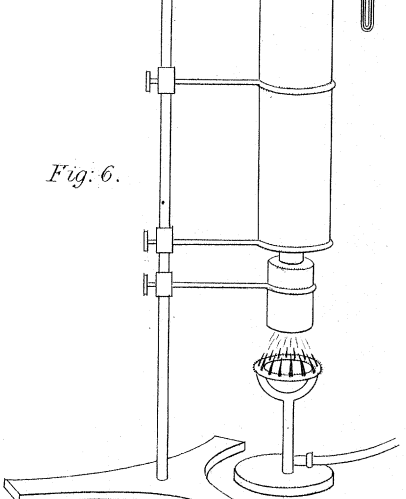


Fig: 6.



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