XXIII. *An Experimental Inquiry on the Action of Electricity on Gases.*—I. *On the Action of Electricity on Oxygen. By Sir* B. C. Brodie, *Bart., F.R.S.*

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The following pages contain the result of a prolonged series of experiments regarding the action of electricity upon certain kinds of gaseous matter. The instrument of this inquiry, by aid of which the gases were submitted to this action, is the induction-tube of W. Siemens*, an admirable and simple piece of apparatus, which enables us not only thus to operate upon the gases, but also to collect the products of the experiment with a view to their estimation and analysis. This instrument renders it practicable to utilize for the purposes of chemical investigation the vast powers of the coil of Ruhmkorff, and places at our disposal a new engine of research. The results at which I have already arrived are of sufficient importance to justify the anticipation that the changes thus produced by the action of electricity upon gases will prove to be a field of inquiry not inferior in interest to the electrolysis of liquids. In this first memoir I shall treat of the action of electricity upon oxygen gas, and in a subsequent inquiry, the results of which I hope speedily to lay before the Society, it is my intention to consider the action of electricity upon carbonic acid and carbonic oxide gas.

The investigations of Schönbein in reference to ozone throw but little light upon its nature, mainly for the reason that this chemist neglected the use of the most fundamental instruments of chemical research, and rarely even attempted any quantitative valuation of its properties; hence it is that we owe our most important knowledge upon this subject, not to Schönbein, who made it the study of his life, but to other investigators.

In a paper published in the Archives of Electricity for 1845†, Marignac and De la Rive established the important fact that ozone is produced by the action of the electric spark upon pure and dry oxygen—a point which was further and conclusively demonstrated by the investigations of Fremy and Becquerel in 1852‡, who also discovered that when electric sparks were passed through pure oxygen gas enclosed in a confined space in contact with a solution of iodide of potassium or with moistened silver, the oxygen was, after the lapse of sufficient time, totally and completely absorbed by those substances. It was thus proved that for the formation of ozone oxygen alone is required; and these investigations effectually disposed of those theories, based upon inadequate or erroneous experiments, according to which the properties conferred upon oxygen by the action of electricity were regarded as due to the formation of minute quantities of nitrous acid or peroxide of hydrogen§. At the same time Marignac and De la Rive

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* Poggendorff's Ann. vol. cii. p. 120.

† Vol. v. p. 5.

‡ Annales de Chimie, 3 S. vol. xxxv. p. 62.

§ Williamson, Ann. Ch. Pharm. vol. lxi. p. 13. Baumert, Poggend. Ann. vol. lxxxix. p. 38.

regarded this change of properties as due not to a special substance, but to a peculiar state or condition of oxygen caused by the electric action in which its "affinities were exalted," and proposed for this reason to discard the term ozone, and to term the gas in this condition simply electrized oxygen. Indeed they do not appear to have had any suspicion of the existence of ozone as an individual chemical entity distinct from oxygen itself.

A further and most important contribution to our knowledge upon this subject was made by ANDREWS and TAIT*, who, by means of a series of delicate and well-contrived experiments, arrived at the following conclusions:—(1) That under the influence of the electric action, which they employed in the form of what is termed the "silent discharge," oxygen undergoes a contraction of volume dependent upon the time for which the gas is thus acted upon, but not transcending a certain limit, the maximum contraction in their experiments being reached when the gas had diminished by one twelfth of its original volume. (2) That when the gas thus contracted was heated to 300° C., it expanded to its former bulk. (3) That when a solution of iodide of potassium was introduced into the contracted gas, an amount of iodine was formed equivalent to the amount of oxygen which disappeared in the contraction without the occurrence of any change in the volume of the gas. (4) That the gas which had been thus operated upon by iodide of potassium did not expand when heated to 300° C.

ANDREWS and TAIT do not offer any adequate interpretation of their remarkable experiments. "To reconcile," they say, "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, from fifty to sixty times that of oxygen, and according to the third series 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"†; and without absolutely rejecting the allotropic hypothesis, they proceed to seek for the origin of ozone in the decomposition of oxygen, and endeavour to explain the phenomena from this point of view.

There is, however, an hypothesis as to the constitution of ozone which would naturally present itself to the mind of a chemist profoundly convinced of the dual nature of oxygen, and by which these results would be accounted for in a simple and probable way. This hypothesis appears to have been first publicly enunciated by ODLING in his 'Manual of Chemistry,' published in 1861, where the following passage occurs (p. 94):—"If we consider ozone to be a compound of oxygen with oxygen and the contraction to be consequent upon their combination, then if one portion of this combined or contracted oxygen were absorbed by the reagent, the other portion would be set free, and by its liberation might expand to the volume of the whole; thus, if we suppose three volumes of oxygen to be condensed by their mutual combination into two volumes, then on absorbing one third of this combined oxygen by mercury the remaining two thirds would be set

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* Philosophical Transactions, 1860, p. 113.

† *Loc. cit.* p. 128.

free, and consequently expand to their normal bulk, or two volumes,

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

SORET* subsequently discovered that if oil of turpentine or oil of cinnamon be brought in contact with oxygen containing ozone as procured by electrolysis, a diminution occurs in the volume of the gas. SORET inferred (from his experiments) this diminution in volume to be equal in amount to twice the expansion which another portion of the same gas underwent when heated, or (what ought to be the same thing) to twice the volume of oxygen absorbed from the same gas by neutral iodide of potassium.

Although I quite agree that this is really the case, at least with the ozone procured by the action of induced electricity upon oxygen, I must be excused for saying that the experiments of SORET by no means justify the conclusion. The mean ratio of the observed diminution in volume to the oxygen absorbed by neutral iodide of potassium was in the case of the first set of five experiments 2·4, a number which cannot be considered even as an approximation to the theoretical number 2; and the similar mean of the second set of seven experiments, in which the ratio was estimated of this diminution to the expansion which the same gas underwent when heated, was 1·81, a number exhibiting a considerable divergence in the other direction from the same theoretical value†. SORET, indeed, gives a preference to these last experiments, and among these to three experiments especially, which show a closer concordance with theory; but this preference seems rather to be based on a foregone conclusion in favour of the theory than from any superiority in the experiments themselves. The truth is that no precise value at all for these contractions is really indicated by the experiments, and the errors are too great for any theory to be based upon them. These deficiencies are doubtless in no way to be attributed to any want of care or skill on the part of the experimenter, but to the unavoidable errors in the method of experiment.

About the time of the publication of SORET's experiments I was myself engaged with the same subject of inquiry, and, indeed, before the publication of these experiments had ascertained the nature of the contraction (hereafter discussed) which an electrized gas undergoes when passed through a solution of neutral hyposulphite of soda. Numerous circumstances, many beyond my control, have unfortunately interfered with the prosecution of these researches, of which, however, I at last am able to lay the results before the Society.

SECTION I.

The chief difficulties in the way of the accurate investigation of this problem have arisen from the absence of any adequate method of experiment; and I shall now proceed to describe an apparatus by which these difficulties may be obviated, and by which I have been enabled to generate and collect the electrized gas in sufficient quantities for examination, to submit successive portions of the same gas to the action of various

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* Ann. Ch. Phys. (4) vol. vii. p. 113.

† *Loc. cit.* pp. 116 & 117.

reagents, and to estimate the variations in volume which the gas undergoes under the influence of these reagents with facility and precision.

The oxygen employed in the following experiments was procured either by the decomposition of pure chlorate of potash or by the electrolysis of dilute sulphuric acid. In the former case the oxygen was collected in one of the sulphuric-acid gas-holders, hereafter described, and thence passed through the induction-tube. In the latter case it was passed through the induction-tube immediately from the apparatus in which it was generated. I shall describe the latter arrangement, which was employed in all but my earliest experiments, and which presents many advantages.

A drawing of the vessel in which the oxygen was generated is given in Plate LI. fig. 1: *a* is a glass vessel, similar to a small gas-jar, open at bottom; this vessel is cemented into a cell of porous earthenware, *b*, by which its aperture is closed; *c* is a ring of coke, being a section of one of the cylinders employed in BUNSEN'S carbon-battery; to this is attached a platinum wire *d*. In the interior of this glass vessel is a platinum plate, to which is attached a second wire (*e*) of the same metal passing through a stopper of caoutchouc. The whole is immersed in a glass jar containing dilute sulphuric acid, with which the vessel *a* is also partially filled. The wire *d* is connected with the zinc, and the wire *e* with the platinum terminal of a voltaic arrangement, consisting of three or four GROVE'S cells; the hydrogen passes into the external air, and the oxygen is delivered through the tube *f*, in which two bulbs (*g*) are inserted containing a solution of iodide of potassium, for the purpose of destroying the traces of ozone which would otherwise be contained in the gas and interfere with the experiment.

The oxygen delivered at *f* is then passed in a slow stream through a tube of the form delineated in figure 2, containing pure and concentrated sulphuric acid, the tube being attached at *g* by a caoutchouc junction to the tube *f*; the gas, thus deprived of moisture by the sulphuric acid, is further and completely dried before entering the induction-tube by anhydrous phosphoric acid contained in three small bulbs attached to the tube.

In figure 3 is given a drawing of the induction-tube, which is fundamentally of the kind originally devised by SIEMENS, and described by him in POGGENDORFF'S 'Annalen' in the place before referred to. The tube, however, is not, as in the arrangement of SIEMENS, coated with tinfoil, but the inner tube is filled with water, in which is placed one of the terminal wires of RUHMKORFF'S coil, while the tube itself is immersed in a vessel of water connected with the other terminal wire of the coil. The gas enters the apparatus at *h*, and passing over anhydrous phosphoric acid contained in the three bulbs *i*, traverses the narrow space *k* between the two tubes, and is there submitted to the electric action, after which the electrized gas is again passed over anhydrous phosphoric acid contained in the three bulbs *l*, and is delivered at *m*.

The gas is thus submitted to the electric action in a very dry condition, which is an essential point for the production of a considerable percentage of ozone. The amount of ozone is also affected by the temperature at which the gas is thus operated on. It is especially desirable to prevent the elevation of temperature consequent on the electric action, which may be done by placing fragments of ice in the interior of the tube, and also in the water contained in the external cylinder in which the induction-tube is immersed. If a lower temperature still be desired, the ice may be replaced by a mixture of ice and salt; in this latter case the precaution of filling the interior tube also with the saline solution must not be omitted. When the tube is thus cooled, either with ice or with ice and salt, the external cylinder containing the refrigerating-mixture should be wrapped in thick flannel. The temperature can readily be thus kept during a long experiment of six or eight hours' duration at 0° C., or even at −10° C.

The electrized gas is collected and preserved for the purpose of experiment in a gas-holder, delineated in Plate LI. fig. 4. On this side of the induction-tube connexions of caoutchouc can no longer be employed, this substance being instantaneously corroded by even the minutest trace of ozone, and the junction between the gas-holder and the induction-tube is effected by means of what may be termed a paraffine-joint. Over the tubes to be connected, which are placed close together, is slipped a piece of glass tube into which they exactly fit, and from which they are separated by a capillary space; a fragment of pure paraffine is placed at the external junction of the tubes; the union of the tubes is effected by gently melting the paraffine; the liquid paraffine is extremely limpid, and runs into and fills up the narrow space between the tubes. When the paraffine is solidified, the tubes are united by a joint, which is perfectly air-tight, which will resist very considerable pressure, and which is quite unaffected by the passage of the ozone. This simple joint is an essential feature of this arrangement, and would doubtless be of great service in many forms of gas-apparatus.

The gas-holder consists of a glass bell (*p*) contained in a glass cylinder (*q*), in which it is suspended, being supported by a knob of glass passing through a wooden cap fitted to the top of the jar; this cap is made in two pieces, which are subsequently united so as to be readily placed in a proper position as a support to the glass bell. The wooden cap was coated internally with paraffine, to protect it from the effects of accidental contact with the acid. It would, however, be far better to make the cap of glass, which could easily be done.

At a superior level is placed a glass jar (*r*) containing pure and concentrated sulphuric acid; this jar is connected by a siphon-tube, *s* (in which is placed a glass stopcock), with the lower cylinder, *q*. This upper jar, which I shall term the reservoir, is closed by a wooden cap, *t*, which also would be better made of glass, through which the siphon-tube passes, and in which is also fitted a second glass tube, *u*. The gas from the induction-tube is delivered at *n*, whence it passes into the gas-holder by an arrangement of tubes, which is best understood from the drawing.

I will now describe the way in which the apparatus is worked. A quantity of concentrated sulphuric acid, just sufficient to fill the glass bell (*p*) and the external cylinder (*q*) to the top of the bell, is placed in the reservoir *r*, the siphon-tube being filled with the same. The stopcock at *v* is closed, and the stopcock *w* open; the glass stopcock in the siphon-tube (*s*) is now opened, the air is expelled from the glass bell (*p*), which is thus filled with sulphuric acid. The stopcock in the siphon-tube is now closed, as also the stopcock *w*; the stopcock *v* is opened, and the gas as delivered from the induction-tube at *n* is allowed to pass into the gas-holder. The sulphuric acid which is thus displaced is drawn back into the reservoir *r*, by creating in the reservoir a partial vacuum; this is effected by means of an air-pump, connected with the glass tube *u* by a caoutchouc tube. Similarly, any required quantity of gas may be delivered from the gas-holder by closing the stopcock *v* and opening the stopcock *w*, the gas being expelled from the gas-holder by the column of sulphuric acid in the jar delivered from the siphon-tube.

The drawing of the apparatus given in the figure is a quarter the actual height; the capacity of this gas-holder is about 3000 cub. centims. The arrangement, although somewhat complicated in description, is easily worked.

The volume of gas submitted to experiment was measured in a glass pipette, of which a drawing is given in Plate LII. fig. 5 to the same scale as the last. The capacity of the pipette between the two marks *b* and *c* was estimated by calibration with mercury, the quantity of mercury required to fill the pipette between the marks being weighed at an observed temperature; its capacity as thus ascertained was 290·8 cub. centims. It was then welded to a glass tube of the form given in the figure: *e* is a reservoir of sulphuric acid with a siphon-tube attached, similar in principle to that previously described; *d* is a cylinder containing water, in which the gas-pipette *a* is immersed, and of which the temperature is observed by means of a thermometer placed in it. The gas-pipette is placed in connexion with the gas-holder by means of a paraffine-joint at *f*; the arrangements for working this pipette are precisely similar to those previously described in the case of the gas-holder. At the commencement of the experiment the pipette is filled with sulphuric acid from the reservoir *e* by means of the siphon-tube, the stopcock *g* being closed and *h* open; this having been effected, the pipette is filled with the electrized gas by closing the stopcock *h* and opening the stopcock *g*, a partial vacuum being made in the reservoir *e* as previously described, and a pressure of 2 or 3 inches of sulphuric acid being put upon the gas in the gas-holder. The pipette is thus filled with gas to some point below the mark *c*; the stopcock *g* is then momentarily lifted so as to allow the sulphuric acid to rise to the mark *c*. The quantity of sulphuric acid in the reservoir was so adjusted that when the siphon-tube was empty the pipette was necessarily filled to this level. It is to be observed that the tubes connected with the apparatus were first filled with the electrized gas by drawing over, at the commencement of the experiment, a certain volume of the gas into the pipette and expelling it into the air. In this manner the pipette was filled to the mark *c* with the electrized gas at atmospheric pressure as observed by the barometer, and at the temperature indicated by the thermometer placed in the water in which the pipette was immersed; the gas was delivered from the pipette at *c*. To effect this the stopcock in the siphon-tube was opened, and a pressure was thus put upon the gas, the stopcock *h* being also open and the stopcock *g* closed: the quantity of sulphuric acid was so arranged that the gas could readily be brought at atmospheric pressure to the mark *b*; the capacity of the pipette having been determined between these points, a definite volume of gas at a known temperature and pressure was thus delivered at the exit-tube *i*. Evidence of the extreme accuracy of this method of measurement will shortly be given. It is, so far as I am aware, the first application to the estimation of the volume of gases of those principles of pipette-measurement which have been of such good service to the chemist in the case of the measurement of liquids.

In order to estimate the changes in bulk which the electrized gas underwent in the various experiments hereafter described, the measuring-apparatus was employed of which a drawing is given in Plate LII. fig. 6. In this apparatus, which I shall term the aspirator, the volume of gas at 0° C. and 760 millims. pressure is ascertained by determining the pressure which it is necessary to put upon the gas in order to cause it to occupy a known space at a known temperature. This is the principle of Regnault's apparatus for gas-analysis, and also of Frankland's apparatus.

The apparatus consists of a cylinder of strong glass (*a*), connected by an iron tube with an iron reservoir (*b*), containing an amount of mercury rather more than sufficient to fill the cylinder *a*. In the iron tube connecting the cylinder and the reservoir is intercalated a stopcock (*c*), by which the connexion between the cylinder and reservoir may at pleasure be made or cut off. In the reservoir *b* a small iron tube (*d*) is inserted, connected by a tube of caoutchouc with a forcing-pump firmly fixed to the table on which the apparatus is placed. By means of this forcing-pump the air contained in the upper part of the reservoir may be compressed, and any required pressure put upon the mercury contained in it. The cylinder *a* is cemented, by means of a resinous cement, into two steel caps (*e* and *f*); the lower cap (*f*) is screwed firmly upon the support of the apparatus, which is made of iron. The cylinder is connected, by means of a channel cut in the lower part of the steel cap (*f*) and continued through the iron frame, with a glass tube (*g*), which is about half an inch in diameter and graduated in millimetres: this tube I shall speak of as the pressure-tube. The cylinder *a* and the pressure-tube *g* are thus in permanent connexion, and constitute one vessel, which is broken into parts solely for facility of construction. This apparatus is supported upon three screws, as shown in the figure, by the adjustment of which the pressure-tube *g* is placed in a perpendicular position before the commencement of the experiment. A piece of strong glass tubing, of fine bore, is cemented into a steel socket which forms part of the steel cap *e*, the upper end of the same glass tube being similarly cemented into a steel socket (*h*), on the upper part of which a screw is cut by which it is connected with a steel stopcock (*k*). Two steel sockets, similar to the socket *h*, are screwed into the stopcock (*k*) and two glass tubes (*l* and *m*) are cemented into these sockets; the steel stopcock *k* is what is termed a three-way stopcock, in which the channels are so cut that a communication may be made between the tube *l* and the cylinder *a*, or between the tube *m* and the cylinder *a*, or between the tubes *l* and *m* (all other communications being shut off), at pleasure, or the communications may be entirely closed.

In the cylinder *a* is placed a thin piece of glass rod, to which seven points are attached, also of glass, as shown in the figure, the points being finely ground. This glass rod is attached to the sides of the tube by a little resinous cement. The rod may be thus fixed after the cylinder *a* has been cemented into the lower cap *f*. The capacity of the cylinder *a*, between each point, is ascertained by calibration with mercury, which is effected before the reservoir is attached to the apparatus. In order to calibrate the cylinder *a*, the stopcock *c* is closed and *k* opened to the air; the cylinder *a* is then filled with mercury (which has been carefully purified, and of which the specific gravity has been determined by experiment) up to the stopcock *k*. The mercury is then run out of the apparatus by means of the stopcock *c* to a level a little below the first point, 1; the stopcock *c* being again closed, a portion of the same mercury, exactly sufficient to bring the level of the mercury to the point 1, is poured back into the apparatus by means of the pressure-tube, the level of the mercury is read on the pressure-tube, and the mercury which has been run out of the apparatus is weighed. From these data the capacity of the cylinder *a*, taken together with the capacity of the pressure-tube *g* from the stopcock *k* to the first point 1, may be calculated. By perfectly similar operations the capacity of the cylinder and pressure-tube at the other points (2, 3, 4, 5, 6, 7) may be ascertained, and the heights of those points upon the pressure-tube *g* determined. In order finally to determine the capacity of the cylinder *a* at the various points, we have to deduct from the capacity of the cylinder and pressure-tube at those points as thus ascertained the capacity of the pressure-tube. This capacity is readily determined by filling the apparatus as before with mercury, closing the stopcock *k*, and running the mercury out, by opening the stopcock *c* (the vessel *b* being detached), from successive portions of the pressure-tube alone, care being taken to run out so much as to pour back in each case a little mercury in order to secure the right reading of the meniscus; this mercury is then weighed. The pressure-tube being graduated in millimetres, a simple calculation informs us of its capacity at any desired interval. Deducting the capacity of the pressure-tube from the capacity of the cylinder and pressure-tube as previously determined, or, rather, deducting the weight of the mercury at a known temperature and of a known density corresponding to the capacity of the pressure-tube from the weight of mercury corresponding to the capacity of the cylinder and pressure-tube, we arrive at the capacity of the cylinder at any desired point.

The cylinder and pressure-tube are enclosed in a second glass cylinder (*n*), which is fastened into an iron ring, by means of which it is attached to the frame of the apparatus; this cylinder is filled with water, in which a thermometer is placed.

The apparatus thus put together is to be carefully examined to ascertain that there is no leakage in the various joints and stopcocks; with this view the reservoir of mercury having been now attached to the apparatus, the stopcock *k* is opened and the cylinder *a* is partially filled with mercury; the stopcock *k* is closed, the stopcock *c* opened, and a considerable pressure put upon the gas by means of the forcing-pump before referred to; the stopcock *c* is then closed, and the height of the mercury in the pressure-tube read: the level of the mercury in the pressure-tube should not appreciably vary for several hours.

In order to determine the volume of a gas enclosed in the cylinder *a*, the gas must be first expanded, if necessary, below the point at which the reading is to be made; this is effected by opening the stopcock *c*, the communications being open between the reservoir *b* and the external air; the stopcock *c* is then closed, and the pressure put upon the mercury in the reservoir by means of the forcing-pump; the stopcock *c* is then partially and carefully opened so as to allow the mercury very slowly to rise until it is brought to the level of the point; the stopcock is instantaneously closed, and the level of the mercury on the pressure-tube read: the temperature of the water in the external cylinder is given by means of the thermometer placed in it; the barometer is also read, and from these data, the capacity of the cylinder at the point at which the observation is made being known, the volume of the gas at 0° C. and 760 millims. pressure may be calculated.

With a view of testing the accuracy of this method of measurement, the ratio of the pressure under which the same volume of air exists at two adjacent points was determined throughout the apparatus, and these ratios were compared with the ratios of the capacities of the same two adjacent points as determined by mercurial calibration; the numbers should be the same in both cases; thus, putting $p_1, p_2, p_3, \ldots.$ as the pressures under which any volume of air exists at the points 1, 2, 3, ..., and $v_1, v_2, v_3, \ldots.$ as the capacities of the apparatus at the same points, as determined by mercurial calibration, the following results were obtained. The ratios of the pressures given below are in each case the mean of not less than three experiments; the several observations at two adjacent points were made with slightly varying volumes of air, so as to get different readings on the pressure tube in each case.

$$\frac{p_1}{p_2}=2\cdot0597, \qquad \frac{v_2}{v_1}=2\cdot0576,$$

$$\frac{p_2}{p_3}=1\cdot6534, \qquad \frac{v_3}{v_2}=1\cdot6541,$$

$$\frac{p_3}{p_4}=1\cdot4464, \qquad \frac{v_4}{v_3}=1\cdot4462,$$

$$\frac{p_4}{p_5}=1\cdot3989, \qquad \frac{v_5}{v_4}=1\cdot3990,$$

$$\frac{p_5}{p_6}=1\cdot4685, \qquad \frac{v_6}{v_5}=1\cdot4696.$$

Now the capacity of the aspirator at the fifth point may also be determined by drawing over into the aspirator a pipette of air, and ascertaining the pressure at which that volume of air exists at that point; assuming this to be the true capacity of the aspirator at that point, and applying the ratios of pressures to the numbers thus obtained for that capacity, the following numbers are arrived at:—

$\frac{72{\cdot}000}{2{\cdot}0597}=34{\cdot}957$ capacity in cub. centims. at point 1,

$\frac{119{\cdot}04}{1{\cdot}6534}=72{\cdot}000$ „ „ „ „ „ „ 2,

$\frac{172{\cdot}19}{1{\cdot}4464}=119{\cdot}04$ „ „ „ „ „ „ 3,

$\frac{240{\cdot}89}{1{\cdot}3989}=172{\cdot}19$ „ „ „ „ „ „ 4,

$240{\cdot}89\times1{\cdot}4685=353{\cdot}75$ „ „ „ „ „ „ 6,

the capacity at point 5, as determined from the pipette, being 240·89 cub. centims. This method of determining the capacity of the aspirator may be termed the method of air calibration.

The capacity of the apparatus at the different points, as determined by the respective methods of mercurial calibration and air calibration, are given in the following Table:—

	By mercurial calibration.	By air calibration.
Capacity in cub. centims. at point 1 . . .	34·93	34·96
„ „ „ „ „ „ 2 . . .	71·87	72·00
„ „ „ „ „ „ 3 . . .	118·88	119·04
„ „ „ „ „ „ 4 . . .	171·92	172·19
„ „ „ „ „ „ 5 . . .	240·51	240·89
„ „ „ „ „ „ 6 . . .	353·45	353·75

The capacities respectively given in these two columns are determined by independent methods; and it must be admitted, if we consider the numerous observations necessary for any one determination, that the concurrence of these numbers is truly surprising, and affords a sufficient guarantee of the accuracy of the method employed for the determination of the volumes of gases in these experiments. It is necessary, however, to observe that the previous description is exactly applicable only to the ultimate form which this apparatus assumed with the various modifications suggested by use. In my earlier experiments the apparatus employed differed in various details from that just described; it was, however, constructed on perfectly similar principles—namely, the measurement of a determinate volume of gas by means of a pipette, and the estimation of the volumes of gases at 0° C. and 760 millims. from the observation of the pressure and temperature at which the same gases occupy a known space. It does not appear to me necessary to trouble the reader with a description of this apparatus, which differed from that just described rather in regard to convenience than precision, the difference in this latter respect, if any, being in no way sufficient to affect the general result.

The pipette was placed on a table, being separated from the aspirator by an interval of about 8 or 10 inches; in this interval the experiment to which the electrized gas was submitted was made. When the gas was passed through a liquid, small glass bulbs were employed of the kind delineated in Plate LII. fig. 7. In bulb *a* the gas is delivered through a capillary tube so as to pass in minute bubbles. It is hardly necessary to observe that the level of the liquid in the bulb was so adjusted at the commencement of the experiment, by drawing a few bubbles of air through it by means of the aspirator, as to occupy the same position as that in which it was finally left at the conclusion of the experiment. Before the commencement of the experiment the aspirator was completely filled with mercury from the reservoir.

In Plate LII. fig. 8 a drawing is given of the whole apparatus as arranged for experiment.

I may here express the obligations which I am under to my assistant, Mr. J. Robinson, for the effectual way in which he has aided me in this investigation, especially in the construction and use of this apparatus for measuring gases, towards the completion and perfecting of which he contributed several valuable suggestions.

Section II.

The action of ozone upon iodide of potassium has been investigated by Andrews and Tait*, and also by Von Babo and Claus†. These experiments were made in both instances with great care; and my own observations entirely confirm the conclusions at which these chemists arrived, and so far present no new feature. It is, however, very desirable in so obscure a subject to multiply experiments; and as the following experiments were conducted in a totally different manner to that in which these chemists operated, and illustrate the working of the apparatus and the degree of precision attained by it, I shall lay them before the reader.

A known volume of the electrized gas was drawn over from the gas-holder into the pipette and there measured. The gas was then passed through a solution of iodide of potassium contained in one of the glass bulbs previously referred to into the aspirator, where the volume was again measured. After the experiment the solution of iodide of potassium was rendered acid by means of a dilute solution of hydrochloric acid, and the iodine formed estimated by a standard solution of hyposulphite of soda. The quantity of oxygen equivalent to this iodine is here termed the "Titre" or "Iodine-titre" of the gas; it is a quantity which for the same gas is constant, and which may be estimated with the greatest precision: I have therefore selected this quantity as the unit with which other analogous quantities are compared.

It is to be observed that ozone is by no means the unstable thing which it is generally imagined to be. The concentrated sulphuric acid over which ozone has been long kept becomes singularly free from colour and of a peculiar brightness. This doubtless arises from the oxidation by the ozone of the particles of organic matter otherwise invariably present in it; but when the sulphuric acid has attained this condition, the electrized gas may be kept over it for many hours at the temperature of the laboratory without appreciable alteration of the "titre." Thus in an experiment not made for this purpose, and made without any special precautions for the preservation of the gas, the "titre" of a gas, twenty-four hours after the gas had been submitted to the electric action, was equivalent to 28·25 cub. centims. of hyposulphite of soda; after sixty-six hours the

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* Philosophical Transactions, 1860, p. 113.

† Annalen der Chemie und Pharmacie, Supplementband ii. (1863), p. 297.

"titre" had sunk to 23 cub. centims., after ninety hours to 20 cub. centims., and after 114 hours to 18·75 cub. centims.; and it is highly probable that the electrized gas might be preserved over perfectly pure sulphuric acid in a cool place with very slight and gradual alteration. In the present experiments, however, no error could arise from such alteration of the gas, as the "titre" of the gas was invariably taken immediately before any series of experiments was made; and if the experiments were extended over a time in which, judging from previous experience, the "titre" of the gas might be altered, this "titre" was again taken at the conclusion of the experiments. The "titre" is quite independent of the strength of the solution of iodide of potassium employed; it is not, however, desirable to operate with a strong solution, as in this case errors may arise from the oxidation of hydriodic acid during the process of titration by means of atmospheric oxygen.

In the following Table the results of eight experiments are given, in which the volumes of the electrized gas before and after passing through a solution of iodide of potassium are compared, the volume before being that read in the pipette, the volume after being that read in the aspirator; these volumes, and all other similar volumes referred to in these experiments, are given in cubic centimetres reduced to 0° C. and 760 millims. pressure. In the first column I have given the "titre" of the quantity of gas employed in cubic centimetres of oxygen similarly reduced.

"Titre."	Volume before the experiment.	Volume after the experiment.
13·58	269·55	269·57
7·53	271·33	271·32
10·52	276·68	276·11
5·82	272·28	271·89
5·47	271·46	271·46
13·17	274·18	273·84
13·17	273·87	273·45
13·17	273·90	274·00
Mean 10·30	Mean 272·906	Mean 272·705

Assuming the mean as the correct result, it appears that for every 100 cub. centims. of gas in the pipette 99·93 cub. centims. appear in the aspirator, and 3·77 cub. centims. of oxygen are absorbed by the iodide of potassium without any appreciable diminution of the volume of the gas, the slight difference found in the mean value of the volumes before and after the experiment being fully accounted for by the absorption by the alkaline liquid of minute quantities of oxygen.

[To increase the percentage of ozone was, for the purpose of the present experiments, no great object; indeed to a certain extent it was even disadvantageous, as a gas rich in ozone is more readily subject to decomposition than a gas containing a smaller proportion. The average amount of ozone in the gas as actually employed in these experiments was about 4 per cent., but occasionally much higher. The following Table contains the record of a few estimations of ozone in the gas after collection in the gas-holder.

Volume of gas at 0° and 760 millims.	"Titre" in cub. centims. at 0° and 960 millims.	"Titre" on 100 volumes of gas.
86·97	4·28	4·92
269·5	13·58	5·04
281·7	14·29	5·07
272·8	15·15	5·55
270·9	14·74	5·44

The actual "titre" of the gas issuing from the induction-tube must, however, in all cases have been somewhat higher than that here given, since several hours were occupied in the collection of the gas, during which time the "titre" was constantly although slowly diminishing. In the last experiment in the Table "the titre" of the gas was not taken until the day after that on which it was prepared, and must, judging from the usual rate of decomposition of the ozone, originally have amounted to at least 6·5 per cent.

The experiments recorded in the following Table were differently conducted, the "titre" of the gas being taken immediately after its exit from the induction-tube The temperature of the experiment is given in the first column.

Temp.	Volume of gas at 0° and 760 millims.	"Titre" in cub. centims. at 0° and 760 millims.	"Titre" on 100 volumes of gas.
0°	88·97	5·27	5·93
−12°	88·97	5·65	6·35
− 9°	88·15	5·71	6·47
−10°	88·15	5·75	6·52

A very powerful coil was employed in these experiments. The passage of the gas in each experiment occupied about thirty minutes. The greatest contraction and highest titre attained in the experiments of Von Babo and Claus was 5·74 per cent.*; but this was reached in only one instance, and the results of their other experiments were far below this amount.

The following experiment was made with the view of ascertaining the effect of the repeated electrization of the gas by passing it several times through the induction-tube. The induction-tube was placed between two of the sulphuric-acid gas-holders previously described, so that the gas operated upon could be drawn through it from the one to the other, by causing a difference of pressure in the gas-holders, and thus submitted to the electric action as often as might be desired. After the passage of the gas through the induction-tube, portions of it were at intervals drawn off into the gas-pipette, and the ozone estimated as usual by iodide of potassium.

A portion of oxygen was thus passed once through the induction-tube and there submitted to the action of the electricity generated by a powerful coil worked by means of five elements of Grove's battery of the usual size.

A pipette of 94 cub. centims. capacity was filled with the gas at barometric pressure and a temperature of 16° C., and the ozone estimated by passing it through iodide of potassium.

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* *Loc. cit.* p 303.

The iodine formed required for titration 28 cub. centims. of the standard solution of hyposulphite, of which 1 cub. centim. was equivalent to 0·1082 cub. centim. of oxygen. This corresponded to a "titre" of about 3·4 per cent. of oxygen.

The gas was again passed three times through the induction-tube and the ozone again estimated, the volume of gas, temperature, and pressure being the same as in the previous experiment. 28 cub. centims. of hyposulphite were again required for the titration.

The gas was now passed five times through the induction-tube, but a comparatively small coil was used in the experiment with five of GROVE'S cells. The same volume as before required for titration 27 cub. centims. of hyposulphite; that is to say, the "titre" of the gas, after having been passed ten times through the induction-tube, was almost, if not quite, the same as the titre of the same gas which had been passed once through the induction-tube.

The gas from the last experiment was again titred after an interval of sixteen hours, during which time the quantity of ozone was materially diminished. The same volume as before now required for titration 17·5 cub. centims. of hyposulphite. The gas was now passed twice through the induction-tube, the same coil being employed as in the last experiment. The same volume of gas as before now required for titration 29 cub. centims. of hyposulphite.

The gas was again passed twice through the induction-tube. The same volume as before required for titration 29·5 cub. centims. of hyposulphite.

It thus appears that there is a fixed limit prescribed by the conditions of the experiment beyond which the formation of the ozone cannot pass, and, moreover, that this limit is reached at once.

In this last respect these results differ essentially from those of Von BABO and CLAUS*, who found that for the production of a high percentage, 3·1 to 5·7 per cent. of ozone, the gas required to be submitted for many hours to the action of the electricity generated by a powerful coil, and that for several hours the gas thus operated upon underwent a regular diminution in volume. A point, however, was ultimately reached at which the volume of the gas remained unaltered.

No difference was detected, by detonation with hydrogen, between the composition of the gas previous to the experiment and its composition after having been submitted in the induction-tube to the electric action and passed through the solution of iodide of potassium. In the following experiment a bulb containing a solution of iodide of potassium was attached to the induction-tube, through which a current of oxygen, prepared by electrolysis and dried by anhydrous phosphoric acid, was passed direct from the generator. The current of oxygen was passed through the tube and solution for from four to five hours before turning on the coil, and a portion collected and detonated with hydrogen. The numbers thus obtained corresponded to 100·06 per cent. of oxygen. The coil was then set to work without disturbing the apparatus, and after half an hour a portion of the gas was again collected and analyzed: it was found to contain 99·1 per cent. of oxygen.

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* *Loc. cit.* p. 304.

In another similar experiment the gas was analyzed in the first instance, after having been submitted to the electric action and passed through the solution of iodide of potassium, and was found by detonation with hydrogen, in two determinations respectively, to contain 99·5 and 99·0 per cent. of oxygen. The action of the coil was stopped, the passage of the current of oxygen continued for an hour, and the gas was again collected and analyzed; it was found to contain 99 per cent. of oxygen.

The experiments of which the results are given in the Table below were instituted with the view of effecting a comparison between the amount of oxygen corresponding to the "titre" of the gas and the increment of weight of the solution of iodide of potassium through which the electrized gas was passed.

The general arrangements were the same as in the experiments last described. A current of pure and dry oxygen was passed direct from the generator through the induction-tube, where it was submitted to the electric action; thence it was passed through a tube containing anhydrous phosphoric acid into the bulb containing the solution of iodide of potassium; to this a second tube, containing anhydrous phosphoric acid, was attached, which was weighed, together with the bulb containing the solution of iodide, before and after the experiment, the exit of the gas being through a fine capillary tube. At the commencement of the experiment a current of oxygen was passed through the apparatus until the weight of the bulb of iodide of potassium and the desiccating tube attached to it became constant; they were similarly weighed after the experiment, the difference of weight in the two cases being the increment of weight due to the passage of the electrized gas.

In column I. this increment of weight is given, W; in column II. the corresponding "titre" (that is to say, the weight of oxygen corresponding to the iodine found), T; in column III. the difference of these two, W—T; in column IV. the increment of weight corresponding to 100 parts of oxygen as estimated by titration, that is $100\times\frac{W}{T}$.

I. W.	II. T.	III. W–T.	IV. $100\times\frac{W}{T}$.
grm.	grm.	grm.	
·0719	·0689	·003	104·3
·1932	·1865	·0067	103·5
·1602	·1548	·0054	103·4
·3338	·3245	·011	103·2
·3939	·3836	·0103	102·7
			103·4=Mean.

The strength of the solution of iodide of potassium was intentionally varied in the last two experiments—the last experiment being made with a very weak solution of iodide of potassium containing 2 grammes of iodide in 25 cub. centims. of water, the preceding experiment with a relatively very strong solution. It hence appears that for every 100 parts of oxygen shown by the "titre" of the solution 103·4 parts of matter are absorbed by that solution. The value of the hyposulphite employed for the titration was estimated with the greatest care; and the difference of these two numbers certainly does not depend on any error in the mode of conducting the experiment. Moreover every chemist who has experimented upon this subject has observed a difference in the same direction. The question is as to the cause of this difference.

It appears, on the face of the results given in the preceding Table, that this difference is proportional, or nearly proportional, to the "iodine-titre," which, again, is itself proportional to the quantity of oxygen employed in the experiment.

It was ascertained by ANDREWS*, and the point has been amply confirmed by MEISSNER, that when the electrized oxygen is passed through an acid solution of iodide of potassium this discrepancy no longer exists, but the increment of weight agrees with the "titre." The same is true when the gas is passed through the solution of neutral iodide until the passage of the ozone is no longer arrested by it, in which case the whole of the iodine is converted into the form of iodic acid†. Two causes may be indicated, both of which tend to create such a discrepancy:—(1) the solution of oxygen in the alkaline solution of iodide of potassium; (2) the formation of oxides of nitrogen in the induction-tube from traces of atmospheric air mixed with the oxygen employed in the experiment. I have ascertained by direct experiment that when atmospheric air, carefully dried, is submitted in the induction-tube to the electric action, very considerable quantities of the oxides of nitrogen are formed. Thus in one experiment in which 2900 cub. centims. of air were thus operated upon, and then passed through a bulb containing a solution of caustic potash, 0·0086 gramme of nitrogen was after the experiment detected in the alkaline solution in the form of nitric and nitrous acids, the nitrogen being carefully estimated in the form of ammonia. Now, assuming the iodine-titre to have amounted in the previous experiments to 4 per cent. of the total gas, in the first experiment (which exhibits the greatest divergence) 1257 cub. centims. of oxygen must have been operated on in the induction-tube. If the gas contained only 1 vol. in 1000 of nitrogen, 1000 cub. centims. would contain 0·00125 gramme of nitrogen, corresponding to ·0034 gramme of the teroxide of nitrogen, which is more than the whole difference.

ANDREWS attributes the discrepancy referred to to the presence of carbonic acid in oxygen formed by electrolysis‡; but, as has been clearly shown by BAUMERT§, the occurrence of carbonic acid was simply a peculiarity in the experiments of ANDREWS, and, moreover, the gas employed by MEISSNER was derived from chlorate of potash, and specially freed from carbonic acid‖. In the case of gas collected, as in the present experiments, over large quantities of sulphuric acid, such traces as might be present, either of the oxides of nitrogen or of carbonic acid, would doubtless be removed by solution in that liquid.

There is still something here to be explained; but I have not pursued the subject

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* Philosophical Transactions, 1856, vol. cxlvi. p. 8.

† MEISSNER, p. 78, Table B.

‡ Philosophical Transactions, 1856, vol. cxlvi. p. 4.

§ Annalen der Physik, vol. xcix. p. 91.

‖ MEISSNER, p. 17.

further, any errors arising from this cause being too minute for satisfactory appreciation by the methods employed, and not essentially affecting the results.—April 1873.]

In the following experiments a pipette of electrized gas was passed through a small glass tube heated with a Bunsen burner, and the volume measured in the aspirator. In experiment 1 a pipette of gas was also passed through a solution of iodide of potassium, and the volume measured with the result given in the first line in the Table below. In column 4 the sum of the volume in the pipette and the "titre" of the gas is given.

	"Titre."	Volume before the experiment.	Volume after the experiment.	Sum of the "Titre" and the volume of the gas before the experiment.
Experiment 1 ...	12·27	270·53	270·49	———
	12·27	270·07	282·55	282·34
*Experiment 2 ...	12·27	290·81	303·24	303·08

This result is in perfect concordance with the experiments of Von Babo and Claus[†], who found, in the series of experiments before referred to, that the contraction which oxygen underwent under the influence of electricity was equal to the volume of oxygen represented by the titre of the gas, the mean of their experiments giving a contraction of 98·27 volumes for every 100 volumes estimated by titration. The experiments also of Andrews and Tait indicate the same conclusion, their last and most concordant and exact series of experiments giving (if I rightly understand them) a contraction of 93 to 95 volumes for every 100 volumes of oxygen thus estimated[‡].

It was a matter of interest to ascertain the way in which the ozone is affected by heat, and the amount of ozone capable of surviving at different temperatures. In the three following experiments a pipette of the electrized gas was passed first through a glass tube heated in a bath of definite and constant temperature, and then through a solution of iodide of potassium, the gas being finally measured in the aspirator; the difference between the original "titre" of the gas and the "titre" after its passage through the heated tube gives the amount of ozone destroyed, which should correspond with the increment of volume as ascertained by measurement in the aspirator.

In the first column of the following Table is given the temperature at which the experiment was made; in column II. is given the "titre" of the gas before the experiment, T; in column III. the volume before the experiment, V; in column IV. the "titre" of the gas after its passage through the heated tube, T_1; in column V. the sum of the "titre" before the experiment, and the volume before the experiment, $T+V$; in column VI. the sum of the "titre" after the experiment, and the volume after the expe-

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[*] Although the "titre" of the gas happens to be the same in these two experiments, they were made with different gases at different times.

[†] Annalen der Chem. u. Pharm., Supplementband ii. p. 303.

[‡] Philosophical Transactions, 1860, vol. cl. p. 123.

riment, V_1, that is, T_1+V_1; in column VII. is given the difference of the "titre" before the experiment and the "titre" after the experiment, $T-T_1$; and in column VIII. the percentage of ozone destroyed as calculated from the equation, $x=100\frac{T-T_1}{T}$, where x is the percentage referred to, and T and $T-T_1$ are the numbers belonging to the experiment in columns II. and VII.

I. Temperature.	II. T.	III. V.	IV. T_1.	V. T+V.	VI. T_1+V_1.	VII. $T-T_1$.	VIII. $x=100\frac{T-T_1}{T}$.
110° C.	14·48	273·64	13·63	288·12	286·21	0·85	5·87
150° C.	14·43	272·96	11·59	287·39	287·08	2·84	19·68
200° C.	14·43	273·50	0·41	287·93	287·08	14·02	97·15

If the experiments were made with perfect accuracy, the numbers in columns V. and VI. should be identical. In the first experiment the difference between these numbers is beyond the usual error of experiment. This, however, does not affect the "titre" of the gas, which is quite independent of any accidental error of measurement. It thus appears that by merely passing the electrized gas through a tube heated to 200° C. 97·15 per cent. of the ozone is destroyed. 270° C. is the temperature given by ANDREWS and TAIT as that at which the ozone is "rapidly destroyed;" the point of rapid decomposition of the ozone lies, however, considerably below this temperature.

The change in volume which the electrized gas undergoes when brought in contact with metallic silver and certain other substances is closely related to the expansion of the gas at an elevated temperature; I have made some experiments on this point also.

When the perfectly dry electrized gas is passed through a tube containing silver leaf, the silver leaf becomes dark in colour at the place where the gas enters the tube, the change in colour appearing as dark specks and also as a transparent film of a purple hue on the surface of the silver. This change in appearance extends, however, but a very little way into the tube, which becomes intensely hot where the gas enters; not a trace of ozone passes out of the tube, and the gas measured in the aspirator is found to have undergone an increment of volume. The silver leaf and other substances employed in the following experiments were contained in small tubes of thin glass. The tube was kept during the experiment at the temperature indicated in column I. of the following Table: in which Table T is the "titre" of the gas; V is the volume of the gas before the experiment; V_1 is the volume of the gas after the experiment; T+V is the sum of the "titre" of the gas and the volume of the gas before the experiment.

Temperature.	T.	V.	V_1.	T+V.
14°·7 C.	14·43	273·17	287·38	287·6
10° C.	9·33	273·22	282·45	282·55
——	9·1	272·97	282·05	282·07
——	8·98	272·23	280·39	281·21

It hence appears that the electrized gas when thus passed over metallic silver undergoes an expansion equal to the "titre" of the gas, precisely as though the gas were passed through a heated tube. The difference between the numbers in columns IV. and V. falls within the unavoidable errors of experiment, and is inappreciable, except perhaps in the last experiment. The quantity of oxygen retained by the silver must therefore in these experiments have been excessively minute. That this oxidation of the silver is nevertheless an integral part of the action, and although minute is still capable of estimation, appears from the following experiment, which was made with every precaution and with a special view of determining this point. The two experiments were made consecutively, without detaching from the apparatus the tube containing the silver.

T.	V.	V_1.	T+V.
9·68	270·27	278·61	279·95
9·68	269·67	277·77	279·35

Regarding these two observations as constituting a single experiment, the total volume measured in the aspirator after the experiment, namely the sum of the volumes in the two experiments headed V_1, is 556·38, whereas the sum of the volumes in the two experiments in the column headed T+V, column V., is 559·30; the difference between these volumes is 2·92 cub. centims., which, if the experiment be correctly conducted, represents the oxygen retained by the silver.

The tube containing the silver was now heated by means of a spirit-lamp, and the gas evolved measured in the aspirator; this gas amounted to 2·5 cub. centims., the difference between this number and the previous deficiency 2·92 cub. centims., that is 0·34 cub. centim., being the total amount of oxygen unaccounted for.

The oxide of silver here formed appears to be a peroxide of silver; for if a tube in which such an experiment has been made be washed out with a solution of iodide of potassium iodine is formed. That the minute quantity of the peroxide of silver thus formed is really an effective agent in determining the decomposition of the ozone, is rendered probable from the circumstance that the binoxide of manganese produces a precisely similar change (as to the decomposition of the ozone and the expansion of the gas) to that produced by silver, a small amount of oxygen being here also (if one experiment may be trusted) retained by the agent by which the decomposition of the ozone is effected, while the contact of the metals copper, gold, and aluminium produces no change whatever in the gas; these points are evident from the following experiments.

An experiment thus made with binoxide of manganese gave the following result:—

T.	V.	V_1.	T+V.
13·45	276·98	288·84	290·43

The difference between the numbers in the fourth and third columns, namely 1·59 cub. centim., represents the oxygen retained by the manganese.

The three following experiments were made in a precisely similar manner with the metals copper, gold, and aluminium, with the exception of a bulb containing iodide of potassium being placed immediately after the tube containing the metal; the "titre" of the gas after the experiment, T_1, as estimated in this bulb, is given in the last column.

	T.	V.	V_1.	T_1.
Copper	14·55	276·48	276·07	——
Gold	14·36	276·10	275·81	14·27
Aluminium...	14·17	275·52	274·61	14·20

It appears from these experiments that the "titre" of the electrized gas is precisely the same after the passage of the gas over these metals as before the experiments, and also that the volume of the gas is unaffected, the results being the same as though the gas had been passed through the solution of iodide of potassium alone.

When the electrized gas is passed through a solution of binoxide of sodium the ozone is destroyed, and a certain portion of the binoxide of sodium also is decomposed. This reaction is constantly referred to as an ascertained fact, but has never been really investigated. It was of great importance, in relation to the theory of this reaction, to ascertain by experiment the relation which exists between the two decompositions.

The points to be ascertained were:—the "titre" of the electrized gas, the oxygen lost by the binoxide of sodium, and the ratio of this oxygen to the "titre," also the expansion undergone by the electrized gas, the difference, that is, of the volumes of the gas after and before the experiment, and the ratio of this difference to the "titre" of the gas.

The oxygen lost by the binoxide of sodium was determined by titration of the solution of the binoxide of sodium before and after the experiment with a standard solution of permanganate of potash, according to the method described by me in a former paper*. From the difference between these two titrations the amount of oxygen lost by the binoxide of sodium may be calculated.

Since ozone is decomposed when brought in contact with a solution of caustic alkali, which substance is always present in the solution of binoxide of sodium, and, indeed, is a product of the decomposition of it by ozone, it was possible that errors in the exact estimation of the reaction might arise from this circumstance, as also from the spontaneous decomposition of the peroxide of sodium, which is especially rapid in a strongly alkaline solution. To guard against such errors, the binoxide of sodium in the first experiment was dissolved in water saturated with carbonic acid. Ozone, although

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* Philosophical Transactions, 1862, vol. clii. p. 840.

destroyed by caustic soda, is totally unaffected even by a strong solution of carbonate of soda. This fact I have ascertained by experiment. In the last two experiments the volume of gas after the experiment was not measured.

In the next Table T is the "titre" of the gas.

V is the volume of the gas before the experiment.

V_1 is the volume after the experiment.

V_1-V is the increment in the volume of the gas.

$\frac{V_1-V}{T}$ is the ratio of this increment to the "titre" of the gas.

P is the amount of oxygen lost by the binoxide of sodium, as estimated by titration calculated in cub. centims. at 0° C. and 760 millims.

$P+T$ is the sum of the oxygen lost by the binoxide of sodium and the "titre" of the gas.

$\frac{P+T}{T}$ is the ratio of this sum to the "titre" of the gas.

T.	V.	V_1.	V_1-V.	$\frac{V_1-V}{T}$.	P.	$P+T$.	$\frac{P+T}{T}$.
3·92	269·84	277·4	7·56	1·93	4·19	8·11	2·06
7·42	273·81	288·62	14·81	1·99	8·70	16·12	2·17
3·23	——	——	——	——	3·26	6·49	2·00
3·34	——	——	——	——	3·61	6·95	2·08

It appears from these experiments that the ozone and the binoxide of sodium are decomposed in exactly equivalent proportions, and that in this decomposition equal volumes of oxygen are evolved from each of the two substances respectively, the reaction in this respect being similar to the decomposition of the peroxide of sodium by permanganic acid and ferrocyanide of potassium, and to the various deoxidations effected by the peroxide of hydrogen previously investigated by me, and discussed in a former communication to the Society*.

That this reaction has all the characters of a normal chemical decomposition occurring according to the law of definite and multiple proportions, is further proved by the following experiments, in which the binoxide of sodium was so dilute as to allow of the passage through it of a certain portion of the electrized gas with its properties unaltered. After the bulb containing the solution of binoxide of sodium a second bulb was placed, containing a solution of iodide of potassium; the difference between the original "titre" of the gas and the "titre" after the experiment of this solution is the "titre" of the ozone by which the decomposition of the binoxide of sodium is actually effected, and the ratio of the amount of oxygen, P, lost by the binoxide of sodium to this difference gives the proportion in which the oxygen is evolved from the two substances respectively.

T is the original "titre" of the gas.

T_1 the "titre" of the gas after its passage through the solution of binoxide of sodium.

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* Philosophical Transactions, 1850, p. 750, and 1862, p. 840.

$T-T_1$ the "titre" of the gas destroyed by the binoxide of sodium.

P the amount of oxygen lost by the binoxide of sodium, ascertained by the titration with permanganate of potash in the way before mentioned.

$\frac{P}{T-T_1}$ the ratio of the volume of oxygen evolved from the binoxide of sodium to the volume of oxygen evolved from the electrized gas.

In these three experiments the solution of binoxide of sodium was saturated with carbonic acid.

T.	T_1.	$T-T_1$.	P.	$\frac{P}{T-T_1}$.
7·98	3·96	4·02	3·99	0·98
2·41	0·08	2·33	2·57	1·11
1·27	0·05	1·22	1·28	1·04

There are doubtless numerous chemical substances which stand towards ozone in the same relation as iodide of potassium, and in which an oxidation may be effected by the electrized gas equal in amount to the "titre" of the gas without any alteration of its volume. Thus in two experiments in which the electrized gas was passed through a solution of the protonitrate of mercury, the two experiments being made consecutively and with the same solution, the following results were obtained:—

Volume of gas in the pipette.	Volume of gas in the aspirator.
268·14	267·21
267·95	268·05

the gas being deprived of its special oxidizing power, and the oxidation effected without alteration of its volume.

In the following experiments also, with protochloride of iron and protosulphate of iron, the oxidation effected is equal to the "titre" of the gas. In the case of protochloride of iron a measured quantity of the solution was "titred" before the experiment with permanganic acid, and the volume of oxygen required to effect its complete oxidation was determined. The solution through which the gas was passed was similarly "titred." From the difference between the "titre" of these solutions the oxidation effected by the electrized gas was estimated.

In the case of the protosulphate of iron, the ozone was not entirely destroyed by its passage through the solution, and a second bulb containing a solution of iodide of potassium was placed after the bulb containing the solution of protosulphate of iron; the difference of the original "titre" of the gas and the "titre" of the gas after its passage through the solution of protosulphate of iron gives the amount of oxidizing power lost by the electrized gas in its passage through that solution. The difference between the "titre" of the solution of the protosulphate of iron before and after the experiment gives the oxidation actually effected. The following is the result of one experiment thus made with protochloride of iron, where T is the "titre" of the electrized gas, S the amount of oxygen corresponding to the actual oxidation effected, and $R=\frac{S}{T}$.

T.	S.	$R=\frac{S}{T}$.
3·197	3·218	1·00

In two experiments with protosulphate of iron, putting T as the original " titre " of the gas and T_1 as the " titre " of the gas after its passage through the solution of protosulphate, $T-T_1$ as the difference of the two " titres," S as the oxidation actually effected in the solution of protosulphate, and $R=\frac{S}{T-T_1}$, the following results were obtained:—

T.	T_1.	$T-T_1$.	S.	$R=\frac{S}{T-T_1}$.
1·124	0·080	1·044	1·003	0·97
1·122	0·134	0·988	1·042	1·05

From the discrepancy which existed between the oxidation of a solution of iodide of potassium, as indicated by the " titre," and the increment of weight of the same solution after the passage of the electrized gas, I was led to make the following experiment with a solution of protosulphate of iron, with the view of ascertaining whether or no a similar discrepancy would be found to exist in this case also. The experiment was arranged precisely as in the previous experiment referred to (p. 449).

A current of electrized gas was passed through a bulb containing a measured quantity of a nearly saturated solution of protosulphate of iron, which was weighed with the drying-tube attached before and after the experiment. The gain in weight was ·2125 grm. The oxidation effected, as estimated by titration with a standard solution of permanganate of potash before and after the experiment, corresponded to ·2184 gramme of oxygen. Now $\frac{\cdot 2184}{\cdot 2125}=\frac{100}{97\cdot 3}$, the oxidation indicated by the titration being rather less than that shown by the gain in weight of the solution, and the discrepancy being in the reverse direction to the discrepancy in the former case.

Hence it appears that the oxidation effected in these solutions exactly corresponds to and is equal to the " titre " of the electrized gas by which that oxidation is effected. The oxidation similarly effected in an acid solution of ferrocyanide of potassium and in a solution of arsenite of soda is of the same character; the experiments, however, which I now proceed to lay before the reader belong to a different order of phenomena.

SECTION III.

According to the statements of ANDREWS and TAIT, the action of ozone upon an acid solution of iodide of potassium is, as regards the amount of oxidation effected, identical with its action upon a neutral solution of iodide of potassium. "In some of the experiments the solution of iodide of potassium was slightly acidulated, in others it was neutral;" but "the results were the same whether the solution was taken in the neutral or in the acid state"[*]. The method is not mentioned by which a comparison was effected between these results; but the assertion is probably to be explained by the circumstance that these chemists experimented only with very dilute solutions of hydriodic acid, in which case the difference between the two oxidations, although by no means imperceptible, may not have been appreciated by their method of estimation. Out of many comparative experiments in no single case have I found the two oxidations to be identical. MEISSNER, on the other hand, who detected the essential difference in the case of the two oxidations, has fallen into an error of a different order, inferring the oxidation effected in the neutral iodide of potassium to be an altogether incorrect measure of the ozone contained in the electrized gas[†]. I shall hereafter recur to his experiments on this point.

The following experiments were among the first made by me as to the quantitative reactions of ozone, and were undertaken before the construction of the apparatus for exact measurement previously described, which accounts for some deficiencies in them.

The volume of gas before the experiment was measured in a gas-pipette, into which the gas was passed from a sulphuric-acid gas-holder substantially of the same construction as that previously described; the actual capacity of this pipette was 265·44 cub. centims., and the pipette contained a volume of gas which, at the temperature and pressure at which the experiments were made, was in round numbers equal to 250 cub. centims. at 0° C. and 760 millims. pressure. This volume does not in any way appear in the result of the experiment, and I shall speak of the volume of gas employed simply as a pipette of the electrized gas: this volume is assumed to be the same in consecutive experiments, which is not exactly true; for although the barometer may be considered constant for the short interval of the experiments, the temperature of the gas was subject to slight variation: this variation in extreme cases amounted to as much as 1° C. I have taken no cognizance of this point in the calculation of the experiments, as it could only affect the results to the extent of $\frac{1}{273}$ part, whence the error in the calculated result would appear only in the second decimal place, and be inappreciable.

The investigation of the action of ozone upon hydriodic acid is complicated by the analogous decomposition effected by the oxygen with which the ozone is invariably associated; in weak solutions of hydriodic acid this latter oxidation is extremely minute, but in strong solutions great errors would arise if it were not taken into account.

The oxidation effected by the passage of a pipette of oxygen through a solution of hydriodic acid of a known degree of concentration was determined by passing a pipette

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[*] Philosophical Transactions, 1860, vol. cl. p. 121.

[†] MEISSNER, 'Neue Untersuchungen über den elektrisirten Sauerstoff,' 1869, p. 82.

of the gas through the solution of hydriodic acid contained in one of the small bulbs previously described, and estimating the oxidation effected with a standard solution of hyposulphite of soda in the usual manner. A strong solution of hydriodic acid invariably contains a certain amount of dissolved iodine; this amount was similarly estimated before the experiment in a quantity of the solution equal to that employed in it, and the number of cub. centims. of hyposulphite of soda employed in this titration was deducted from the number of cub. centims. of the same solution employed in the final titration. The difference represents the oxidation effected. The hydriodic acid was made of a definite strength by suspending in water a weighed quantity of iodine, and passing through the solution a current of sulphide of hydrogen, the acid being purified in the usual manner, a method sufficiently exact for the object in view.

The solution of hydriodic acid employed was measured, in all cases, in a small pipette of the same capacity, namely about 15 cub. centims. This quantity will be here termed a bulb of the solution.

The following experiments were made in the way described at a temperature of 18° C.

I. 16 cub. centims. of the solution contained about one gramme of iodine in the form of hydriodic acid; a bulb of this solution required for titration before the experiment 0·72 cub. centim. of the standard solution of hyposulphite. After the passage of the oxygen, the bulb of hydriodic acid required for titration 1 cub. centim. of the same standard solution, which gives 0·28 cub. centim. of hyposulphite as equivalent to the oxidation effected by the pipette of pure oxygen. One cub. centim. of the hyposulphite employed was equivalent to 0·0002814 gramme of oxygen. The oxygen therefore operative in the experiment for the decomposition of the hydriodic acid was certainly not more than ·000093 gramme. It was useless to attempt to follow the oxidation beyond this point.

II. 8 cub. centims. of the solution contained one gramme of iodine; the bulb of solution before the experiment required for titration 1·4 cub. centim. of hyposulphite and after the passage of the gas in two experiments 3·25 and 4 cub. centims. of the same. Taking the mean of these two experiments, 3·62 cub. centims., and deducting 1·4 cub. centim., we have 2·22 cub. centims. of the standard solution of hyposulphite of soda as the measure of the oxidation.

III. 4 cub. centims. of the solution contained one gramme of iodine in three experiments: the "titres" after the experiment were respectively 5, 7·5, and 6·75 cub. centims.; the "titre" before the experiment was 2·8 cub. centims., and the mean oxidation effected was equivalent to 3·61 cub. centims.

IV. 2 cub. centims. of the solution contained one grain of iodine; the "titre" after the experiment was in three determinations respectively 9·75, 9·75, and 10 cub. centims., and before the experiment 5·75, the oxidation effected being equivalent to 4·08 cub centims.

V. In the case of a very strong solution of hydriodic acid, of which 1 cub. centim. contained one gramme of iodine, 22·75 cub. centims. of hyposulphite were required for titration after the experiment and 14·2 before the experiment, the oxidation being equivalent to 8·5 cub. centims.

These numbers exhibit in experiments made under the same general conditions very appreciable differences, and in the case of very concentrated solutions of hydriodic acid, as in experiment V., undoubtedly become inaccurate from the oxidation of the hydriodic acid during the process of titration, and also to a certain extent from variations dependent on the rate of the passage of the gas through the solution, and the time for which the surface of the solution is consequently exposed to an atmosphere of oxygen. These differences, however, although undoubtedly a source of error, nevertheless are very small as compared with the total oxidation in the analogous experiments made with an electrized gas, and would hardly affect the result to more than one per cent., except in the extreme case given in experiment V.

The mean results of the preceding experiments are given in the two columns below. The numbers in column II. indicate the amount of oxidation effected by the passage of a pipette (that is about 250 cub. centims.) of pure oxygen at a temperature of 18° through a bulb, or (15 cub. centims.) of hydriodic acid, as estimated in cub. centims. of the standard solution of hyposulphite of soda. The degree of concentration of the hydriodic acid employed is indicated in column I., in which is given the number of cub. centims. of the solution containing one gramme of iodine. One cub. centim. of the hyposulphite employed was equivalent to 0·0002814 gramme of oxygen, whence the actual oxidation effected can be readily calculated. For the present object this is not necessary. The numbers marked † are interpolated from calculation, and are the mean of the two experiments between which they appear.

I.	II.
1 cub. centim.	——
2 „	4·08
†3 „	3·80
4 „	3·61
†6 „	3·00
8 „	2·22
†12 „	1·25
16 „	0·28

In determining the oxidation effected by the action of the electrized gas upon the solution of hydriodic acid, the total oxidation was estimated precisely as in the experiments just described; and a correction was made for the effect of the oxygen associated with the ozone by deducting from the number of cub. centims. of the standard solution of hyposulphite of soda which represented the total oxidation, the number of cub. centims. of the same hyposulphite of soda which represented the oxidation due to the passage of the pipette of oxygen through a solution of hydriodic acid of the strength employed in the experiment according to the preceding Table. This correction is made upon the hypothesis that the oxidation effected in the hydriodic acid is constituted of two distinct parts—namely, the oxidation effected by the ozone and the oxidation effected by the oxygen with which it is associated, which are assumed to be separate and independent occurrences. The truth of this assumption, however probable it may appear, cannot be demonstrated by *à priori* reasoning; but if, proceeding upon this principle, it should be found that the ratio of the oxidation effected by the ozone to the "titre" of the gas under varying conditions has a constant value, there is every reason to believe the assumption to be substantially correct.

It is unnecessary to give the details of these experiments; but I will offer one or two examples to explain the mode of proceeding.

A pipette of electrized gas was passed through a neutral solution of iodide of potassium, which required for titration, after the passage of the gas, 12·5 cub. centims. of the standard solution of hyposulphite of soda.

A pipette of the same gas was passed through a bulb of hydriodic acid, 4 cub. centims. of which contained one gramme of iodine. The "titre" of the hydriodic acid, after the passage of the gas, was in two experiments respectively represented by 28·2 and 28·7 cub. centims. of the same hyposulphite of soda, deduction for the "titre" of the solution before the experiment having been made on the principles previously explained. Now 3·61 is the number given in the Table as that of the cub. centims. of the same hyposulphite of soda, which represents the oxidation due to the passage of a pipette of pure oxygen through a bulb of hydriodic acid of the degree of concentration employed in the experiment; subtracting this number from 28·2 and 28·7 respectively, we have 24·6 and 25·1 as the numbers representing the oxidation due to the action of the ozone; and putting R as the ratio of the oxidation of the hydriodic acid to the "titre" of the gas, we have, in the two experiments respectively, $R=\frac{24·6}{12·5}=1·96$, and $R=\frac{25·1}{12·5}=2·00$.

A similar experiment made with a solution of hydriodic acid, of which 2 cub. centims. contained one gramme, gave the following results:—

The "titre" of a pipette of the electrized gas with neutral iodide of potassium was represented by 19 cub. centims. of the standard solution of hyposulphite of soda.

The "titre" of a pipette of the same gas passed through the bulb of hydriodic acid was represented by 41·8 and 41·3 cub. centims. of the same hyposulphite; the correction for the influence of the associated oxygen is 4·1 cub. centims.; whence, subtracting this number from 41·8 and 41·3 respectively, we have 37·7 and 37·2 as the cub. centims. of the standard solution of hyposulphite representing the oxidation effected by the ozone in the several experiments, and we have for the values of R, $R=\frac{37·2}{19}=1·96$, and $R=\frac{35·6}{19}=1·87$.

The following experiment was made with a dilute solution of hydriodic acid, of which 16 cub. centims. contained one gramme of iodine, on which the action of pure oxygen would be almost imperceptible, the deduction according to the Table amounting to no more than 0·28 cub. centim.

The "titre" of a pipette of gas passed through neutral iodide of potassium was 12·5 cub. centims.; the "titre" of a pipette of the same gas passed through the solution of hydriodic acid was 23·8 cub. centims.; deducting from this 0·3 cub. centim., we have 23·5 cub. centims. as representing the oxidation effected by the ozone, whence $R=\frac{23·5}{12·5}=1·88$.

An experiment conducted in a perfectly similar manner, but with an exceedingly dilute solution of hydriodic acid, of which 256 cub. centims. contained one gramme of iodine, gave for the value of R, $R=\frac{14·25}{12·5}=1·14$.

The following Table contains the record of a series of experiments made, precisely as were the experiments just described, with solutions of hydriodic acid, varying in their degree of concentration, which ranged from a solution containing one gramme of iodine in one cub. centim. to a solution containing one gramme of iodine in 256 cub. centims. For reasons which will presently appear, I have recorded in this Table all the experiments, without exception, which I have made upon this subject in the same way.

In column I. is given the degree of concentration of the hydriodic acid employed. In column II. is given the "titre" of a pipette of the gas with neutral iodide of potassium, T, as represented by the cub. centim. of hyposulphite of soda necessary for the titration. In column III. is given the "titre" of a pipette of the same gas with hydriodic acid, S, similarly represented. In column IV. is given the ratio of the oxidation effected in the hydriodic acid to the oxidation effected in neutral iodide of potassium, $R=\frac{S}{T}$.

I. Degree of concentration of the solution of hydriodic acid employed.	II. T.	III. S.	IV. $R=\frac{S}{T}$.
1. 1 gramme of Iodine in 1 cub. centim.	19	36	1·89
2. ,, ,, ...	19	36	1·89
3. 1 gramme of Iodine in 2 cub. centims.............	19	37·7	1·98
4. ,, ,, ...	19	37·2	1·96
5. ,, ,, ...	14·7	33·3	2·24
6. ,, ,, ...	14·7	32·3	2·20
7. ,, ,, ...	12·5	29·7	2·37
8. ,, ,, ...	12·5	29·7	2·37
9. 1 gramme of Iodine in 3 cub. centims.............	23	42·2	1·83
10. ,, ,, ...	23	46·7	2·03
11. ,, ,, ...	23	48·7	2·11
12. ,, ,, ...	23	47·2	2·05
13. ,, ,, ...	15	27·6	1·84
14. ,, ,, ...	15	28·2	1·88
15. 1 gramme of Iodine in 4 cub. centims.............	19	35·6	1·87
16. ,, ,, ...	15·5	33·3	2·15
17. ,, ,, ...	12·5	24·6	1·96
18. ,, ,, ...	12·5	25·1	2·00
19. ,, ,, ...	14·7	32·3	2·20
20. 1 gramme of Iodine in 6 cub. centims.............	23	46·1	2·00
21. ,, ,, ...	23	44·1	1·91
22. ,, ,, ...	20	35·5	1·77
23. ,, ,, ...	18·7	40	2·13
24. ,, ,, ...	18·7	38·5	2·05
25. ,, ,, ...	15	27·2	1·81
26.	15	29·5	1·70

TABLE (continued).

I. Degree of concentration of the solution of hydriodic acid employed.	II. T.	III. S.	IV. $R=\frac{S}{T}$.
27. 1 gramme of Iodine in 8 cub. centims.............	15·5	31·4	2·02
28. " "	15·5	30·9	2·00
29. " "	12·5	25·4	2·03
30. 1 gramme of Iodine in 12 cub. centims.	23	42	1·82
31. " "	23	42·4	1·84
32. 1 gramme of Iodine in 16 cub. centims.	15	28·3	1·88
33. " "	15	28·5	1·88
34. 1 gramme of Iodine in 24 cub. centims.	23	37·7	1·64
35. " "	23	38·8	1·69
36. 1 gramme of Iodine in 48 cub. centims.	20	32·1	1·61
37. " "	20	31·3	1·57
38. 1 gramme of Iodine in 64 cub. centims.	12·5	18·9	1·51
39. 1 gramme of Iodine in 96 cub. centims.	20	28·1	1·40
40. " "	20	28·8	1·44
41. 1 gramme of Iodine in 128 cub. centims..........	12·5	17·2	1·40
42. 1 gramme of Iodine in 192 cub. centims..........	20	22·4	1·12
43. 1 gramme of Iodine in 256 cub. centims..........	12·5	14·2	1·14

It is evident on inspection of the Table that there is an appreciable diminution in the value of R in these experiments made with solutions of hydriodic acid containing less than one gramme of iodine in 16 cub. centims., and that in the last two experiments given, experiments 42 and 43, made with excessively dilute solutions, the oxidation in the solution of hydriodic acid closely approximates to the oxidation effected by the same gas in a solution of neutral iodide of potassium. This value, however, diminishes very gradually—the mean value of R in experiments 34 to 41 being 1·53, and the extreme values of R in experiments made the one with a solution of hydriodic acid containing 1 gramme of iodine in 24 cub. centims. and the other 1 gramme of iodine in 128 cub. centims. respectively being 1·66 and 1·40, the difference of which, 0·26, lies almost within the errors of experiment. In experiments 1 to 33 no regular variation is seen in the value of R, the mean value of this ratio for the first nineteen experiments given in the Table being 2·04, and the mean value of the same ratio for the following fourteen experiments being 1·92, the mean of the thirty-three experiments taken together being 1·99.

There are numerous causes of uncertainty in these experiments, several of which have already been pointed out; but it is impossible for us to apply any conjectural correction to the experiments, or to say how these causes have affected any particular experiment. With the view of determining the probable error of the result, I have applied to the system of experiments the method of least squares. Some of these experiments exhibit very considerable divergences from the mean result, but I have not ventured to reject any. A singular example of this divergence is exhibited in experiments 7 and 8, both of which give 2·37 as the value of R. It might be thought at first sight that these experiments should be rejected, as affected by some special source of error; but, on the other hand, there is one value of R in the Table which exhibits a nearly equal divergence from the mean in the other direction, namely 1·7, experiment 26: also if we reject on these grounds the number 2·37, no adequate reason can be given for retaining such a number as 2·24; and I find, on turning to my note-book, that experiments 7, 17, 18, 8 were made successively on the same day, by the same method, under the same conditions, and by the same observer in the order of the preceding numbers, the value of R in the several experiments being (7) 2·37, (17) 1·96, (18) 2·00, (8) 2·37; and I cannot but attribute the divergence of these numbers from the mean to an accidental accumulation of errors in one direction.

In column I. of the following Table is given the value of R in each of the thirty-three experiments referred to; column II. contains the differences of these values from the mean value of R, and column III. the squares of the differences.

Experiments with Hydriodic Acid.

I. $R=\frac{S}{T}$.	II. Difference from the mean.	III. Squares of the differences.
1·89	−·1	·01
1·89	−·1	·01
1·98	−·01	·0001
1·96	−·03	·0009
2·24	+·25	·0625
2·20	+·21	·0441
2·37	+·38	·1444
2·37	+·38	·1444
1·83	−·16	·0256
2·03	+·04	·0016
2·11	+·12	·0144
2·05	+·06	·0036
1·84	−·15	·0225
1·88	−·11	·0121
1·87	−·12	·0144
2·15	+·16	·0256
1·96	−·03	·0009
2·00	+·01	·0001
2·20	+·21	·0441
2·00	+·01	·0001
1·91	−·08	·0064
1·77	−·22	·0484
2·13	+·14	·0256
2·05	+·06	·0036
1·81	−·18	·0324
1·70	−·29	·0841
2·02	+·03	·0009
2·00	+·01	·0001
2·03	+·04	·0016
1·82	−·17	·0289
1·84	−·15	·0225
1·88	−·11	·0121
1·88	−·11	·0121
Mean =1·99 cub. centim.		Sum=·8601

The number of these experiments is thirty-three.

Hence the probable error of the result $=0{\cdot}6745\sqrt{\frac{0{\cdot}8601}{33\times 32}}$

$=0{\cdot}02$ cub. centim.;

and also

the probable error of a single experiment $=\sqrt{33}\times$ the probable error of the result

$=\sqrt{33}\times 0{\cdot}02$

$=0{\cdot}11$ cub. centim.

It appears, therefore, from these experiments that it is an equal chance that the true value sought of the ratio R lies between the values 2·01 and 1·97. The value of this ratio indicated by chemical theory is 2; the preceding experiments, therefore, entirely agree with this theory. We may also infer, from the calculated value 0·11 of the error of a single experiment, that if we should proceed to make another experiment by the same method it is an equal chance that the value of R in that experiment will lie between the values 1·88 and 2·10; and half the values of R found by the preceding observations should lie between the same limits. As a matter of fact, out of these 33 experiments 17 experiments are within these limits, and 16 experiments are outside these limits. The experiments, therefore, are in perfect accordance with the calculated value of the probable error of a single result.

These experiments are fully confirmed by certain experiments of MEISSNER[*] previously referred to, which really throw great light upon the subject, although this chemist has the art of singularly misinterpreting his results. The object of the experiments was to effect a comparison between the weight of a volume of oxygen equal to the contraction of the electrized gas and the increment of weight of a solution of iodide of potassium, acidulated with sulphuric acid, when the same electrized gas was passed through the solution. The contraction was (as I understand the experiment) estimated by comparing the volume of the oxygen before and after its passage through the induction-tube, which was an induction-tube of the form devised by VON BABO; the weight corresponding to this contraction was then calculated, and the increment of weight of the acid solution of iodide of potassium was determined by weighing the apparatus in which it was contained before and after the experiment. I shall not pretend to criticise these experiments, the uncertainty of which is fully admitted by the author. Among other sources of error, however, the total increment of weight of the acid solution of iodide of potassium is comprised in the several experiments between a maximum of 0·016 gramme and a minimum of 0·005 gramme, quantities which it is evidently very difficult to estimate with precision in this way. I would rather direct the attention of the reader to the mean result of these twelve experiments, which gives 2·02 as the ratio of the increment of weight of the acid solution of iodide of potassium to the weight of a volume of oxygen equal to the contraction of the electrized gas. From these observations, taken in connexion with the Table of experiments before given, we may consider it as conclusively proved, not only that the oxidation

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[*] Neue Untersuchungen über den elektrisirten Sauerstoff, 1869, p. 95, Tabelle F.

effected by the passage of an electrized gas through a solution of hydriodic acid amounts to twice the oxidation effected by the passage of the same gas through a solution of neutral iodide of potassium, but also that that oxidation is attended by an actual absorption of oxygen, the weight of which is equal to twice the weight of oxygen similarly absorbed by the neutral iodide.

The previous observations were made at the temperature of the laboratory, which was about 18° C. to 19° C. It was important to ascertain whether by varying the temperature the oxidation effected by the ozone could be carried beyond the limit thus reached. The following experiments were instituted with the view of determining this point; the gas was measured in a small pipette, the capacity of which was 94 cub. centims.

The influence of variation of temperature upon the oxidation of hydriodic acid effected by pure oxygen was first determined. In three concordant experiments made at the temperature of the laboratory, in which 92 cub. centims. of oxygen were passed through 15 cub. centims. of a concentrated solution of hydriodic acid, of which solution 2 cub. centims. contained 1 gramme of iodine, an oxidation was effected equivalent to 1·7 cub. centim. of the standard solution of hyposulphite. This oxidation is very nearly in the same proportion, in relation to the volume of oxygen passed through the solution, as that arrived at in the previous experiments, and would amount on 250 cub. centims. of oxygen to an oxidation represented by 4·6 cub. centims. of the hyposulphite, the number given in the Table for a solution of hydriodic acid of this strength being 4·1. The oxidation as similarly determined for the temperature of 53° C. to 55° C. (the mean being taken of four experiments) was equivalent to 4·6 cub. centims. of hyposulphite, and at 80° C., in two experiments, of which the results were nearly identical, to 6·35 cub. centims.

At a temperature, however, of 0° C., the bulb being immersed in water containing ice, the oxidation in four experiments was equivalent to 1·8, 1·9, 1·7, and 2·1 cub. centims. of hyposulphite, the mean of the four experiments being 1·9 cub. centim., a number slightly higher than that representing the oxidation at 18° C. to 19° C., namely 1·7 cub. centim. We may conclude, therefore, that the oxidation effected by the action of pure oxygen on a solution of hydriodic acid of the above strength is not materially affected by lowering the temperature from 18° C. to zero.

The two following experiments were made with a small pipette of the electrized gas at 55° C. In estimating the oxidation due to the influence of the ozone, a correction was made for the oxidation effected by the oxygen associated with it by deducting 4·6 from the number representing the total oxidation.

Experiments at 55° C.

I. Degree of concentration of the solution of hydriodic acid employed.	II. T.	III. S.	IV. $R=\frac{S}{T}$.
2 grammes of Iodine in 2 cub. centims.	31·4	59·8	1·90
,, ,, ,,	31·4	60·4	1·92

The value of the ratio R is essentially the same as that previously arrived at. We may conclude, therefore, that while the oxidation effected by pure oxygen is raised from 1·7 at 18° C. to 4·6 at 55° C. (that is, nearly in the proportion of 1 to 3), the oxidation effected by the ozone is not appreciably altered by the same variation of conditions.

At the temperature of 0° C., however, exactly the reverse occurs; for while, as has been shown, the oxidation effected by pure oxygen at 0° does not sensibly differ from the similar oxidation at 18° C., the oxidation effected by the ozone is materially increased, as appears from the following experiments. The correction for the effect of the associated oxygen is here made by deducting 1·9 cub. centim. from the total oxidation.

Experiments with Hydriodic Acid at 0° C.

I. Degree of concentration of the solution of hydriodic acid employed.	II. T.	III. S.	IV. $R=\frac{S}{T}$.
2 grammes of Iodine in 2 cub. centims. ...	31·4	78·2	2·49
" " " ...	31·4	77·7	2·47
" " " ...	27·1	63·2	2·33
" " " ...	14·9	34·6	2·32
" " " ...	8·78	22·1	2·52
			Mean ... 2·43

When the electrized gas is passed through a solution of hyposulphite of soda, a certain oxidation of the hyposulphite is effected, and the gas undergoes a diminution in volume. These effects differ in neutral and alkaline solutions of the hyposulphite, and in the latter case vary with the amount of the alkali (carbonate of soda) contained in the solution. Of the action on neutral and slightly alkaline solutions I shall speak hereafter. The experiments of which the results are given in the following Table were made with a solution of hyposulphite of soda rendered strongly alkaline with carbonate of soda. The gas before the experiment was measured in the gas-pipette, and thence drawn through a bulb containing in most cases about 30 cub. centims. of the alkaline hyposulphite of soda into the aspirator, where the gas was again measured, the experiments being conducted precisely as described in Section II., p. 446.

In column I. of the following Table the relative strengths of the solutions of hyposulphite of soda are given in terms of the cub. centims. of oxygen at 0° C. and 760 millims., equivalent to the iodine employed for the titration of 1 cub. centim. of the solution, that is, in terms of the volume of oxygen required to effect the oxidation to tetrathionate of the amount of hyposulphite contained in 1 cub. centim. of the solution. In column II. is given the "titre" of the gas, T; in column III. the volume before the experiment, V; in column IV. the volume after the experiment, V_1; in column V. is given the contraction, $V-V_1$; in column VI. is given the ratio of the contraction to the "titre" of the gas, $\frac{V-V_1}{T}$. The temperature at which the experiment was made is also given.

Experiments with strongly alkaline Hyposulphite of Soda.

	I.	II.	III.	IV.	V.	VI.
Temperature of experiment.	Strength of the solution.	T.	V.	V_1.	$V-V_1$.	$\frac{V-V_1}{T}$.
	grm.					
0° C.		3·47	87·16	83·85	3·31	0·95
0°	·89	10·98	273·00	264·84	8·16	0·74
0°	……	10·98	272·84	262·34	10·50	0·96
0°	……	10·98	272·09	262·89	9·20	0·84
0°	·94	12·95	273·73	262·39	11·34	0·87
0°	……	12·95	273·42	261·74	11·68	0·90
0°	2·45	7·53	273·76	264·69	9·07	1·20
15°	……	13·48	274·85	258·35	16·50	1·22
15°	……	13·48	274·57	257·95	16·62	1·23
15°	……	9·18	273·99	265·11	8·88	0·96
0°	……	7·53	270·94	262·43	8·51	1·13
0°	……	7·53	273·86	265·32	8·54	1·13
0°	……	9·79	275·71	266·12	9·59	0·98
0°	……	9·79	275·25	265·36	9·89	1·01
0°	……	9·79	274·94	265·60	9·34	0·95
0°	……	9·23	277·74	268·43	9·31	1·01
0°	……	9·23	277·25	265·22	12·03	1·33
14°	……	10·52	276·30	265·56	10·74	1·02
14°	……	8·37	270·48	261·17	9·31	1·11
16°	……	5·82	271·71	264·97	6·74	1·16
17°	……	9·44	275·93	264·97	10·96	1·16
18°	……	5·47	271·31	267·15	4·16	0·76
						Mean… 1·03

The conditions under which the experiments here given were made were greatly varied. They differ widely in the "titre" of the gas employed in the experiment, in the temperature at which the experiment was made, in the strength of the solution of hyposulphite through which the gas was passed, and in the amount of carbonate of soda present in that solution; but it is impossible to infer from these experiments that the ratio $\frac{V-V_1}{T}$ varies in any definite and regular manner with any one of these circumstances; and I have in this case also calculated, by the method of least squares, the probable error of the result.

In column I. of the following Table the values are given of the ratio $\frac{V-V_1}{T}$. In column II. the differences are given of the several values from the mean value of that ratio. In column III. the squares of these differences are given.

Experiments with strongly alkaline Hyposulphite of Soda.

I. $\frac{V-V_1}{T}$.	II. Differences from the mean.	III. Squares of the differences.
0·95	−·08	·0064
0·74	−·29	·0841
0·96	−·07	·0049
0·84	−·19	·0361
0·87	−·16	·0256
0·90	−·13	·0169
1·20	+·17	·0289
1·22	+·19	·0361
1·23	+·2	·04
0·96	−·07	·0049
1·13	+·1	·01
1·13	+·1	·01
0·98	−·05	·0025
1·01	−·02	·0004
0·95	−·08	·0064
1·01	−·02	·0004
1·33	+·3	·09
1·02	−·01	·0001
1·11	+·08	·0064
1·16	+·13	·0169
1·16	+·13	·0169
0·76	−·27	·0729
Mean= 1·03 cub. centim.		Sum=·5168

The number of these experiments is twenty-two.

$$\text{The probable error of the result} = 0{\cdot}6745\sqrt{\frac{0{\cdot}5168}{22\times 21}}$$
$$= 0{\cdot}022 \text{ cub. centim.};$$

and also

$$\text{the probable error of a single experiment} = \sqrt{22}\times\text{the probable error of the result}$$
$$= \sqrt{22}\times 0{\cdot}22$$
$$= 0{\cdot}1 \text{ cub. centim.}$$

We may conclude, therefore, from these experiments that it is an equal chance that the true value of the ratio $\frac{V-V_1}{T}$ lies between the value 1·01 and 1·05; also, if we should proceed to make another experiment by the same method, it is an equal chance that the value of the same ratio in that experiment would lie between the limits 1·13 and 0·93; and half the values of this ratio in the preceding twenty-two experiments should lie between the same limits. There actually are 11 values of $\frac{V-V_1}{T}$ in the preceding Table within these limits, and 11 of these values outside those limits. In this point, therefore, the experiments are in entire accordance with theory.

The theoretical value of the ratio $\frac{V-V_1}{T}$ lies just outside the limits of probable error; but there is no doubt that the mean value of $\frac{V-V_1}{T}$ in these experiments is somewhat too high. I may especially notice two sources of error as constantly affecting these experiments in this direction for which I have not been able to apply a correction. When pure oxygen is passed through a solution of hyposulphite of soda, either alkaline or neutral, a minute but nevertheless real amount of oxidation occurs: this oxidation is far too minute to be estimated by measurement in the aspirator; but I endeavoured to gain some notion of its magnitude in the following way. A small pipette of oxygen, being 87 cub. centims. at 0° C. and 760 millims., was passed at a temperature of 14° C. in two experiments through an alkaline and a neutral solution of hyposulphite of soda respectively; the hyposulphite of soda was "titred" with a standard iodine solution before and after the experiment. In the case of the alkaline solution, the difference between the two titrations amounted to 0·7, and in the case of the neutral solution to 0·8 division of the burette; this would correspond in the previous experiments, in which about three times the amount of oxygen was passed through the solution, to an oxidation represented in the two experiments respectively by 2·1 and 2·4 divisions of the burette, representing an absorption of about 0·1 cub. centim. of oxygen by the alkaline solution of hyposulphite. The error from this source, although very small, affects every experiment in the same direction, and would appreciably affect the mean result—the value of the mean result, on the hypothesis that the contraction $V-V_1$ is in every case 0·1 cub. centim. in excess, being, as I have ascertained by calculation, 1·02. I have not, however, applied this correction, as there is no positive evidence that the oxygen, as thus calculated from the difference of the two titrations, represents the oxygen actually employed in the oxidation of the hyposulphite. The point also is immaterial. Another source of error is found in the gas simply dissolved by the solution of hyposulphite, which would not be estimated by this method of titration. Some idea of the magnitude of the error from this source may be derived from the experiments given in Section II. (page 446) with neutral iodide of potassium, where the volumes before and after the experiment (much the same quantity of gas being employed as in the present experiments), which theoretically should be identical, show a difference in their mean value of 0·2 cub. centim., for which difference we have an adequate cause in the absorption of 0·2 cub. centim. of oxygen by the neutral solution of iodide of potassium. Here, again, I have hesitated to apply a correction, which would be to a certain extent of an arbitrary character; but this is undoubtedly a real and constant cause of error operating in the same direction as the preceding; and if from these data we assume the contraction $V-V_1$ to be in all cases in excess by 0·3 cub. centim., the mean value of R would, after applying this correction, be as nearly as possible 1·00. The probable error of the result would not be appreciably affected.

In the experiments of which the result is given in the following Table the electrized gas was passed through a solution of polysulphide of barium, made by boiling a solution of the neutral sulphide with an excess of sulphur out of contact of air. The passage of the gas is attended with a deposition of large quantities of sulphur. The experiment was conducted in all respects as the experiments with hyposulphite of soda last described, but the temperature was kept at 0° C. I have no record of the amount of polysulphide of barium contained in the solution; but the proportion of the polysulphide of barium in the several experiments was greatly varied, the relative amounts of the polysulphide contained in the bulb being, assuming the amount in experiment 1 as the unit of comparison, in experiments 2 and 3 twice that amount, in experiment 4 three times that amount, and in experiments 5 and 6 six times that amount.

Experiments with Polysulphide of Barium.

Experiment.	I. T.	II. V.	III. V_1.	IV. $V-V_1$.	V. $\frac{V-V_1}{T}$.
1.	12·60	267·97	254·73	13·24	1·05
2.	12·60	267·34	254·33	13·01	1·03
3.	11·94	268·68	255·79	12·89	1·08
4.	12·60	267·7	255·53	12·17	0·96
5.	12·60	268·15	254·33	13·82	1·09
6.	11·94	268·41	256·36	12·05	1·01
					Mean ... 1·04

The following experiments were conducted in a manner precisely similar to the preceding, but with a solution of polysulphide of sodium. The experiments were made at 0° C. In this case also the degree of concentration of the solution was very greatly varied, the amount of polysulphide of sodium employed being in experiment 11 six times that in experiments 2, 3, and 4, in experiments 8, 9, and 10 three times that in the same experiments, in experiments 5, 6, and 7 twice that in the same, and in experiment 1 two thirds that in the same. In experiment 1 a slight trace of ozone escaped the action of the polysulphide. With a solution half the strength of that in experiments 2, 3, 4 the ozone came distinctly through the solution when about half the gas had passed over.

Experiments with Polysulphide of Sodium.

Experiment.	I. T.	II. V.	III. V_1.	IV. $V-V_1$.	V. $\frac{V-V_1}{T}$.
1.	11·41	270·16	256·86	13·3	1·16
2.	15·15	272·84	257·04	15·80	1·04
3.	11·04	270·65	257·96	12·69	1·15
4.	13·24	272·37	257·15	15·22	1·15
5.	11·41	269·92	257·82	12·10	1·06
6.	10·2	271·04	258·4	12·64	1·24
7.	10·2	270·76	259·03	11·73	1·15
8.	13·24	273·57	258·74	14·83	1·12
9.	10·2	271·04	259·62	11·42	1·12
10.	11·04	270·65	258·68	11·97	1·08
11.	15·15	272·66	255·43	17·23	1·14
					Mean ... 1·13

The mean of these experiments is distinctly higher than the mean 1·04 of the previous experiments with polysulphide of barium; and while they point to the same general result, they also indicate the operation of a constant cause, causing a deviation in excess of the theoretical number 1.

The action of ozone upon the hydrosulphide of sodium (Na H S) appears to be of a different order. The following experiments were made with that substance at the temperature of the laboratory, which was about 20° C. The concentration of the solution in the five experiments severally commencing with experiment 1 was proportional to the numbers 1, 2, 4, 8, 16. The solution in experiment 5 was extremely concentrated.

Experiments with Hydrosulphide of Sodium.

Experiment.	I. T.	II. V.	III. V_1.	IV. $V-V_1$.	V. $\frac{V-V_1}{T}$.
1.	12·81	273·10	254·62	18·47	1·44
2.	12·81	273·37	253·19	20·18	1·57
3.	12·81	273·74	254·12	19·62	1·53
4.	12·81	274·29	252·71	21·58	1·68
5.	13·21	272·28	250·45	21·83	1·65
					Mean... 1·57

These experiments, made with solutions of such very different degrees of concentration, are nearly uniform in their result; at the same time they indicate a slight progression as the solution becomes more concentrated. An experiment made with a much weaker solution gave 1·21 for the value of $\frac{V-V_1}{T}$, while with a solution half the strength of this last the ozone came through. Considering these experiments in connexion with those made with hydriodic acid at the temperature of 0° C. (Section III. p. 459), I am inclined to believe that the ratio 1·5 indicates a definite pause in the oxidation. I have not pursued this part of the subject further; but I may mention that, in the case of two similar experiments made with the neutral sulphide of barium, 1·47 and 1·45 were obtained as the values of $\frac{V-V_1}{T}$; and in the case of one experiment with sulphide of potassium 1·62 was obtained for that value.

It would be very desirable to determine not only the contraction which the electrized gas undergoes in its passage through these various solutions, but also the oxidation actually effected in them. In the case of hyposulphite of soda I have made various attempts, and in different ways, to determine this point; but for some reason, which I do not quite understand, without satisfactory results, the different experiments not being so concordant as to be of much value: there can, however, be no reasonable doubt as to the amount of the oxidation effected—namely, that while the contraction is equal in amount to the "titre" of the gas, the oxidation is equal to twice that "titre;" for the ozone after its passage through the solution of the alkaline hyposulphite is found to have lost its special oxidizing properties, and to have no effect whatever upon a solution of neutral iodide of potassium. Hence, to arrive at the amount of oxygen actually retained by the solution, we have to add the "titre" of the gas which is absorbed without change of volume to the contraction; moreover, in one case, namely that of hydriodic acid, this oxidation has been actually determined and found by experiment to be equal in amount to twice the "titre" of the gas with neutral iodide of potassium. In the case of the polysulphide of barium, again, the contraction is exactly equal in amount to the "titre" of the gas; and we may conclude from these experiments with certainty that, besides that class of oxidations of which examples were given in the last section, and which are attended with no change of volume in the gas, ozone is capable of acting upon various chemical substances in a totally different, but still perfectly definite way, and of effecting an oxidation equal to twice the amount effected in those cases where no change of volume occurs, and which oxidation is attended by a diminution in the volume of the gas equal to half the volume of the oxygen employed in effecting the oxidation.

Besides this there is in all probability another definite form of oxidation effected by ozone, which is represented by the oxidation of hydriodic acid at 0° C., and by the oxidation of hydrosulphide of sodium, and possibly also by the neutral sulphide of potassium and neutral sulphide of barium, in which the oxidation effected is equal to twice and a half the "titre" of the gas, and the contraction is equal to once and a half that "titre." In the next section I shall bring before the reader yet another definite class of reactions of ozone.

SECTION IV.

When the electrized gas is passed through a solution of neutral hyposulphite of soda, the gas undergoes a diminution of volume, as in the case of the alkaline hyposulphite, but different in amount. In the following Table I have collected the results of various experiments made by me at different times upon this subject. The experiments were conducted in the way previously described, and the conditions of the experiments were very greatly varied. The first four experiments in the Table were made without any special measuring-apparatus, the gas being simply collected in an ordinary graduated gas-jar and measured. In some cases the gas was passed very rapidly, and in others very slowly, through the solution; the strength of the solution of hyposulphite was also varied from an extreme degree of dilution, as in the first four experiments, to a degree of concentration of ten times that amount; the temperature also was varied from 0° C. in some experiments to 14° C. in others; but none of these variations produced any appreciable effect whatever upon the contraction of the gas.

The numbers in the second column represent the cubic centimetres of oxygen equivalent to the iodine required for titration of 1 cubic centimetre of the solution. About 30 cubic centimetres of the solution was the quantity usually employed.

Experiments with neutral Hyposulphite of Soda.

Temperature.	Strength of the solution.	T.	V.	V_1.	$V-V_1$.	$\frac{V-V_1}{T}$.
13°·5 C.	·36	3·95	87·84	79·66	8·18	2·07
13°·5	......	3·18	87·56	81·32	7·24	1·97
12°	......	3·50	87·47	80·45	7·02	2·00
14°	......	4·19	86·76	78·23	8·53	2·03
0°	·47	13·17	274·00	256·58	23·42	1·78
18°·6	·62	10·29	270·06	250·12	19·94	1·94
19°	......	10·29	269·69	249·38	20·31	1·97
0°	1·23	10·78	271·72	248·16	23·56	2·18
0°	1·75	12·06	273·18	248·53	24·65	2·04
0°	1·89	12·14	272·92	247·06	25·86	2·13
0°	......	12·14	272·70	246·34	26·36	2·17
0°	2·45	13·58	269·36	241·82	27·54	2·03
0°	......	13·58	268·78	240·45	28·33	2·08
0°	......	13·58	268·78	243·80	24·98	1·83
0°	......	12·61	268·15	240·74	27·41	2·17
0°	3·78	13·17	273·07	246·51	26·56	2·02
0°	......	12·14	273·82	249·17	24·65	2·03
						Mean ... 2·02

In the following Table the data are given for the calculation of the probable error in the result of these experiments.

Experiments with neutral Hyposulphite of Soda.

$\frac{V-V_1}{T}$.	Differences from the mean.	Squares of the differences.
2·07	+·05	·0025
1·97	—·05	·0025
2·00	—·02	·0004
2·03	+·01	·0001
1·78	—·24	·0576
1·94	—·08	·0064
1·97	—·05	·0025
2·18	+·16	·0256
2·04	+·02	·0004
2·13	+·11	·0121
2·17	+·15	·0225
2·03	+·01	·0001
2·08	+·06	·0036
1·83	—·19	·0361
2·17	+·15	·0225
2·02	·00	·0000
2·03	+·01	·0001
Mean = 2·02 cub. centims.		Sum = ·1950

The number of these experiments is seventeen.

The probable error of the result $=0{\cdot}6745\sqrt{\frac{0{\cdot}195}{17\times16}}$

$=0{\cdot}017$ cub. centim.;

$$
\begin{aligned}
\text{the probable error of a single experiment} &= \sqrt{17}\times\text{the probable error of the result}\\
&= \sqrt{17}\times 0{\cdot}017\\
&= 0{\cdot}07 \text{ cub. centim.}
\end{aligned}
$$

It appears, therefore, from these experiments that it is an equal chance that the true value of the ratio $\frac{V-V_1}{T}$ lies between the limits 2·00 and 2·04. The theoretical value of this ratio, 2, is within these limits, and the experiments are in accordance with theory. At the same time it cannot be doubted that here also, from the causes previously indicated in the case of the similar experiments made with alkaline hyposulphite (Section III.), the mean experimental value of this ratio, 2·02, is somewhat too high; also, from the calculated value of the probable error of a single experiment, 0·07, half the values of $\frac{V-V_1}{T}$ given in the preceding Table might theoretically be expected to be found within the limits 2·09 and 1·95. Of the seventeen experiments, nine are within these limits, and eight outside them. The experiments, therefore, in this point also agree with theory.

The solution of hyposulphite of soda, originally neutral, is found, after the passage of the ozone, to have become strongly acid. Considering that the acid thus formed might exercise some important influence upon the reaction, I experimented with solutions of hyposulphite of soda rendered slightly alkaline with carbonate of soda. The influence of a great excess of carbonate of soda is, as has been shown, to reduce the oxidation, so that the contraction in the case of the strongly alkaline solution is only half the contraction in the case of the neutral solution. I therefore (with the view of adding only a slight excess of alkali) estimated by titration the amount of carbonate of soda required to render the solution neutral after the passage of the gas, and added to the solution employed in the experiment two or three times that amount. This amount of carbonate of soda was sufficient to keep the solution alkaline during the experiment, without, as will be seen, sensibly reducing the oxidation effected by the electrized gas. When about this quantity of carbonate is added the solution is spoken of as slightly alkaline. The following ten experiments were thus conducted. The Table below is of the same nature as the preceding.

Experiments with slightly alkaline Hyposulphite of Soda.

Temperature.	Strength of the solution.	T.	V.	V_1.	$V-V_1$.	$\frac{V-V_1}{T}$.
0° C.	·05	1·60	87·34	83·96	3·38	2·09
16°	·50	13·41	272·31	243·93	28·38	2·10
0°	·94	12·95	274·11	250·49	23·62	1·82
0°	......	12·95	273·89	249·31	24·58	1·90
16°	·85	13·81	272·50	243·69	28·81	2·13
0°	1·75	9·79	274·75	254·44	20·31	2·07
0°	......	9·79	274·66	254·12	20·54	2·10
14°·5	......	10·52	274·92	255·89	20·03	1·90
15°	......	13·81	273·63	245·18	28·45	2·06
15°	......	13·81	272·88	244·95	27·93	2·02
						Mean 2·02

The following Table contains the differences of the value of $\frac{V-V_1}{T}$ in the case of the several experiments from the mean value of that ratio and the squares of the differences.

$\frac{V-V_1}{T}$.	Differences from the mean.	Squares of the differences.
2·09	+·07	·0049
2·10	+·08	·0064
1·82	−·2	·04
1·90	−·12	·0144
2·13	+·11	·0121
2·07	+·05	·0025
2·10	+·08	·0064
1·90	−·12	·0144
2·06	+·04	·0016
2·02	·0	·0
Mean =2·02		Sum =·1027

The number of these experiments is ten.

$$\text{The probable error of the result} = 0{\cdot}6745\sqrt{\frac{0{\cdot}1027}{10\times 9}}$$
$$= 0{\cdot}023 \text{ cub. centim.;}$$

and also

$$\text{the probable error of a single experiment} = \sqrt{10}\times\text{the probable error of the result}$$
$$= \sqrt{10}\times 0{\cdot}023$$
$$= 0{\cdot}07 \text{ cub. centim.}$$

We may, therefore, from these experiments regard it as an equal chance that the true value of the ratio $\frac{V-V_1}{T}$ is included between the limits 2·00 and 2·04.

From the value of the probable error of a single experiment, 0·07, half the above observations would theoretically be included within the limits 1·95 and 2·09; four of the ten observations are actually within these limits, and six external to them.

In none of the previous experiments have I rejected any experiment as untrustworthy; but in the case of these experiments, made with the slightly alkaline solution of hyposulphite of soda, I have rejected seven experiments which were made successively at the same period, and which from some cause, of which I am not aware, but possibly some slight derangement of the measuring-apparatus, gave a mean result considerably above the average of the preceding experiments. I do not believe that these seven experiments are to be relied on; but as it is an important question whether any definite contraction greater than that found in the preceding experiments can actually occur, and as the discrepancy between these seven experiments and the preceding may possibly be otherwise accounted for, it appears to be desirable to notice the circumstance, and I have given in the following Table the record of the observations.

Temperature.	Strength of the solution.	T.	V.	V_1.	$V-V_1$.	$\frac{V-V_1}{T}$.
16° C.	1·75	8·37	270·29	250·99	19·30	2·30
16°	......	5·82	272·18	259·66	12·52	2·15
16°	......	5·82	271·89	259·03	12·86	2·21
17°	......	13·44	274·01	245·89	28·12	2·09
17°	......	9·44	275·84	253·23	22·61	2·39
18°	......	5·42	271·04	259·00	12·04	2·20
17°	......	4·92	273·13	262·17	10·96	2·22
						Mean ... 2·22

It is to be observed, that not only is the mean value in these experiments, 2·22, considerably greater than the mean value in the preceding experiments, 2·02, but that every one of these experiments gives a result greater than that mean value. As no intentional difference was made in the mode of conducting the two sets of experiments, and as the previous set are in entire accordance with the experiments made with neutral hyposulphite of soda, the obvious conclusion is that the discrepancy in the latter set arises from the operation of some constant and accidental cause of error peculiar to those experiments.

I now repeated the experiment of Soret*, and passed the electrized gas through a bulb of oil of turpentine, measuring the volume before and after the experiment in the usual manner; the tension of the vapour of oil of turpentine was taken into account in the calculation of the volume of the gas in the aspirator after the experiment, care being taken to saturate the gas with it. Although I speak of this experiment as a repetition of the experiment of Soret, it really differs from that experiment, not only in the method employed for measuring the gas, but also in the gas operated on, the gas used by Soret being the ozone procured by electrolysis, and his experiments, moreover, being always made with a moist gas.

It was desirable to ascertain whether any change in volume was caused in pure oxygen by passing a pipette of that gas through a bulb of oil of turpentine. The results of three experiments made with this view were as follows: the several pipettes of oxygen were passed successively through the same oil of turpentine at a temperature of 9° C.

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* Annales de Chimie, 4e série, vol. vii. p. 113.

V.	V_1.	$V-V_1$.
282·33	282·09	+0·24
282·00	282·14	−0·14
282·13	282·12	+0·01

The differences in the last column are hardly appreciable by the method employed, and we may conclude that any error in the following experiments arising from the oxidation of oil of turpentine by oxygen in its ordinary condition must be very small.

In the first two experiments given in the following Table the gas was rendered moist before its passage through the oil of turpentine; in the other experiments the gas was, as usual, dry.

Experiments with Oil of Turpentine.

Temperature.	T.	V.	V_1.	$V-V_1$.	$\frac{V-V_1}{T}$.
11° C.	14·29	281·27	251·24	30·03	2·09
11°	14·29	281·16	254·16	27·00	1·88
0°	13·93	280·85	250·60	30·25	2·17
0°	13·93	280·55	252·57	27·98	2·01
10°	14·22	280·14	251·04	29·10	2·04
10°	14·22	279·74	253·39	26·35	1·85
0°	9·16	282·45	263·52	18·93	2·06
0°	9·16	282·35	262·95	19·40	2·11
					Mean 2·02

In the following Table the differences from the mean and the squares of the differences are calculated.

$\frac{V-V_1}{T}$.	Differences from the mean.	Squares of the differences.
2·09	+0·07	·0049
1·88	−0·14	·0196
2·17	+0·15	·0225
2·01	−0·01	·0001
2·04	+0·02	·0004
1·85	−0·17	·0289
2·06	+0·04	·0016
2·11	+0·09	·0081
Mean =2·02 cub. centims.		Sum =·0861

The number of these experiments is eight.

The probable error of the result $=0·6745\sqrt{\frac{·0861}{8\times7}}$

$=0·03$ cub. centim.;

and also

the probable error of a single experiment $=\sqrt{8}\times$ the probable error of the result

$=\sqrt{8}\times0·03$

$=0·08$ cub. centim.

These experiments are also in accordance with theory; for it appears from them that it is an equal chance that the true value of the ratio $\frac{V-V_1}{T}$ is included within the limits 1·99 and 2·05.

Also, from the probable error of a single experiment, half the preceding observations would theoretically be included within the limits 1·94 and 2·10; four out of the eight experiments are within these limits, and four external to them.

Sufficient evidence is afforded of the value of the oxidation which occurs in the case of the contractions considered in Section III. (where the contraction is equal to the "titre" of the gas) by the experimental determination of the oxidation effected in the case of hydriodic acid; which oxidation is exactly represented by an amount of oxygen equal to that which disappears in the contraction in the case of the strongly alkaline hyposulphite of soda, together with the titre of the gas. With the view of determining this point in the class of contractions considered in the present Section, I have made various experiments with protochloride of tin, in the case of which substance the oxidation effected, as well as the change in the volume of the gas, may be determined with considerable accuracy. These experiments, however, are attended with peculiar difficulties, not only from the facility with which the protochloride of tin is oxidized and the influence which very slight variations of circumstances (such as the strength of the tin solution and the rate of the passage of the gas) have upon the oxidation, affecting the result in various ways, but also from the circumstance that the oxidation effected by the action of the ozone and that effected by the oxygen associated with it are in all probability not independent of one another—owing to the occurrence of that remarkable induced oxidation which has been noticed and made the subject of investigation, in the case of the oxidation of the protochloride of tin by chromic and permanganic acids, by F. KESSLER*, and also by LENSSEN and LÖWENTHAL†, so that we cannot apply a correction for the oxidation effected by the associated oxygen on the simple principle employed in the case of hydriodic acid. However, by operating with very dilute solutions the influence of these sources of error may be, if not entirely destroyed, at any rate very greatly reduced; and the following experiments afford conclusive evidence as to the actual oxidation effected in those cases also where the contraction is equal in amount to twice the "titre" of the gas.

It appears from the three following experiments, that when an electrized gas is passed through an acid solution of protochloride of tin, the total oxidation which takes place is equal in amount to that due to the "titre" of the gas, together with the oxidation due to a volume of oxygen equal to the contraction which occurs in the experiment.

The oxidation of the protochloride of tin was determined by running an amount of the tin solution equal to that employed in the experiment into a measured quantity of a standard iodine solution greater in amount than that required to effect the oxidation of the tin. The excess of iodine was estimated with a standard solution of hypo-

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* POGG. Ann. xcvi. 332, and cxix. 218.

† J. Pr. Chem. lxxxvi. 193; Jahresbericht, 1862, p. 38.

sulphite of soda; a similar estimation was made with the solution after the experiment. From the difference between the amounts of hyposulphite respectively employed in the two cases, the oxidation effected in the tin solution was calculated in cub. centims. of oxygen.

The volume of the gas before the experiment was measured in a small gas-pipette; the gas after the experiment was collected and measured in an ordinary graduated jar.

In the following Table S is the oxidation effected in the protochloride of tin as experimentally determined, T, V, V_1 have their previous signification.

T.	V.	V_1.	$V-V_1$.	S.	$\frac{V-V_1}{T}$.	$\frac{S}{T}$.
3·86	90·40	80·02	10·38	15·31	2·69	3·93
3·24	89·24	81·30	7·94	11·75	2·45	3·63
2·92	88·37	80·25	8·12	11·09	2·78	3·78

If the experimental results absolutely coincided with the view above given, we should have $\frac{S}{T}=1+\frac{V-V_1}{T}$.

Also, if we deduct the "titre" of the gas from the total oxidation, the difference gives the oxidation due to the gas which disappears in the contraction, and the ratio of this difference to the contraction gives the density of this gas as compared with the density of oxygen. Calling this density Δ, we have in the three experiments successively:

$$(1)\ \Delta=\frac{11{\cdot}45}{10{\cdot}38}=1{\cdot}10.$$

$$(2)\ \Delta=\frac{8{\cdot}51}{7{\cdot}94}=1{\cdot}07.$$

$$(3)\ \Delta=\frac{8{\cdot}17}{8{\cdot}12}=1{\cdot}00.$$

We may conclude from these experiments that, by the oxidation of the solution of protochloride of tin, nothing whatever is removed from the electrized gas, except the quantity of oxygen estimated in the "titre" of the gas, together with a certain volume of gas of the density and properties of oxygen.

In the two following experiments I attempted to discriminate between the oxidation effected by the ozone and the oxidation due to the oxygen associated with it; this was done by causing the gas, after being deprived of ozone by its passage through the bulb of protochloride of tin, to pass through a second bulb of the same solution, in which also the oxidation was afterwards estimated. The oxidation in the second bulb was taken as the measure of the oxidation due to the oxygen associated with the ozone, and the difference between the oxidation effected in the two bulbs respectively was assumed to be the true oxidation effected by the ozone. In this mode of operating the two oxidations were effected under precisely similar circumstances as regards the temperature and rate of passage of the gas, and are strictly comparable.

Before the experiment the oxygen required to effect the complete oxidation of the bulb of protochloride of tin was estimated by running a bulb of the solution into a measured quantity of hypochlorite of soda, of which the oxidizing value had been previously determined by effecting its decomposition by means of an acid solution of iodide of potassium, and estimating the iodine formed with a standard solution of hyposulphite of soda. A solution of iodide of potassium was added to the solution of hypochlorite of soda before the addition of the protochloride of tin. The bulb of protochloride of tin was then run into the solution, which was immediately acidified with hydrochloric acid, and the iodine estimated as before. A similar experiment was made after the completion of the experiment with each of the two bulbs of protochloride of tin employed in it; the oxidation effected was calculated, as in the former method, from the difference between the two titrations. This method gives good and accurate results; the contraction was not estimated.

The experiments were made at 0° C. The strength of the protochloride of tin is given in the first column: Q is the oxidation in the second bulb, S—Q is the oxidation estimated as due to the ozone, and the ratio $\frac{S-Q}{T}$ given in the last column is the ratio of this oxidation to the "titre" of the gas.

Strength of the solution.	T.	S.	Q.	S—Q.	$\frac{S-Q}{T}$.
3·78	8·98	30·95	1·28	29·67	3·3
7·07	8·98	37·36	7·06	30·3	3·37

It will be observed that in the second of the two experiments the strength of the tin solution employed was nearly double the strength of the solution employed in the former of the two experiments; and the oxidation effected by the passage of the associated oxygen was so greatly increased that the oxidation in the second bulb, in the latter experiment, amounted to nearly as much as six times the oxidation effected in the same bulb in the former experiment: nevertheless, when the correction has been applied for this oxidation, the number representing the oxidation due to the ozone is almost the same as in the former experiment; and this oxidation, thus calculated, closely approximates to three times the "titre" of the gas. The coincidence of this result in the two experiments affords a guarantee of the accuracy of the principles on which the process depends.

The two following experiments were made with an extremely dilute solution of protochloride of tin, on which, under the circumstances of the experiment, pure oxygen has but very little action. In the second of the two experiments the solution was so dilute that no inconsiderable portion of the ozone passed unaltered through the solution. To estimate the amount of ozone actually effective for the oxidation of the tin, the gas after its passage through the bulb of protochloride of tin was passed through a second bulb of neutral iodide of potassium, in which the ozone which escaped from the deoxidizing influence of the tin salt was arrested and estimated.

In these experiments the contraction as well as the oxidation was estimated with the following results:—

Strength of the solution.	T.	V.	S.	T_1.	V_1.	$T-T_1$.	$V-V_1$.	$\frac{V-V_1}{T-T_1}$.	$\frac{S}{T-T_1}$.
·96	8·15	269·55	25·41	0	251·69	8·15	17·86	2·19	3·12
·7	8·15	268·92	19·83	1·68	253·85	6·47	15·07	2·33	3·07

We thus, through two perfectly independent methods of experiment, arrive at the same conclusion—namely, that when a current of electrized oxygen is passed through a solution of protochloride of tin, the amount of oxidation effected in that solution by the ozone present in the gas is equal to three times that effected by the "titre" of that gas, and also that the gas undergoes a diminution in volume equal to the space occupied under normal conditions by a quantity of oxygen equal to twice that "titre."

If the experimental results were perfectly concordant with theory, we should have

$$\frac{S}{T-T_1}=1+\frac{V-V_1}{T-T_1}.$$

We have also for the value of Δ, the density of the gas absorbed, as compared with the density of oxygen, after subtraction of the "titre" in these two experiments, as estimated from the equation

$$\Delta=\frac{S-(T-T_1)}{V-V_1}:$$

$$(1)\ \Delta=\frac{17·26}{17·86}=0·97,$$

$$(2)\ \Delta=\frac{13·37}{15·07}=0·88,$$

against the theoretical value $\Delta=1$.

These results depend in each case upon the successful performance of at least five independent experiments, each of which again depends upon various other observations. The successive performance of these numerous experiments without any considerable error or mistake is truly difficult, and we need not be surprised if a certain divergence appears between the actual and the theoretical result.

The various experiments recorded in the three preceding sections constitute a body of exact information as to the chemical properties of ozone, through which it may be hoped that this important question will be finally removed from the domain of arbitrary speculation and brought within the precincts of science. It only remains to consider the bearing which these facts have upon the theory of the subject.

We may first remark that in the total system of experiments no evidence whatever is afforded of the existence in the electrized gas of any other "simple weight" than the "simple weight"[*] ξ, and the hypothesis of ANDREWS and TAIT as to the decomposition of oxygen by the electric discharge has no support in facts. I shall therefore assume the unit of ozone to be constituted of some number of these "simple weights;" and as a

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[*] Philosophical Transactions, 1866, pp. 792, 805, 810; J. Chem. Soc. 1868, vol. vi. p. 367.

diminution of volume occurs when the oxygen is submitted to the action of electricity, I shall further assume that (the unit of oxygen being symbolized as ξ^2) ozone is some denser form of oxygen, to which the symbol ξ^{2+n} (where n is a positive integer) is to be assigned. Writing also $[\xi]$ as the symbol of that "simple weight" ξ which is transferred to the oxidized substance in the various oxidations effected by ozone, the result of the total system of experiments, of which an account has here been given, may be expressed, so far as regards the distribution of the matter of the unit of ozone in those reactions, by the general equation

$$(p+q)\xi^{2+n}=q\xi^2+(p(2+n)+qn)[\xi],$$

where p, q, n are positive integers, $p+q$ the number of units of ozone which are effective in the reaction, q the number of units of oxygen formed, and $p(2+n)+qn$ the number of the "simple weights" $[\xi]$ transferred.

We have, then, putting T as the "titre" of the gas, $V-V_1$ as the contraction, S as the oxidation, and $R=\frac{V-V_1}{T}$ and $r=\frac{S}{T}$, since $T=\frac{(p+q)n}{2}$,

$$R=\frac{2p}{(p+q)n},\quad r=\frac{p(2+n)+qn}{(p+q)n}=R+1.$$

Considering the preceding experiments we have four cases brought before us.

$$\text{Case I.}\quad R=0,\ r=1,$$
$$p=0;\ \text{the equation becomes}$$
$$\xi^{2+n}=\xi^2+n[\xi].$$

In this case no diminution occurs in the volume of the gas. Examples of this case are afforded in the various experiments given in Section II.,—namely, the oxidation of neutral iodide of potassium, the oxidation of the protochloride and protosulphate of iron, and other similar phenomena. These experiments throw no light whatever on the value of n, and any assumption as to this value based upon them is purely speculative and conjectural.

$$\text{Case II.}\quad R=1,\ r=2,$$
$$p(2-n)=qn.$$

Examples of this class are supplied in Section III.; such are the oxidation of hydriodic acid, the oxidation of the strongly alkaline solution of hyposulphite of soda and of the pentasulphide of barium.

We may here make two hypotheses as to the value of n:

$$\text{Hypothesis (1)}\quad n=1,\ p=q,\ \text{whence}$$
$$2\xi^3=\xi^2+4[\xi];$$
$$\text{Hypothesis (2)}\quad n=2,\ q=0,\ \text{whence}$$
$$\xi^4=4[\xi].$$

According to hypothesis (1) the density of ozone is once and a half that of oxygen;

according to hypothesis (2) the density of ozone is twice that of oxygen. The experiments are perfectly consistent with either of these two assumptions, and both hypotheses are equally tenable.

$$\text{Case III.}\quad R=\tfrac{3}{2},\ r=\tfrac{5}{2},$$

$$p(4-3n)=3qn.$$

The experiments with hydriodic acid at zero, and also the experiments with hydrosulphide of sodium, given in Section III., are to be referred to this case; only one hypothesis is possible:

$$\text{Hypothesis, } n=1,\quad p=3q;\ \text{whence}$$

$$4\xi^3=\xi^2+10[\xi].$$

$$\text{Case IV.}\quad R=2,\ r=3,$$

$$p(1-n)=qn.$$

The experiments comprised in Section IV. (namely, the oxidation of neutral and slightly alkaline solutions of hyposulphite of soda, the oxidation of oil of turpentine and of protochloride of tin) are examples of this class.

But one hypothesis is possible:

$$\text{Hypothesis, } n=1,\ q=0;\ \text{whence}$$

$$\xi^3=3[\xi].$$

The hypothesis, therefore, that the unit of ozone is constituted of three "simple weights" ξ is both necessary and sufficient for the explanation of the total system of phenomena, and no other hypothesis of this order is tenable.

Fig. 1.

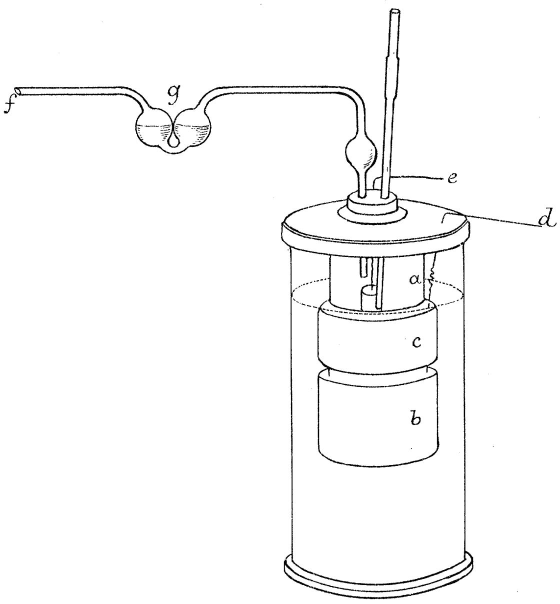


Fig. 4.

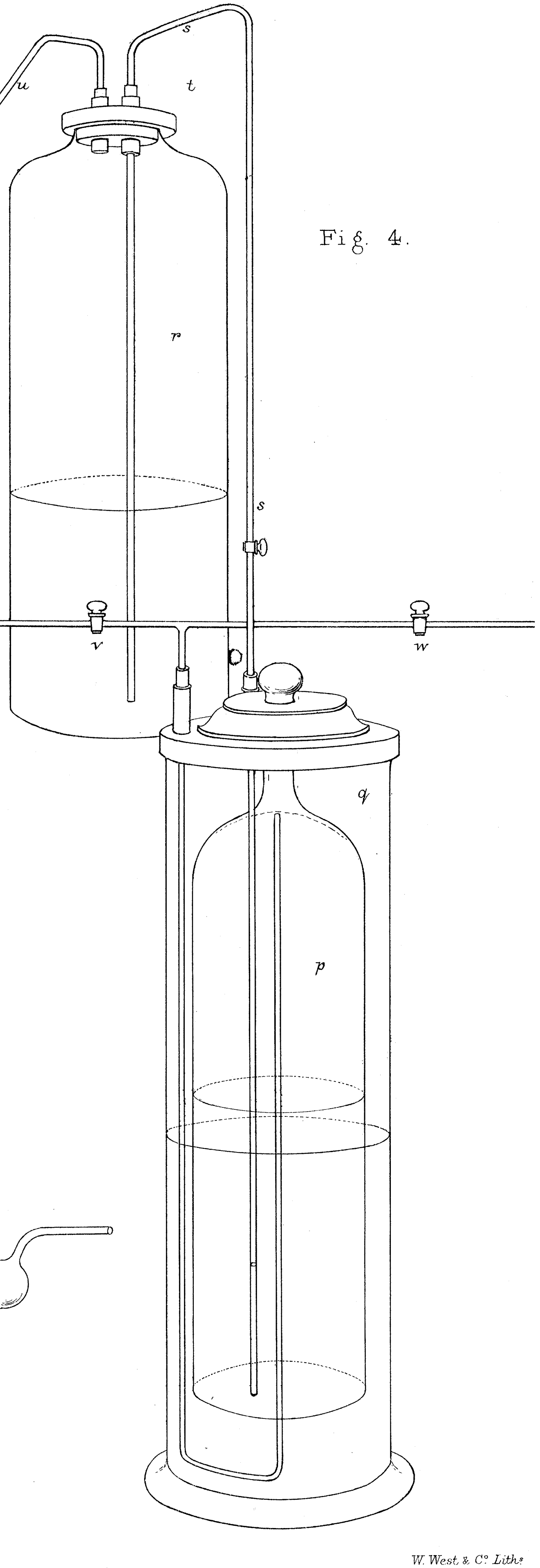


Fig. 3.

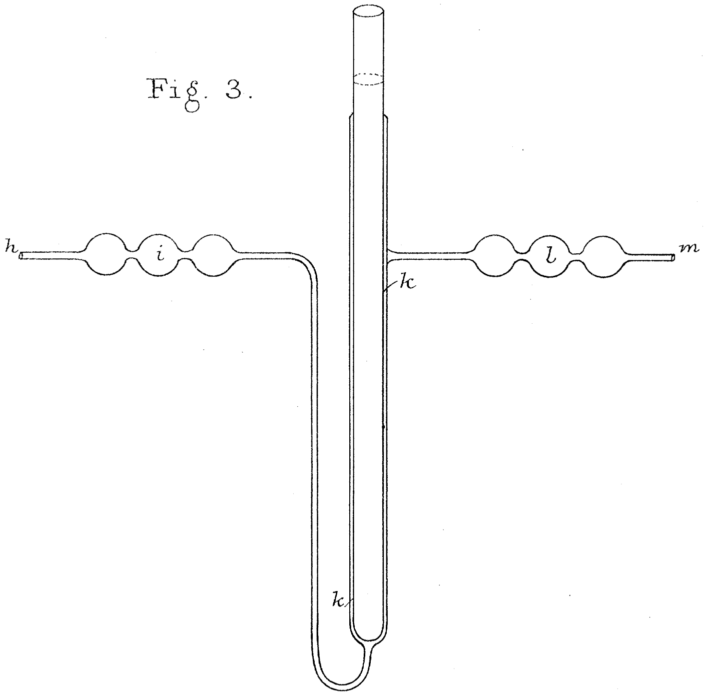
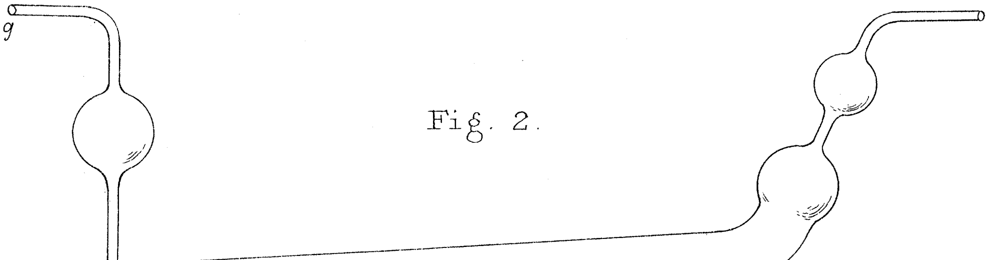


Fig. 2.



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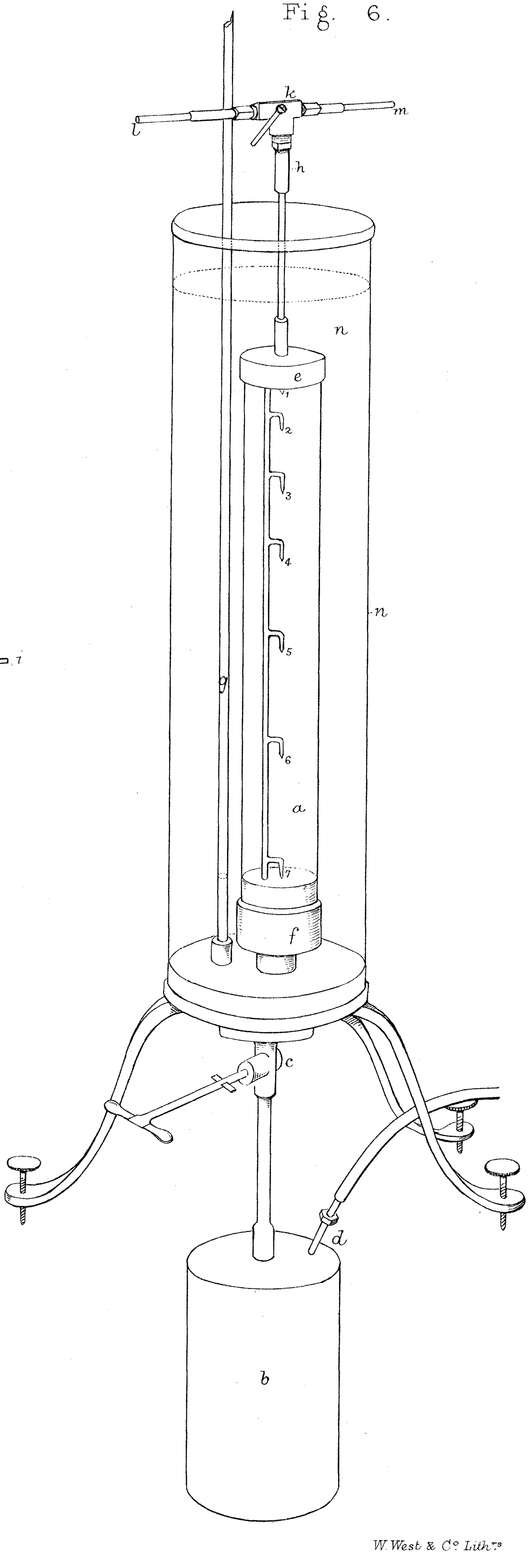

Fig. 6.

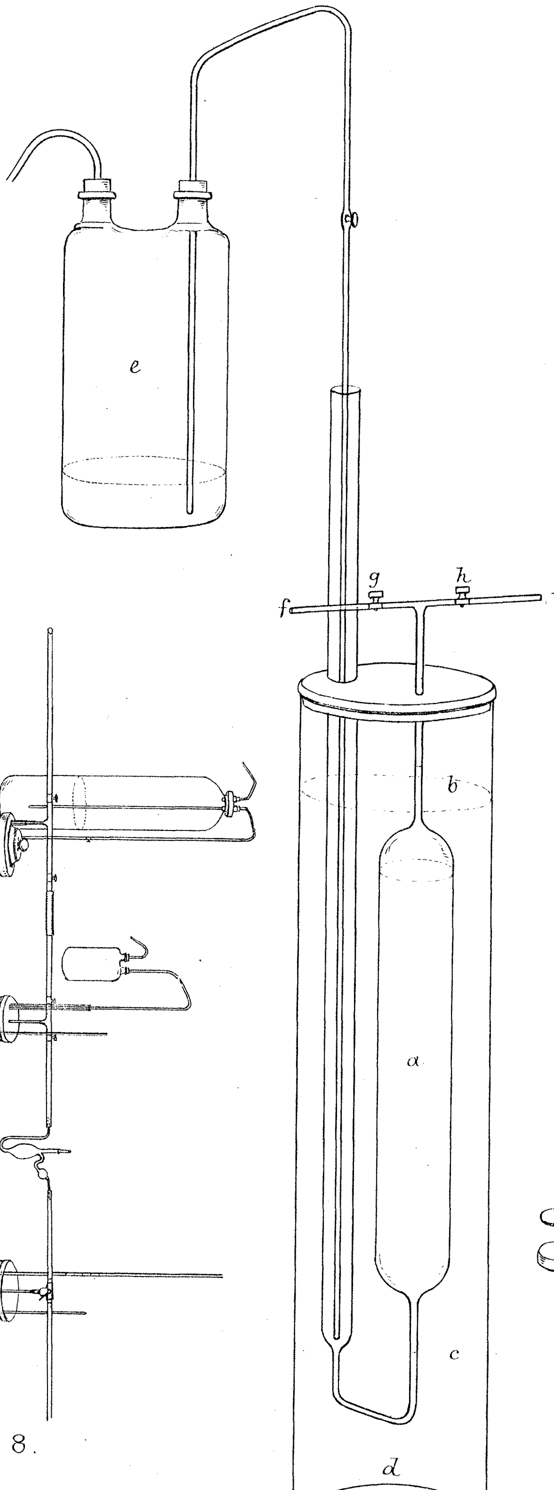

Fig. 5.

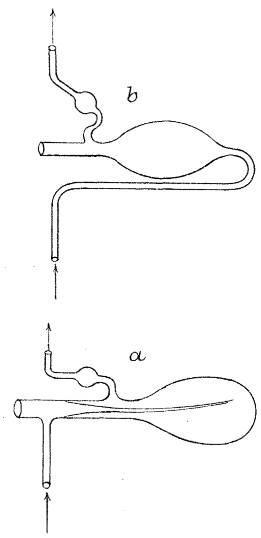

Fig. 7.

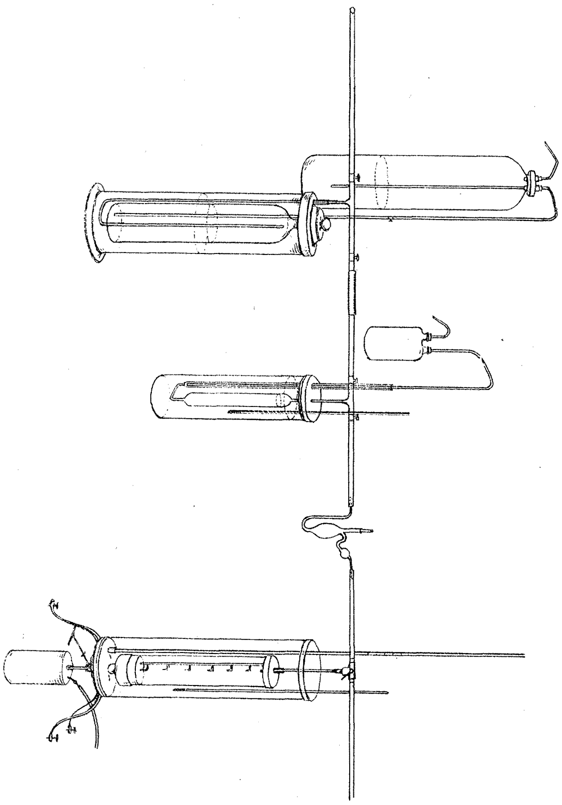

Fig. 8.

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