IV. *On the Action of Electricity on Gases.*—II. *On the Electric Decomposition of Carbonic-acid Gas. By Sir* B. C. Brodie, *Bart., D.C.L., F.R.S., late Waynflete Professor of Chemistry in the University of Oxford.*

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At a very early period of the investigation on the action of electricity upon oxygen, which formed the subject of my previous memoir*, the idea occurred to me that although but a small and limited proportion of the total oxygen passed through the induction-tube was converted into ozone (which proportion could not be exceeded by any modification I had been able to effect in the conditions of the experiment), it might be practicable to replace that portion of the oxygen which was unaffected by the action of electricity by an indifferent gas, and thus effect the total conversion of oxygen into ozone, or even the actual isolation of the ozone by the subsequent removal of the gas by which it was diluted. Thus, for example, by the passage of 100 cub. centims. of oxygen through the induction-tube, a gas can readily be obtained of which the iodine-titre is 5 cub. centims. This corresponds, according to my previous experiments, to an absorption by hyposulphite of soda of 10 cub. centims. of a gas containing in that space the matter of 15 cub. centims. of oxygen. If, therefore, we were to mix 15 cub. centims. of oxygen with 85 cub. centims. of an indifferent gas which should be unaffected by the action of the electricity, and pass the mixed gases through the induction-tube (assuming the same proportion of ozone to be still formed as in the case of the passage through the tube of pure oxygen), the total amount of oxygen in the gas would be converted into ozone, and be removed in that form by passing the gas though a solution of hyposulphite of soda. With the view of testing this idea by a critical experiment, I passed such a mixture of carbonic-acid gas and oxygen through the induction-tube. The formation of ozone was at once apparent, and was rendered evident by the action of the gas issuing from the induction-tube upon a neutral solution of iodide of potassium. But on examining the composition of the gas I soon discovered that the proportion of oxygen in it had actually increased, owing to the decomposition in the induction-tube of the carbonic-acid gas into oxygen and carbonic oxide. I did not publish this experiment; but the apparatus by which it was effected long stood upon my laboratory table, and, together with the results, has repeatedly been explained by me to other chemists. Since that time, as appears from the pages of the 'Comptes Rendus,' this decomposition of carbonic-acid gas under the influence of electricity has been cited as a novel discovery. So far as the bare fact of the decomposition of carbonic-acid gas, under the influence

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* Philosophical Transactions, Part II. 1872, p. 435.

of electricity, in the induction-tube into oxygen and carbonic oxide is concerned, the results of this experiment might, even at the time it was made by me, have reasonably been anticipated, not only from the circumstance that carbonic-acid gas is, as is well known, decomposed by the passage of the electric spark, but also that PLÜCKER* had already observed (although I was unaware of the observation) that when the electric discharge was passed through rarefied carbonic-acid gas, the spectrum of the gas after a short time changed into the spectrum of carbonic oxide, and from this circumstance had inferred the decomposition of the gas. But the observations of this eminent investigator were made under very different circumstances to mine; and he was not cognizant of the formation of ozone, which was the critical point of my experiment, and a result which could not have been ascertained by his method of observation.

The experiment having failed in its immediate object was for a time laid aside by me. Subsequently, however, I reverted to it under a somewhat modified form. It occurred to me, instead of mixing oxygen with carbonic acid, to endeavour to generate in the very atmosphere of the carbonic acid itself, by the electric decomposition of the gas, the requisite amount of oxygen. I passed, therefore, pure and dry carbonic acid through the induction-tube, and examined the gases resulting from its decomposition, estimating the ozone by the titre of the gas, and also the oxygen and carbonic oxide formed. This examination at once convinced me of the importance of the experiment in reference to the problem of the isolation of ozone, and became the foundation of the following research, which has gradually been extended in more than one direction.

SECTION I.

The subject will be conveniently considered in two divisions.

I will first lay before the Society the results of four experiments, in which the quantities were carefully measured, which may serve to define the general features of the decomposition and the methods of operation.

A measured volume of carbonic-acid gas was passed through the induction-tube and there submitted to the electric action. On quitting the tube the gas traversed a bulb containing a solution of neutral iodide of potassium, the decomposition in which afforded a measure of the ozone present in the gas. The gas was then passed into a bulb containing a strong solution of caustic potash, which absorbed the carbonic acid, while the oxygen and carbonic oxide were collected in it.

The carbonic acid was made, in the usual way, from pure marble and dilute hydrochloric acid in a (so called) KIPP'S apparatus. Having been washed with water and dried by passing through a system of tubes containing sulphuric acid and pumice imbued with sulphuric acid, the gas was collected in a sulphuric-acid gas-holder. A description of this gas-holder and of the other apparatus here employed for the collection of and measurement of gases is given in my previous paper, to which the reader is referred for information on the subject†. The carbonic acid before its passage through the induction-

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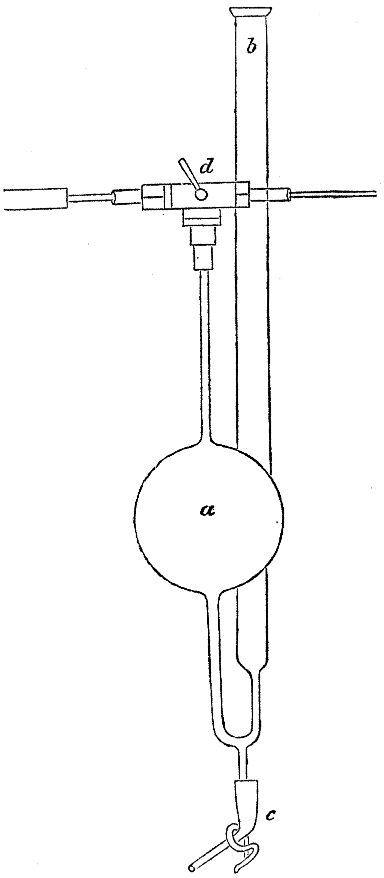
* POGG. Ann. vol. cv. p. 82.

† Philosophical Transactions, *loc. cit.* p. 437.

tube was transferred to a large gas-pipette and there measured, the pipette being filled with the gas at atmospheric pressure and a known temperature. The arrangement of the induction-tube was precisely as in my previous experiments with oxygen, the tube being in all cases placed between two sets of small bulbs permanently attached to it containing anhydrous phosphoric acid. The bulb also containing the solution of potassium iodide was of the form previously employed. A sketch is here annexed of the absorption-bulb, from which this part of the arrangement will be easily understood.



The stopcock (*d*) was a three-way stopcock of steel similar to that attached to the aspirator. Before the experiment the bulb *a* was filled with mercury by means of the tube *b*, the stopcock being open to the air; it was then closed, and a partial vacuum created in the bulb by running out a portion of mercury at *c*, where an india-rubber tube closed by a clamp was attached. The solution of caustic potash was introduced by pouring the solution into the absorption-bulb through the tube *b*. The upper part of the bulb and the capillary tube were filled with the solution to within about half an inch of the stopcock, which should not be allowed to come in contact with the alkali.

At the commencement of the experiment the apparatus was thoroughly swept out with carbonic acid, the connexion with the absorption-bulb being shut off and a suitable channel provided for the gas by means of the three-way stopcock. The pipette having been filled with the gas and the requisite observations made for its measurement, the gas was drawn through the induction-tube, which may readily be effected at any required rate by opening the communication with the interior of the bulb and running mercury from it. The absorption at first is very rapid, and some management is required not to expose at once too great a surface of the alkaline solution to the action of the gas. The connexion having been made with the coil, iodine speedily appears in the titre-bulb, and after a short time a sensible quantity of permanent gas is collected in the absorption-apparatus. After the first pipette of gas had thus been passed through the tube, the coil was temporarily disconnected, a second pipette filled and drawn over as before. The experiment was continued until in each case five pipettes of carbonic-acid gas had been thus acted on.

This part of the experiment having been completed, the absorption-bulb was disconnected, and having been attached to the aspirator described in my former memoir, the total gas was transferred to it and measured. A small quantity of an alkaline solution of pyrogallic acid was now introduced into the absorption-bulb and the gas drawn back from the aspirator into the bulb, in which it was allowed to remain for some time until no further change in the volume of the gas occurred; the gas was then retransferred to the aspirator and again measured: the difference between the two measurements gives the volume of oxygen in the gas. The total volume of oxygen due to the changes occurring in the induction-tube is represented by the sum of this difference and the titre of the gas. The whole gas, or a portion of it, was transferred to a eudiometer of known capacity, oxygen added, and the mixed gases detonated. The contraction which occurs affords another and independent measure of the oxygen formed, the oxygen which disappears on this contraction being the volume of oxygen required to restore the gas to its original condition and reconstitute the state of things broken up in the induction-tube. I shall not now enter upon the further analysis of the gas, which presents peculiarities better reserved for future consideration; but evidence will hereafter be given, in Section II., of the substantial identity of the results afforded by these two modes of estimation, although of the two measures that afforded by the contraction is undoubtedly the more exact.

The following Table contains the experimental results obtained in these four experiments, which were made with the same coil, the same battery-power, and under the same general circumstances, no intentional variation being made in any of the conditions of the experiment.

In column I. is given the volume of carbonic acid passed through the induction-tube, estimated (as are all other volumes of gas in these experiments) in cub. centims. at 0° C. and a pressure of 760 millims. In column II. is given the volume of gas unabsorbed by potash; in III. the titre of the gas; in IV. the oxygen absorbed by pyrogallate of potash; in V. the total oxygen found by actual experiment—namely, the sum of the titre and the gas absorbed by pyrogallate. In column VI. the contraction is given which occurred on detonation with oxygen of the unabsorbed gas.

Experiment.	I. Carbonic acid.	II. Unabsorbed gas.	III. Titre.	IV. Gas absorbed by pyrogallate.	V. Total oxygen.	VI. Contraction.
1.	1413	29·89	2·44	7·98	10·42	10·49
2.	1385	26·67	1·55	7·08	8·63	8·88
3.	1347	37·66	1·61	10·99	12·6	13·47
4.	1390	54·99	3·38	15·6	18·98	19·8

Now if we assume two thirds of the sum of the titre and unabsorbed gas in the several experiments to be carbonic oxide, which is nearly although not quite the case, we have for the amount of carbonic oxide formed, and therefore of carbonic acid decomposed, in the induction-tube in the four experiments respectively

(1)	21·56
(2)	18·81
(3)	26·18
(4)	38·92

and for the amount per cent. of carbonic acid decomposed

(1)	1·52
(2)	1·35
(3)	1·94
(4)	2·68

Also the iodine-titre on 100 volumes of carbonic acid passed through the induction-tube in the four experiments is

(1)	0·17
(2)	0·11
(3)	0·12
(4)	0·12.

Similarly, the iodine-titre on 100 volumes of the sum of the titre and unabsorbed gas is

(1)	7·54
(2)	5·44
(3)	4·1
(4)	5·79

And the iodine-titre on 100 volumes of oxygen formed in the induction-tube, as represented by the contraction given in the last column, is

(1)	23·29
(2)	17·47
(3)	11·97
(4)	17·05

The titre on 100 volumes of the sum of the titre and unabsorbed gas, although somewhat higher than the titre on 100 volumes of pure oxygen as arrived at by my previous experiments, in which the maximum value of this titre was 6·52 per cent., is nevertheless not far removed from that titre; but the titre on 100 volumes of the oxygen thus generated by the decomposition of carbonic acid in the induction-tube is fully three times as great as that titre; and the proportion of 100 parts of oxygen converted into ozone is in the four experiments severally

(1)	69·87
(2)	52·41
(3)	35·91
(4)	51·15

It is assumed in these remarks not only that the ozone thus produced in the decomposition of carbonic acid is an ozone essentially the same in kind as that formed by the action of electricity on pure oxygen, but also that no other substance is associated with it capable of decomposing iodide of potassium. But these assumptions might, for aught we know to the contrary, be incorrect: there may be more than one variety of ozone itself; or, again, some higher oxide of carbon might, in such an experiment, be formed by the oxidation of carbonic acid, analogous in properties to the organic peroxides of the bibasic acids and capable of decomposing iodide of potassium. No definite conclusion could be drawn from these experiments until this point was ascertained.

In my previous investigation certain definite quantitative reactions of ozone have been established, which may be submitted to exact measurement, by which this gas is discriminated from all other known gases, and by which it may be effectually recognized and estimated. Of these, the following reaction is perhaps the most certain and characteristic[*].

When oxygen which has been submitted in the induction-tube to the electric action is passed through a solution of neutral hyposulphite of soda a diminution of bulk occurs, and a volume of gas is absorbed by the hyposulphite of soda equal to twice the volume which would be occupied by the quantity of oxygen absorbed, under similar circumstances, when an equal volume of the same gas is passed through a solution of neutral iodide of potassium. This critical test was applied in the present instance as follows.

Five pipettes of the electrized carbonic acid (the capacity of the pipette being 290·8 cub. centims.) were successively passed through a bulb containing a solution of neutral iodide of potassium, by which the "titre" of the gas was estimated. After the experiment the carbonic acid was, as before, absorbed in the absorption-bulb, and the unabsorbed gas transferred to the aspirator and measured. It was demonstrated in my previous experiments that the volume of electrized oxygen is not affected by the passage of the gas through a solution of neutral iodide of potassium.

In the first column of the following Table is given the "titre" of the gas, T; in column II. the volume of the gas unabsorbed by potash after the passage of the five pipettes of gas through the solution of iodide of potassium, V. In column III. is given the volume of unabsorbed gas after the passage of an equal volume of the electrized gas through the solution of hyposulphite of soda, V_1; in column. IV. the difference of these volumes, $V-V_1$; in column V. the ratio of this difference to the "titre" of the gas, $R=\frac{V-V_1}{T}$. The strength of the solution of hyposulphite of soda employed in the several experiments was greatly varied, but, as in the case of my previous experiments with electrized oxygen, without producing any appreciable effect on the result.

I. T.	II. V.	III. V_1.	IV. $V-V_1$.	V. $R=\frac{V-V_1}{T}$.
2·44	29·89	26·37	3·52	1·44
1·55	26·66	23·56	3·10	2·00
3·69	67·93	62·17	5·76	1·55
3·69	67·93	60·22	7·71	2·08
3·47	64·94	56·78	8·16	2·35
3·47	64·94	57·49	7·45	2·14
1·61	37·66	34·51	3·15	1·95
3·38	54·99	48·94	6·05	1·79
1·94	43·50	39·46	4·04	2·08
1·06	39·04	36·84	2·20	2·07
4·34	59·49	52·96	6·53	1·50
3·47	47·33	40·86	6·47	1·86

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[*] Philosophical Transactions, *loc. cit.* p. 473.

In order to form a just estimate of the value to be attached to these experiments, which exhibit considerable divergences from the mean, I have calculated the probable error of the result, as in the Tables given in my previous paper, by the method of least squares. The data for the calculation are given below.

$R=\frac{V-V_1}{T}$.	Differences from the mean.	Squares of the differences.
1·44	$-·46$	·2116
2·00	$+·1$	·01
1·55	$-·35$	·1225
2·08	$+·18$	·0324
2·35	$+·45$	·2025
2·14	$+·24$	·0576
1·95	$+·05$	·0025
1·79	$+·11$	·0121
2·08	$+·18$	·0324
2·07	$+·17$	·0289
1·50	$-·4$	·16
1·86	$-·04$	·0016
Mean = 1·90		Sum = ·8741

The number of these experiments is 12.

$$\text{The probable error of the result} = 0·6745\sqrt{\frac{8741}{12\times 11}}$$

$$= ·054 \text{ cub. centim.};$$

and also

$$\text{the probable error of a single experiment} = \sqrt{12}\times ·054$$

$$= ·19 \text{ cub. centim.}$$

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 1·95 and 1·85; also, from the calculated value of the probable error of a single experiment ·19, half the values of this ratio given in the preceding Table might theoretically be expected to be found within the limits 2·09 and 1·71. Of the twelve experiments, seven experiments are within these limits, and five experiments outside these limits.

As might be expected from the comparatively rough method of experimentation and the small quantities of gas operated upon, the probable error in these experiments is much greater than in the case of the similar experiments made with the electrized oxygen, where, in the case of a set of seventeen such experiments, the probable error amounted only to ·017 cub. centim. In the case of those experiments the limits of probable error were 2 and 2·04, which agree with theory; whereas in the case of the present experiments the theoretical value 2 is not contained within the limits of probable error, and indeed lies considerably outside those limits. These experiments, therefore, are not in themselves adequate to sustain this theory, and we should not be justified in basing it upon them; but the theory has been conclusively demonstrated by perfectly independent methods; and, taken in conjunction with the previous experiments referred to, we may confidently infer that the fundamental reaction is the same as in the case of the experiment with pure oxygen, but that the experiments are affected by the operation of a constant cause which depresses the mean value of the ratio R.

Such a cause is to be found in the absorption of oxygen by the strongly alkaline solution employed in the absorption-bulb for the removal of the carbonic acid from the mixed gases. The gas passed through the hyposulphite of soda and the gas passed through iodide of potassium have, it is true, been subjected to a similar treatment in this respect; and if the same quantity of oxygen were absorbed by the alkaline solution in the two cases, the value of the difference between the volumes of the gases, which is the numerator of the fraction $\frac{V-V_1}{T}$ in the preceding calculation, would not be affected by this circumstance. But this cannot on the average be the case; for the relative volume of oxygen present in the latter gas being considerably greater than that present in the former, a larger quantity of it will be absorbed by the solution. Now we have (as has been explained) in the contraction which the unabsorbed gas undergoes on detonation with oxygen an independent measure of the total oxygen formed in the induction-tube; and, in fact, if we compare the average values thus actually obtained for the total oxygen in the gas, it will be found that the sum of the "titre" and the oxygen absorbed by pyrogallate of potash is sensibly less than the contraction. This, however, only appears when we consider the mean result, as there are many causes of error which affect the individual experiments. The comparison of these values in the case of fourteen experiments is given below. In column I. is given the sum of the oxygen absorbed by pyrogallate of potash and the "titre" of the gas; in column II. the contraction which the same gas underwent when detonated with oxygen—the results of the experiments being calculated on equal volumes of gas in the two experiments respectively.

I.	II.
15·76	16·17
14·49	14·62
11·20	10·78
10·53	10·84
9·21	9·75
10·42	10·49
8·63	8·89
12·60	13·47
16·83	17·62
16·10	17·68
11·80	12·05
17·34	18·42
3·20	3·61
14·96	15·42
Sum =172·17	Sum =179·81

It hence appears that for every 100 volumes of oxygen found in the induction-tube as estimated by the contraction, only 95·8 volumes are found by the other method, showing a diminution in the amount of oxygen, due to the absorption of that gas by the alkaline solution in the absorption-bulb or to some equivalent cause, of somewhat over 4 per cent. Another cause operating in the same direction as the preceding is the absorption of oxygen by the alkaline solution of iodide of potassium, which (as appears from my previous experiments) although very small in amount is yet an appreciable quantity.

As the question of the identity of the ozone thus formed by the action of electricity on carbonic acid with the ozone similarly formed from oxygen is of great importance in relation to the present inquiry, and as the comparison of the diminution in volume which the electrized gas undergoes when passed through neutral hyposulphite of soda with the "titre" of the gas affords the most satisfactory evidence we can apply to establish or negative this identity, I do not hesitate to lay before the Society the results of a set of experiments in which the diminution in volume which the electrized gas undergoes when passed through hyposulphite of soda is calculated on both hypotheses:—(1) on the hypothesis that the total oxygen formed in the induction-tube is equal to the "titre" of the gas together with the gas absorbed by pyrogallate of potash, and (2) on the hypothesis that the total oxygen is equal to the contraction which the gas after its passage through hyposulphite of soda undergoes on detonation with oxygen. These results are given in the two following Tables; the experiments to which the same number is attached are comparable with each other, having been made with different portions of the same gas.

In column I. of the first Table given below is given the "titre" of the gas; in column II. V_1, the volume absorbed by pyrogallate of potash in the case of the experiment with hyposulphite of soda—that is to say, the oxygen present in the gas after its passage through the solution of hyposulphite by this mode of estimation. In column III. is given the sum of the "titre" of the gas and the oxygen absorbed by pyrogallate in the case of the experiment with iodide of potassium—that is, the total oxygen formed in the induction-tube by this method of estimation. In column IV. is given the difference of these volumes—that is to say, the gas absorbed by hyposulphite of soda according to this mode of estimation, $V-V_1$; and in column V. is given the ratio of this difference to the "titre" of the gas, $r=\frac{V-V_1}{T}$.

I.

Experiment.	I. T.	II. V_1.	III. V.	IV. $V-V_1$.	V. $r=\frac{V-V_1}{T}$.
1.	1·61	7·91	12·60	4·69	2·91
2.	3·38	9·74	18·98	9·24	2·71
3.	3·43	8·87	17·34	9·47	2·76
4.	1·94	9·53	14·96	5·43	2·80
5.	4·34	9·91	20·41	10·50	2·42
					Mean=2·72

The probable error in these experiments is ·055, and we have for the limits of probable error

$$2{\cdot}72+0{\cdot}05=2{\cdot}77,$$
$$2{\cdot}72-0{\cdot}05=2{\cdot}67,$$

the theoretical number 3 being external to these limits.

In the second Table the value C, given in the third column, is the contraction which the gas after its passage through hyposulphite of soda underwent on detonation with oxygen, which is taken as representing the total oxygen formed in the induction-tube*, the value $r=\frac{C-V_1}{T}$ in the last column being calculated on that assumption.

II.

Experiment.	I. T.	II. V_1.	III. C.	IV. $C-V_1$.	V. $r=\frac{C-V_1}{T}$.
1.	1·61	7·91	13·50	5·59	3·41
2.	3·38	9·74	20·32	10·58	3·10
3.	3·43	8·87	18·59	9·72	2·83
4.	1·94	9·53	15·07	5·54	2·85
5.	4·34	9·91	22·23	12·32	2·84
					Mean=3·01

Now, proceeding to calculate the value of the probable error in these experiments, we have as the data for this calculation

Differences from the mean.	Squares of differences.
+·4	·16
+·09	·0081
—·18	·0324
—·16	·0256
—·17	·0309
	Sum=·2570

whence the probable error$=0{\cdot}6745\sqrt{\frac{{\cdot}257}{5\times4}}$
$=0{\cdot}076$;

and we have for the limits of probable error

$$3{\cdot}01+0{\cdot}08=3{\cdot}09,$$
$$3{\cdot}01-0{\cdot}08=2{\cdot}93.$$

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* [Since the above was written I have ascertained that the unabsorbed gas contains a very small proportion of hydrogen. This proportion, under the circumstances under which these experiments were made, is excessively minute, and would not affect the contraction to an extent to interfere with the conclusions as here given. The subject will be fully discussed in my next memoir.—B. C. B., March 16, 1874.]

We have also for the probable error of a single experiment:—

$$\begin{aligned}\text{probable error of a single experiment} &= \sqrt{5}\times \text{p. e. of result}\\ &= \sqrt{5}\times \cdot076\\ &= 0\cdot17,\end{aligned}$$

$$3\cdot01+0\cdot17=3\cdot18,$$
$$3\cdot01-0\cdot17=2\cdot84.$$

Three experiments are within and four experiments outside these limits.

If in the case of these five experiments we compare the total oxygen in the gas as estimated by these two methods (that is to say, the sum of the quantities given in column III. in the two Tables respectively), it appears that this total oxygen, estimated by the contraction, amounts to 89·71 cub. centims. against 84·21 cub. centims. as the same quantity estimated by the other method. These quantities are proportional to the numbers 100 and 93·95. The number 93·95 is below the average arrived at from the fourteen experiments before given, namely 95·8; and it may be noticed that the value of the ratio r in the first Table is below the average value of the same ratio in the former system of experiments, 2·9. But the result, in the case of so few experiments, is less trustworthy than the preceding.

These experiments supply an important link in the chain of evidence absent in my previous experiments, and demonstrate that not only does the gas absorbed by hyposulphite occupy twice the space occupied by the volume of oxygen absorbed by neutral iodide of potassium, but also that it consists of three times that quantity of oxygen and of oxygen alone.

I may here mention that when the electrized carbonic acid is passed through a solution of hyposulphite of soda rendered strongly alkaline with carbonate of soda, the diminution in volume is the same as when the gas is passed through neutral hyposulphite—a result quite different to that observed in the case of electrized oxygen*, and due doubtless to the presence of the large proportion of carbonic acid, which, as will be seen, modifies other reactions also.

In my previous memoir I have investigated the action of ozone upon a solution of protochloride of tin†, and I have shown that the oxidation there effected by the ozone is equal in value to three times the "titre" of the gas, and also that a diminution in the volume of the gas occurs equal to twice that "titre." The evidence which I have given of these facts is, I believe, perfectly valid; but the result is not easily ascertained, owing to the difficulty of disengaging and separating the effects of the ozone from the effects of the oxygen with which it is associated; but in the present form of experiment, in which the ozone is so largely diluted with carbonic-acid gas, and in which the proportion of oxygen present in relation to the total volume of gas is so small, the influence of the associated oxygen is reduced to a minimum, and the oxidation and diminution in volume are those due to the ozone alone. This point is demonstrated by the concordance of the

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* Philosophical Transactions, *loc. cit.* p. 468.

† Ibid. *loc. cit.* p. 479.

results of various experiments made under different conditions. The oxidation effected by the passage of the ozone was estimated as follows.

Before the experiment a volume of the tin solution equal to that employed in it was run from a pipette into a measured volume of a standard solution of iodine, and the excess of iodine was estimated by titration with hyposulphite of soda. A similar estimation was made after the experiment with the tin solution through which the gas had been passed; the oxidation effected is measured by the difference between the two titrations. One pipette of the electrized carbonic-acid gas was employed for each experiment, and was passed through 10 cub. centims. of the tin solution. The experiments were made successively; and no appreciable change in temperature or barometric pressure occurred during the course of the experiments, so that the same volume of gas was always operated upon.

In the first column of the following Table the strength of the tin solution as measured by the volume of oxygen required to effect the complete oxidation of 1 cub. centim. of the solution is given. Column I. contains the "titre" of the gas, T*; column II. the oxidation effected in the tin solution, S; column III. the ratio of this oxidation to the "titre" of the solution, $r=\frac{S}{T}$.

In experiment 5 the bulb containing the tin solution was placed in ice; the other experiments were made at the temperature of the air, about 16° C.

Experiment.	Strength of the tin solution.	I. T.	II. S.	III. $r=\frac{S}{T}$.
1.	15·4	2·8	7·59	2·71
2.	15·4	2·8	7·87	2·81
3.	4·2	2·8	7·9	2·83
4.	4·2	4·73	13·56	2·87
5.	4·2	4·73	12·77	2·70
6.	0·84	4·73	12·66	2·72
				Mean=2·77

In the two following experiments, besides the oxidation effected, the diminution in volume also which the gas underwent by its passage through the tin solution was determined, the diminution being estimated, as in the case of the previous experiments, with hyposulphite of soda. In column IV. is given the total gas unabsorbed by potash after the passage of the electrized gas through the solution of iodide of potassium, V. In column V. is given the volume of gas similarly unabsorbed after the passage of the electrized gas through the tin solution, V_1; in VI. the difference of these volumes, $V-V_1$, being the volume of gas absorbed by the tin solution; in VII. the ratio of this difference to the "titre" of the gas, $R=\frac{V-V_1}{T}$. Two pipettes of gas were employed in these two experiments.

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* The titre and oxidation in columns I. and II. are given in terms of the cub. centims. of hyposulphite of soda employed for their estimation.

Experiment.	Strength of the tin solution.	I. T.	II. S.	III. $r=\frac{S}{T}$.	IV. V.	V. V_1.	VI. $V-V_1$.	VII. $R=\frac{V-V_1}{T}$.
1.	4·2	3·22	8·87	2·75	56·07	49·94	6·13	1·9
2.	2·1	3·22	8·68	2·69	56·07	50·25	5·82	1·8

The density of the gas thus absorbed by the protochloride of tin may be calculated from these data. Putting Δ as this density, the density of oxygen being the unit of comparison, we have for the value of Δ, in the two experiments respectively,

$$(1) \qquad \Delta=\frac{8{\cdot}87}{6{\cdot}13}=1{\cdot}45,$$

$$(2) \qquad \Delta=\frac{8{\cdot}68}{5{\cdot}82}=1{\cdot}49;$$

that is, once and a half the density of oxygen. It is to be observed that the value of Δ here given is quite independent of the "titre" of the gas and unaffected by any errors in its estimation.

The volumes of gas operated upon in these experiments were altogether too small to bring out very sharp results, and the agreement between theory and experiment is perhaps as close as could be anticipated. I am, however, inclined to believe the somewhat low value of the mean, 2·77, to be due to a real although slight diminution in the oxidation, owing to the dilution of the ozone with carbonic-acid gas. In the two following experiments, in which the solution of the tin salt was excessively dilute, a much lower number for the comparative oxidation was obtained.

Strength of the tin solution.	I. T.	II. S.	III. $r=\frac{S}{T}$.
·42	3·24	8·18	2·51
·21	3·24	7·98	2·45

The following experiments were made with an electrized gas obtained by passing a mixture of one volume of oxygen and four volumes of carbonic-acid gas through the induction-tube, S and T being the weight in grammes of the oxygen found by titration.

Experiment.	I. T.	II. S.	III. $r=\frac{S}{T}$.
1.	·0084	0273	3·25
2.	·0079	0241	3·05
3.	·0079	0257	3·26
4.	·0073	0242	3·29

In experiment 3 the concentration of the solution of the tin salt was twice that of the solution employed in the two previous experiments. In experiment 4 that solution was diluted with $\frac{1}{6}$ of its bulk of a solution of strong hydrochloric acid. The reaction was unaffected by these circumstances. But in the case of similar experiments made with electrized oxygen very different results were obtained. In three experiments thus made, in which the strength of the solution of the tin salt was the same as in experiments 1 and 2, 5·89, 6·49, 7·14 were severally obtained for the value of the ratio $\frac{S}{T}$. The conclusion to be drawn from these experiments, taken in connexion with those on the same subject given in my previous paper, is that the oxidation effected in a solution of protochloride of tin by oxygen gas is greatly diminished and retarded when the oxygen is diluted with a large proportion of carbonic-acid gas, whereas the oxidation effected in the protochloride of tin by passing ozone through the solution is unaffected by such dilution. The influence of the carbonic-acid gas in thus preventing the combination of oxygen may be compared to the influence of even a small proportion of the same gas in extinguishing combustion.

When ozone prepared from pure oxygen is passed through a solution of hydriodic acid of such a degree of concentration that not less than one gramme of iodine is contained in 8 cub. centims. of the solution, the average oxidation effected was found to be equal to twice that effected by the passage of an equal volume of the same gas through a solution of neutral iodide of potassium*. But this oxidation is considerably reduced when the electrized oxygen is largely diluted with carbonic-acid gas, as is shown by the following experiments, which were made with an electrized gas obtained by passing through the induction-tube a mixture of oxygen and carbonic acid in the proportion of one volume of the former to nine volumes of the latter gas. A pipette of the capacity of about 100 cub. centims. was employed to measure the gas; the temperature and pressure were constant throughout the several experiments.

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. centims. 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 the neutral iodide of potassium, $R=\frac{S}{T}$.

The independent oxidation effected under these circumstances by the oxygen mixed with the ozone must be very small, since in an experiment similarly conducted, in which a bulb containing the solution of hydriodic acid was placed after the bulb of neutral iodide employed for the titration of the gas, no oxidation whatever was effected in the second bulb by the passage of the oxygen. I have therefore not attempted to make any allowance for this oxidation; in other respects the experiments were conducted as those before referred to. In the case of the last four experiments in the Table I have no memorandum of the degree of concentration of the hydriodic acid employed.

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[*] Philosophical Transactions, *loc. cit.* p. 462.

I. Degree of concentration of the solution of hydriodic acid employed.	II. T.	III. S.	IV. $R=\frac{S}{T}$.
1 gramme of Iodine in 3 cub. centims. ...	26·2	41·5	1·54
1 gramme of Iodine in 6 cub. centims. ...	26·2	38·8	1·47
„ „ ...	26·2	39·2	1·48
„ „ ...	26·2	40	1·52
1 gramme of Iodine in 12 cub. centims. ...	26·2	38·7	1·47
„ „ ...	26·2	37·5	1·42
	20	28·7	1·4
	14	21·5	1·53
	14	22·5	1·6
	27·7	42	1·51
			Mean=1·49

The oxidation, therefore, of the hydriodic acid effected by the ozone, when thus largely diluted with carbonic acid, is exactly intermediate between the oxidation effected in the case of neutral iodide of potassium and the oxidation effected in hydriodic acid of the same concentration by undiluted ozone. When, in the case of the experiments with electrized oxygen, the concentration of the solution of hydriodic acid is less than that indicated by one gramme of iodine in 16 cub. centims. of the solution, the oxidation effected is very appreciably diminished, and appears (for the experiments do not enable us to pronounce with certainty on the point) to pass continuously through all the intermediate stages until an oxidation is reached closely approximating to (but still in no case reaching) the oxidation effected in neutral iodide of potassium, the smallest oxidation obtained in my experiments by an excessive dilution being $1\frac{1}{10}$ that oxidation; but in the present case the reaction is of a different character, being perfectly definite and not subject to variation, with the variation of those conditions by which it is affected in the other instance referred to. We need not conclude that these conditions are here altogether inoperative, but only that the influence of the dilution of the ozone is so predominant as to render these causes insignificant as regards the total result. The experiments were made with a gas of which $\frac{1}{10}$ consisted of oxygen, the rest being carbonic acid; and this proportion was constant in the several experiments. In the case, however, of two experiments with gas derived from the decomposition of pure carbonic acid, 1·71 and 1·79 were obtained as the value of the ratio $\frac{S}{T}$; and it is quite likely that the reaction may vary with the degree of dilution of the ozone and the proportion of the several gases present, just as it varies with the degree of dilution of the hydriodic acid. Using the notation employed in my previous memoir* (to which the reader is referred for explanation) in addition to the two forms of the decomposition of ozone by hydriodic acid there mentioned, namely, $r=\frac{5}{2}$, in which the unit of ozone is

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* Philosophical Transactions, *loc. cit.* p. 482, and 1866, pp. 792, 805, 810. Journ. Chem. Soc. 1868, vol. vi. p. 367.

distributed according to the equation

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

and $r=2$, in which

$$2\xi^3=\xi^2+4[\xi],$$

we have here an example of a third form of decomposition, $r=\frac{3}{2}$, in which

$$4\xi^3=3\xi^2+6[\xi].$$

These various experiments lead to one and the same conclusion, and demonstrate that the ozone produced in the electric decomposition of carbonic-acid gas in the induction-tube is the same in kind as that produced by the action of electricity upon pure oxygen, but that its quantitative reactions are in certain cases, and to a limited extent, modified by the circumstances peculiar to the experiment.

It was of special importance, in reference to the primary object of this investigation, to ascertain the combination of conditions most favourable to the production in the unabsorbed gas of a high percentage of ozone. From the numerous circumstances of the experiment, and the variety of ways in which these circumstances may be varied and combined, this question is of a very complex order, and can only be fully and satisfactorily answered by a careful special investigation, which I have not attempted.

The following experiments, however, throw considerable light upon the problem.

I. The question which most obviously comes before us is, as to the result of the prolonged action upon the gas of the electricity generated by a coil of high intensity. This question is answered by the following experiment, although it did not happen to have been instituted in reference to it. A very slow current of pure carbonic-acid gas, carefully dried, was passed through the induction-tube and there submitted to the action of the electricity generated by a coil of the above description; the gas was collected in a sulphuric-acid gas-holder. A pipette of this gas was drawn over into the absorption-bulb, and there allowed to stand for some time over a strong solution of caustic potash. The ozone in this case undergoes an expansion in presence of the alkali similar to that which it undergoes by the action of heat. I may observe that I had first tried to expand the gas, as in the case of electrized oxygen, by passing it through a heated tube, but had found reason to believe that a small portion of the oxygen present in the gas was removed by this operation. The gas was then transferred from the aspirator to a eudiometer and there detonated (without any addition of oxygen), the contraction noted, and the carbonic acid determined by removal with potash. Two experiments thus conducted gave the following results:—

Volume of gas in pipette.	Titre.	Volume of unabsorbed gas.
249·14	2·52	
250·5	......	64·81
249·6	......	63·77

The 63·77 cub. centims. of gas from the last experiment, when detonated in the manner mentioned, underwent a diminution in volume of 19·58 cub. centims., and 40·14 cub. centims. of carbonic acid were formed, leaving a residue of 4·05 cub. centims.; the theoretical volume of the oxygen is 19·9 cub. centims. We may hence infer that 230 cub. centims. of carbonic acid were passed through the induction-tube. Further, out of every 100 volumes of carbonic acid passed through the induction-tube, 17·4 volumes were decomposed. The iodine-titre on the same 100 volumes was ·11, and the iodine-titre on 100 volumes of oxygen formed was 12·8.

Now if these numbers be compared with those found in the previous experiments given on page 86, say with experiment (3) there given, it will be seen that although the proportion of carbonic acid decomposed is increased tenfold, the iodine-titre, as estimated on 100 volumes of oxygen, is nearly the same in the two experiments—that is to say, the result of the electric action, after a certain point has been reached in the decomposition, is simply to decompose the carbonic-acid gas without effecting any corresponding increase in the proportion of ozone. It is therefore to be inferred that the prolonged action of a powerful coil is by no means favourable to the object of these experiments.

II. I now proceeded to ascertain the result of repeating the electric action upon the same gas. This was effected by placing the induction-tube between two sulphuric-acid gas-holders, and passing the electrized gas forwards and backwards between the gas-holders in the manner elsewhere described in the case of an analogous experiment with electrized oxygen*. The gas was thus passed ten times through the induction-tube. An undetermined quantity of the electrized gas was then passed through a solution of iodide of potassium, and collected as usual in the absorption-bulb. When the absorption of carbonic acid was complete, the volume of unabsorbed gas was measured. The oxygen was then absorbed by pyrogallate of potash, the gas again measured, and lastly detonated in the eudiometer with excess of oxygen.

The second experiment, given below, was made in a similar manner, all the conditions being preserved as nearly as possible the same as in that just described; but the carbonic acid was passed once only through the induction-tube immediately from the vessel in which it was generated. The coil employed in these experiments was of high intensity.

In column I. of the Table below the titre of the gas is given; in II. the volume of gas after absorption of the carbonic acid; in III. the volume absorbed by pyrogallate of potash; in IV. the sum of the gas absorbed by pyrogallate and the titre of the gas; in V. the contraction on detonation with oxygen.

Experiment.	I.	II.	III.	IV.	V.
1.	3·18	58·03	16·89	20·07	20·27
2.	3·55	44·58	12·21	15·76	16·18

From these data the titre calculated on 100 volumes of the oxygen formed in the two experiments respectively is

(1) . . 15·6, (2) . . 21·9.

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* Philosophical Transactions, *loc. cit.* p. 447.

These experiments confirm the result last obtained, and indicate that the frequent repetition of the electric action on the same gas operates in the same direction as the prolongation of that action by passing the gas very slowly through the induction-tube—namely, to diminish the proportion of ozone in the gas*. They afford, moreover, a satisfactory explanation of the very different amount of decomposition and very different proportion of ozone formed in experiments made under conditions apparently the same.

III. Another important question is, as to the effect upon the electric decomposition of the presence of moisture in the gas. The following three experiments were instituted with this object; and although not made in immediate connexion with the preceding experiments, but from another point of view, may find a place here. In experiment 1 the carbonic-acid gas was saturated with moisture immediately before entering the induction-tube. In experiment 2 the gas was not dried in the usual manner by sulphuric acid, but was only partially dried by a short tube containing chloride of calcium, by which desiccating agent a large proportion, it is true, but by no means the whole moisture in a gas, is removed. In experiment 3 the gas was dried first by sulphuric acid, and subsequently by passing it through a tube about 12 inches long, containing anhydrous phosphoric acid. The induction-tube was in every case kept at nearly the same temperature by immersion in water containing ice. In experiments 2 and 3 five pipettes of the electrized gas were employed for the titration and subsequent estimations. In experiment 1, where the volume of carbonic acid decomposed was comparatively small, eight pipettes of the gas were employed with a view of securing greater accuracy; but the results of that experiment, for the sake of comparison, are calculated on five pipettes of the gas—that is to say, the numbers are $\frac{5}{8}$ of those actually obtained.

Experiment.	I.	II.	III.	IV.	V.
1.	·48	21·95	6·89	7·37	7·53
2.	2·75	48·88	14·09	16·83	17·62
3.	3·43	51·47	13·91	17·34	18·42

From these data the titre calculated on 100 volumes of oxygen as measured by the contraction given in column V. is, in the three experiments respectively,

(1) . . 6·38, (2) . . 15·6, (3) . . 18·62.

These quantities are proportional to the numbers 1, 2·45, 3·76, indicating a progressive increase in the proportion of ozone formed corresponding to the more perfect desiccation of the gas. In experiment 3, where the gas was most completely deprived of moisture, 55·86 per cent. of the total oxygen formed was converted into ozone.

The conclusion at which I arrived from the preceding experiments was, that the mode of conducting the experiment most favourable to the production of a large proportion of ozone in the electrized gas would be (1) to operate upon the gas by means of electricity of feeble tension, (2) to submit the gas for as short a time as possible to the

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* For the account of similar experiments in the electrized oxygen, conf. Philosophical Transactions, *loc. cit.* p. 447.

electric action, (3) rigorously to dry the carbonic acid employed, (4) to keep the induction-tube at a low temperature. These conditions I endeavoured to realize in the following manner.

The carbonic-acid gas was generated in a KIPP'S apparatus, and having been washed and dried, as in experiment 3 in the last Table, was passed immediately through the induction-tube, which was placed in a glass cylinder, surrounded with flannel, containing a mixture of ice and salt, by which means the temperature could readily be kept during the experiment at from −10° C. to −14° C. On leaving the induction-tube the gas traversed three bulbs containing anhydrous phosphoric acid (which were permanently attached to the tube to preclude the entrance by diffusion of aqueous vapour), and, passing through the solution of iodide of potassium contained in the titre-bulb, entered the absorption-apparatus, where the carbonic acid was absorbed by a strong solution of caustic potash. The gas was passed through the induction-tube in as rapid a current as possible consistent with the absorption of the carbonic acid. When a sufficient quantity of gas for analysis had been collected in the absorption-bulb, for which several hours were required, the experiment was stopped, the iodine separated in the titre-bulb was estimated with hyposulphite of soda, the gas contained in the absorption-bulb was measured, and the whole or a portion of it transferred to a eudiometer and there detonated with oxygen. The oxygen originally present in the gas was assumed to be equal to the contraction occurring on detonation. These data supply all the elements necessary for the calculation of the proportion of that oxygen converted into ozone in the induction-tube.

It is not difficult, by this mode of experiment, to effect the conversion of as much as 75 per cent. of the total oxygen eliminated in the induction-tube into ozone, in which case the ratio $\frac{C}{T}=4$; and the gases formed are constituted of ozone and oxygen in the proportion of two units of the former gas to one of the latter, the matter of the oxygen being thus distributed, $2\xi^3+\xi^2$; but it is difficult to increase the proportion of the ozone beyond this limit; however, I have made several experiments, conducted with all possible care, in which this limit has been exceeded. The results of these experiments are given in the following Table. In column I. is given the total gas unabsorbed by potash; in column II. the titre, T; in III. the contraction on detonation (that is to say, the total oxygen), C; in IV. the ratio, $R=\frac{C}{T}$; and in V. the proportion of the matter of oxygen converted into ozone calculated on 100 parts of the total oxygen, as measured by the quantity of the matter of oxygen which would be absorbed by a solution of neutral hyposulphite of soda were the gas passed through such a solution, which has been proved to be a quantity equal to three times the titre of the gas.

I. Unabsorbed gas.	II. T.	III. C.	IV. $R=\frac{C}{T}$.	V. Ozone per cent.
22·6	2·06	7·63	3·7	81·3
32·73	3·01	10·63	3·53	85·5
15·92	1·46	5·48	3·75	79·8
31·42	3·0	10·78	3·59	83·5
28·14	2·55	9·76	3·82	78·3
11·03	1·13	4·32	3·82	78·3
16·57	1·58	6·19	3·91	76·6
9·43	0·97	3·46	3·57	84·1
10·51	1·09	3·88	3·56	84·3

The maximum result attained in these experiments is that in which 85·5 per cent. of the matter of oxygen is converted into ozone, in which case the value of the ratio $\frac{C}{T}$ is 3·53. The value of this ratio, 3·5, corresponds to a gas in which 85·7 per cent. of that matter has been thus converted, and which is constituted of ozone and oxygen in the proportion of four units of the former to one of the latter gas, thus $4\xi^3+\xi^2$. The numbers, it is to be observed, given in the last column are undoubtedly somewhat too low, from the circumstance, already mentioned, that the unabsorbed gas contains a minute quantity of hydrogen[*], and also possibly from the removal of traces of iodine from the absorption-bulb by the rapid current of carbonic acid, so that the proportion of ozone found is certainly not less than is there indicated.

These experiments, taken in connexion with those described in my previous investigation, leave no room for doubt as to the true nature of the unit of ozone, the composition of which must henceforth be regarded as established on evidence hardly less conclusive than that on which our knowledge rests of the composition of the unit of water. Nevertheless it is not to be anticipated that this result will be equally clear to all minds. As in the analogous case of the dual nature of oxygen, it is not a point to be demonstrated by any single experiment, but is a conclusion derived from various trains of reasoning, each of which has to be separately mastered and appreciated. In interpreting the experiments on which this conclusion is based, I have made frequent use of the well-known method of the science of probabilities, the method of least squares, which (so far as I am aware) has not hitherto found any serious application in chemistry; but in such cases as the present, where the experiments are complicated and where an exact result can only be obtained by the successful performance of numerous operations, each of which is liable to error, this method is of essential service. We cannot, indeed, get rid of accidental errors from our experiments; but instead we eliminate from our conclusion the result of those errors considered individually. It has, moreover, the very great advantage of enabling us to estimate the numerical result of our experiments at neither more nor less than its true value; and removing that value from the uncertainties incidental to the appraisement of individuals, assigns to it its true position according to an external standard.

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[*] Conf. note, p. 92.

No discovery has ever, perhaps, been made more calculated to throw light upon the nature of the elemental bodies than the discovery of the chemical constitution of ozone. Since the time when the molecular constitution of the elements first seriously engaged the attention of chemists, the opinion has prevailed that the units of oxygen and chlorine are of the same class, being each constituted of two similar atoms, between which we cannot discriminate. This view, notwithstanding the real and cogent arguments by which it is supported, had for many years to struggle against the prepossessions of the electro-chemical theory. It is, however, now paramount, and the opinion that we have no alternative in the matter is almost universal. I myself have, however, distinctly proved* that there is such an alternative, and that chlorine may at least with equal probability be regarded as a triad element constituted of three "simple weights," of which the unit is to be symbolized as $\alpha\chi^2$. Now in ozone, ξ^3, we have actually before us an element of this peculiar triad class, to which not only is the unit of chlorine analogous in form, but to which it is also analogous in properties. The formation of this triad element places beyond a doubt the possibility of the existence of such a class. Another chemical substance which stands in the most intimate relation to ozone is the binoxide of hydrogen, the artificial element "hydroxyl," $\alpha\xi^2$, which is connected on the one hand with the unit of ozone, on the other with the unit of chlorine†, being derived from the unit of ozone by the substitution in that unit of the simple weight α for one of the simple weight ξ, and derived from the unit of chlorine by the substitution in that unit of the simple weight ξ for the simple weight χ, the three substances being also connected by the closest analogy in their chemical properties.

The complete analysis of the electrized gas will be considered in another communication.

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* Philosophical Transactions, 1866, vol. clvi. p. 818.

† In relation to the analogies of chlorine and the binoxide of hydrogen, see Chem. Soc. Q. J. vol. xvii. (1864) p. 281, "The Organic Peroxides theoretically considered," by the author.