XXXII.—SOME ADDITIONAL NOTES ON OZONE.

BY ALBERT R. LEEDS. PH. D.

I.—COMPARATIVE RESULTS OBTAINED WITH PREVIOUS ELECTRICAL OZONISERS, WITH DESCRIPTION OF A MODIFIED AND POWERFUL FORM.

In pursuing this inquiry, three objects were kept prominently in view:

1st. To obtain ozone by a method which could be relied upon at all times, and which would not only be practically independent of changes in temperature, humidity, etc., but require little or no supervision from the experimenter, after once being set in operation.

2nd. To be able both to ozonise to a maximum the air or oxygen employed, and to employ large volumes of the ozonised gas.

3rd. To render the apparatus simple and inexpensive, using the appliances at present found in a well appointed chemical laboratory.

The considerations summarized under the first head, finally caused the abandonment of a large Holtz machine, with which the experiments had been originally instituted. For, granting that by the use of suitable precautions, the disturbing influences of atmospheric variations are eliminated, there still remains the necessity of a considerable amount of mechanical power to drive the machine.

As to the second point, there was little to guide us except the results of our own comparative experiments with the various forms of ozonisers hitherto proposed, and Dr. Siemens' theoretical discussion of the principle involved in the construction of the induction tube which bears his name. In the experiments of von Babo and Claus, with an ozoniser devised by the first named, a very small volume of oxygen, confined within the apparatus, was subjected for many hours to the action of electricity, generated by a powerful coil.* The maximum degree of ozonation was reached under these circumstances, when the confined gas ceased to contract, and this maximum in various trials corresponded to 3.1 to 5.74 per cent. of ozone. Brodie employed a Siemens' tube, the interior and exterior surfaces being cooled to 0°, or even —10° by ice, or a mixture of ice and salt.†

---

* Researches on the Constitution of Ozone, Ann. d. Chem. u. Pharm., **140**, 248.

† Sir B. C. Brodie, on the Action of Electricity on Gases, Phil. Trans., 1872, 435.

The highest percentage of oxygen obtained in this manner was 6.5 per cent. A very powerful coil was employed (how powerful is not stated), the passage of the gas in each experiment occupying about 30 minutes; and the volume of oxygen, varying from about 100 cc to less than 300 cc. Experiments were made with the view of ascertaining the effect of repeated electrization of the gas, on passing it several times through the induction tube. It was found that on its fourth or fifth passage, it contained no higher percentage of ozone than it did at the end of the first. These experiments agree, therefore, with those of von Babo and Claus, in so far as they likewise appeared to show that there was a fixed limit prescribed by the conditions of the experiments, beyond which the ozonation cannot pass, but differed in the respect that this limit was reached at once; while in von Babo and Claus, it was not obtained until after powerful electrization for many hours.

But the object in the present inquiry, was not to ozonise to a maximum, a small volume of confined gas, with the view of studying the properties of the gas itself. It was rather to ozonise to a maximum a *current* of air or oxygen, with a view of studying the reactions produced by it in the various substances with which it was brought in contact. It was also desirable, if possible, to employ a large volume of oxygen, and to keep it flowing rapidly, so that the total amount of ozone produced might be considerable. With these ends in view, the various forms of ozonisers hitherto proposed, were tried, and failed to give, in our hands, the character of results sought for, until eventually, after many modifications, a development of the Siemens' induction tube was arrived at, which has proved satisfactory.

After discarding the Holtz machine, an induction coil with a battery of 10 Bunsen elements set up as two large cells, was employed The axis of the wheel which operated the hammer used in making and breaking connections, was also the axis of a pulley connected by a belt with another pulley, run by a small electro-magnetic machine. This latter was driven by two additional Bunsen cells, and the speed so regulated that about 60 sparks would pass between the terminals of the coil per minute. As thus arranged, the coil was used to supply the electricity employed in making the trials on the various ozonisers employed. And, without claiming that the results in each case were the best possible, yet they were the best which we could obtain, and as such are put on record, without attempting to explain why in some instances, they are so low. With these words of explanation, we shall give a brief description of the ozonisers experimented upon, and their performances.

Wright's Ozoniser.[*]

The first tried was that of Prof. Wright, who, however, had made use in his own experiments of a Holtz machine, as the source of electricity. The original description was followed closely. A straight glass tube, 20 cm in length and 2.5 cm diam., was closed at each end with paraffined corks, through the axis of which stout copper wires were passed, one carrying a terminal in the form of a ball, the other a terminal disc. Inlet and exit tubes were also let into the corks eccentrically, to provide for the flow of gas.

A very slow stream of perfectly dry oxygen was made to flow through the apparatus. The maximum result was 0.76 mgm of ozone per liter. The oxygen used contained about two per cent. of nitrogen. It was dried in this and the subsequent experiments, by passage through a series of sulphuric acid dryers.[†]

Houzeau's Ozoniser.

According to M. Houzeau's description (Compt. Rend., **74**, 256), this is constructed of a straight tube, in the interior of which is a wire of copper, lead, or better, of platinum, 40 to 60 cms long, passing through the upper side. A wire is wrapped around the exterior, which is a little longer than the interior wire, and connects with the other pole of the induction coil. With such an apparatus, and with a coil giving 2 to 3 cm sparks, Houzeau states that he readily obtained 60 to 120 mgms of ozone per liter of ozonised air, according as the experiment was performed at + 15° or — 30°. In one case he obtained 180 mgms, and expressed the opinion that the complete conversion of oxygen into ozone was to be regarded as possible.

---

[*] Amer. Journ. Sci., 3, **4**, 29.

[†] NOTE.—Gianetti and Volta (Ber. d. d. chem. Gesell., **7**, 1,462), with a similar apparatus, employing the Holtz machine, obtained 15 mgms of ozone per liter. Later (ib., **9**, 84) they employed a form of Siemens' induction tube, with the inner and outer tube 2 cms and 2½ cms respectively, in connection with a Holtz machine. They found that the slower the stream, and the lower the temperature, the larger the percentage. Between 5 and 10°, ½ liter of oxygen flowing per hour, they obtained 40 mgms ozone per liter. On substituting a Ruhmkorff coil, they obtained, under like circumstances, only ½ this amount.

Two ozonisers of this form were made. The first, of a tube 55 cm long and 15 mm diameter. A spiral of platinum wire 90 cm long, coiled around the middle portion of the exterior of the tube, formed one pole; a straight platinum wire passing along the axis of the interior of the tube, the other.

Result.—Oxygen used, a slow current flowing, 3.25 liters; ozone obtained, 16.07 mgms, or 4.95 mgms per liter; temp., 20°.

Second trial.—Oxygen used, 5.125 liters; ozone obtained, 19.85 mgms, or 3.9 mgms per liter; temp., 21°.

These results being highly disappointing, a more elaborate ozoniser of this class was constructed. The outside tube was 60 cm long and 18 mm diameter. Around the middle portion of this exterior tube, for a length of 40 cm, was coiled a platinum spiral, 177 cm long, with 32 turns. In the axis of this tube, another glass tube 6 mm in diameter was placed, with a similar platinum spiral, but having 70 turns, and coiled in the opposite direction. The inner tube was kept concentric with the outer by two rings of glass beads.

Result.—Placed in a mixture of ice and salt; oxygen used, 4¼ liters; ozone obtained, 10.03 mgms, or 4.6 mgms per liter. No better result on second trial.

Repeated.—Temp., 22°; spark-length, 30 mm; oxygen used, 1.6 liters; ozone obtained, 3.78 mgms, or 2.4 mgms per liter.

Since in these and subsequent trials, Houzeau's ozoniser in my hands, yielded equally unsatisfactory results, its use was abandoned.

Boillot's Ozoniser.

Its peculiar features are: 1st. The use of gas-carbon as the material constituting the poles. 2d. The ozonised oxygen is allowed to flow through and in contact with one of these poles, instead of isolating the gas-carbon in a glass tube. The apparatus was constructed so as to embody the ideas of its author, as far as we understood them.*

The oxygen was conveyed through a glass tube, 60 cm long and 15 mm in diameter. This was closed with paraffined corks at both ends, through which smaller glass tubes were passed for inlet and outflow of gas. It was filled with coarse fragments of gas-carbon, each about the size of a pea. These were connected with one pole by a

---

* Compt. Rend., **75**, 214 and 1,712; Chem. News. **26**, 312; Journ. Chem. Soc. N. S., **10**, 879.

copper wire passing through the cork. The middle of this tube was surrounded by another tube 19 mm in diameter, the space between them being filled with pulverized gas-carbon, and connected by a copper wire with the other pole.

Result.—Length of spark, 60 mm at beginning, 50 mm at close of experiment ; temp., 20° ; time, 2 hours ; amount of oxygen used, 4½ liters ; of ozone obtained, 11.01 mgms. This is equivalent to 2.77 mgms, or 1.29 cc per liter.

*Von Babo's Ozoniser.**

The instrument of this description, as constructed by ourselves, was made as follows : 14 small thin tubes, 2.5 mm wide, and 900 mm long, were joined together two by two, and thrust into a large tube, 21 mm inside diameter, and 975 mm long. The thin tubes were kept apart by means of little pieces of tubing about 10 mm long, and just large enough to fit over the other tubes. In each tube was placed a copper wire, running through nearly its entire length, and connected with a platinum wire. They were then sealed by the gas flame. The tubes in couples were so arranged that the platinum wire of one projected from one end of the large tube, and the platinum wire of the other projected from the other end. The bundles of wire were connected at each end with copper wires going off to the coil, the junction being made outside of the enveloping tube, which was provided with an inlet and outlet for the gas.

Result.—Spark-length, 70 mm ; time, 35 minutes ; oxygen used, 1 liter ; ozone obtained, 9.15 mgms. In the dark it was found that the discharge was not altogether silent, a few points of light being visible.

Thinking that a better result might be obtained by spreading the charge over a lesser extent, another ozoniser of this pattern was fitted up with only 5 pairs of tubes, all the other arrangements being the same.

Result.—Time, 70 minutes ; oxygen used, 1 liter ; ozone obtained, 2.5 mgms. Minute points of light were also noticeable in the dark, along the sides of some of these tubes.

After these trials, the attempt to employ ozonisers of Von Babo's form was abandoned.

---

* "Volumetric Relations of Ozone." Ann. der Chem. u. Pharm., Suppl., 2, 297

Will's Ozoniser.[*]

This is a Siemens' ozoniser, modified by making the inside of the inner tube a portion of a worm, through which a current of cold water is kept flowing. The object of this arrangement, it is stated (*loc. cit.*), is to prevent the heating which takes place on continued use of the Siemens' apparatus, the heating being attended with a diminution in the quantity of ozone.

We constructed an ozoniser in accordance with this description, the diameter of the exterior tube being 42 mm; of the inner tube, 20 mm; and the length of the opposed surfaces, where the tin pipe forming a portion of the worm on the inside of the inner tube, was opposed to the tinfoil on the outside of the outer tube, 30 cm. But the apparatus, as we used it, did not give results of such a character as to compensate for the increased complication brought about by the introduction of a current of water. There appeared, also, to be a considerable loss of electricity from the pole connected with the stream; and in the Siemens' ozoniser, properly constructed, there is so slight a heating of the surfaces, and so little gained from artificially cooling them (I am now speaking of the ozonation of a large volume of gas in motion, not of a small confined volume), that the employment of Will's modification was abandoned.

Siemens' Ozoniser.

The original description of this ozoniser, which was designed and constructed according to certain theoretical conceptions by W. Siemens (Ann. der Phys. u. Chem., **102**, 120), more than 20 years ago, is as follows. It is made of two tubes of the thinnest suitable glass. One of them, which is closed, and the narrower of the two, is set inside the other in such a way, that the annular space between them is of uniform width throughout. The outer is melted to the inner tube at one end, and at the other is narrowed down into an exit tube. The inlet tube is joined to the other end of the outer tube. The inner and outer surfaces of the glass tube are coated with metallic foil, and oppositely electrified.

With the objects in view, which were set forth at the beginning of this article, a very large number of ozonisers of this description were made, and the successive improvements, as shown by the increase in the amount of ozone obtained, rapidly led to the modification, which was finally adopted. The first was constructed of a tube 50 cm in length and 35 mm in diameter, narrowed down at each end so

---

[*] Chem. News, **27**, 292; Ber d. d. chem. Gesell., **6**, 769.

as to unite with a straight tube passing through its middle, 17 mm in diameter. The inside of this second tube was covered with tinfoil and formed one pole; the exterior of the outer tube was covered with 378 cm of tinfoil, and constituted the outer pole. The lateral inlet and exit tubes for the passage of the gas, were closed with small wash-bottles made of test tubes and containing sulphuric acid. This simple arrangement prevents backward diffusion of the ozone, and consequent destruction of the rubber connections.

Result.—Oxygen employed, 1 liter ; ozone obtained, 7.18 mgms.

After the experiments given in the present article, were concluded, a Siemens' ozoniser of the pattern known as Geissler's, was received from Bonn. The interior tube was 18 mm, the exterior tube 27 mm, in diameter, and the exterior surface of the latter over a length of 30 cm, was coated with foil. About the same length of foil was contained in the inner tube. The outer tube was again surrounded by a final enveloping glass tube. All the joints and connections in this difficult piece of glass-blowing were of glass. In our own trials we were compelled to make the joints of sealing-wax and paraffine. As this lowered all the quantities found, their relative value and significance would still remain.

Result.—Spark-length, 31 mm ; time, 40 minutes; oxygen used, 1 liter ; ozone obtained, 28.16 mgms.

A series of experiments was now instituted to determine the influence of the extent of electrified surface, its separating distance, duration of exposure of the current of oxygen to the silent discharge, and of the spark length, upon the amount of ozone obtained. With these objects we employed :

I. Ozoniser of one meter in length, of which 850 mm were covered with tinfoil. Diameter of outer tube, 25 mm ; width of annular space intervening, 1 mm ; both inside and outside tubes of very thin glass.

Result.—Oxygen employed, 1 liter ; ozone obtained, 23.65 mgms; spark-length, 85 mm ; temp., 20° ; duration of experiment, 10 minutes.

II. Length of tube, 1 meter ; length of exterior of outer tube covered by tinfoil, 925 mm ; diameter of outside tube, 47 mm ; diameter of inside tube, 25 mm ; width of the annular space intervening, 11 mm ; walls of the glass tubes thicker than the preceding.

Result.—Oxygen employed, 1 liter ; ozone obtained, 5.8 mgms ; time, 10 minutes ; temp., 22° ; spark-length, 60 mm.

Therefore, in the construction of tubes subsequently made, glass tubes as thin as could be obtained, and with as small an annular space between them as possible, were employed.

III. Using the same (II.) ozoniser, an experiment was made to determine the effect of prolonged exposure to the silent discharge upon the degree of ozonation. After filling with oxygen, the coil was put into operation for 15 minutes, and then, the coil being still active, a current started and allowed to flow until 1 liter of oxygen had passed through the ozoniser, the time required being 10 minutes.

Result.—Oxygen employed,. 1 liter ; ozone obtained, 10.2 mgms ; time, 15 + 10 = 25 minutes ; temp., 22° ; spark-length, 55 mm.

In this experiment, a lower result in the total amount of ozone obtained is very noticeable as compared with I., in which, however, the spark-length was 85 mm.

IV. Using, therefore, the same ozoniser (I.) with the spark-length of 55 mm, the experiment was repeated without setting the coil into action prior to beginning of the flow.

Result.—Oxygen employed, 1 liter ; ozone obtained, 14.93 mgms ; time, 10 minutes ; temp., 25° ; spark-length, 55 mm.

The foregoing experiments point out the proper directions in which to modify the apparatus, in order, under given circumstances, to bring the degree of ozonation to a maximum :

(*a.*) To diminish the distance between the electrified surfaces, both by diminishing the thickness of the glass, and by lessening the annular space between the two tubes.

(*b.*) By prolonging the interval during which the oxygen is subjected to the silent discharge. There are evidently two ways of doing this ; either by lessening the rate of flow, or, the intensity of static charge being preserved the same upon each unit of electrified surface, by increasing the length of the tubes. The latter method was adopted, since the principal object in view was that of obtaining the largest possible total quantity of ozone.

(*c.*) Along with the increase in the length of the tubes, to raise correspondingly the length and number of the sparks (within the limits of the silent discharge).

(*d.*) As no notable elevation of temperature was perceived, in the case of large tubes operated in this manner, it was deemed important not to complicate the apparatus by arrangements for depressing the temperature.

Since considerable time was required to line the inside of the inner tubes with tinfoil, some trials were made to learn whether a simpler arrangement would answer.

V. The outside of the inner tube, this time of heavy glass, was coated with tinfoil, and the outside of the inner tube with the same, the length covered by the tinfoil being 900 mm, and the annular space between the tubes 1 mm.

Result.—Spark-length, 62 mm; time, 10 minutes ; temp., 21°; oxygen used, 1 liter ; ozone obtained, 1.89.

VI. The tinfoil was transferred from the outside to the inside of the inner tube, everything else remaining the same.

Result.—Oxygen used, 1 liter ; ozone obtained, 10.58 mgms.

These trials demonstrated the importance of separating the electrified surfaces by glass walls. The tin was not noticeably affected, and the diminution of ozonation was probably due to the loss of tension consequent on removing one of the insulating surfaces.

VII. To study the effect of prolonging the interval, during which a certain volume of oxygen was subjected to ozonation, the ozoniser used in VI. was charged for 15 minutes, the gas not flowing. The volume of oxygen contained in the annular space and ozonised in this manner, was 70 cc.

Result.—Spark-length, 55 mm ; time, 15 minutes ; oxygen used, 70 cc ; ozone obtained, 2.31 mgms, corresponding to 33 mgms per liter.

Since an increase in the length of the tube would also have the effect of prolonging the duration of ozonation, the foregoing experiment suggested those which follow, and ultimately led to a satisfactory solution of the problem in hand.

VIII. A thin glass tube, 25 mm wide and 1 meter long, was coated with tinfoil over 815 mm of its outside surface. An inner tube was similarly coated on the inside over 815 mm. Its inner coating was connected by copper wire with one pole. Both ends of each tube were sealed with paraffined corks, the outer tube enclosing the inner, and the inner separated by glass rings by an annular interval of 1 mm, from the outer. A duplicate ozonising tube was prepared, and the outer surfaces of the two connected together, and with one pole of the coil, and likewise their inner surfaces with the other pole.

Result.—Spark-length, 50 mm ; temp., 21.5° ; time, 30 minutes ; oxygen used, 1 liter ; ozone obtained, 52.54 mgms.

Repeated, but the ozoniser charged for 15 minutes before beginning the flow of oxygen ; ozone obtained, 57.83 mgms.

Repeated.—The charging being begun 15 minutes before flow ; ozone obtained, 71.82 mgms.

Finding, as the result of other variations in the lengths and proportions of the tube, the conclusions arrived at above were confirmed, the form of ozoniser as finally used and adopted, was constructed, and will be found figured in the text. Each induction tube is a modified Siemens' tube, and may be called a Siemens' element. Six of these elements are connected together, and supported on a frame, constituting what we may term an ozonising battery. One of these frames is fitted on above another, the end elements of the two batteries being suitably connected: and in this way, by repetition of similar parts, an ozonising tube of as great a length as desired, can be made and handled without inconvenience. Or, the electrical charge can be divided between several ozonising batteries, and the supply of oxygen, as well, so that a number of currents of ozonised gas can be used at the same time.

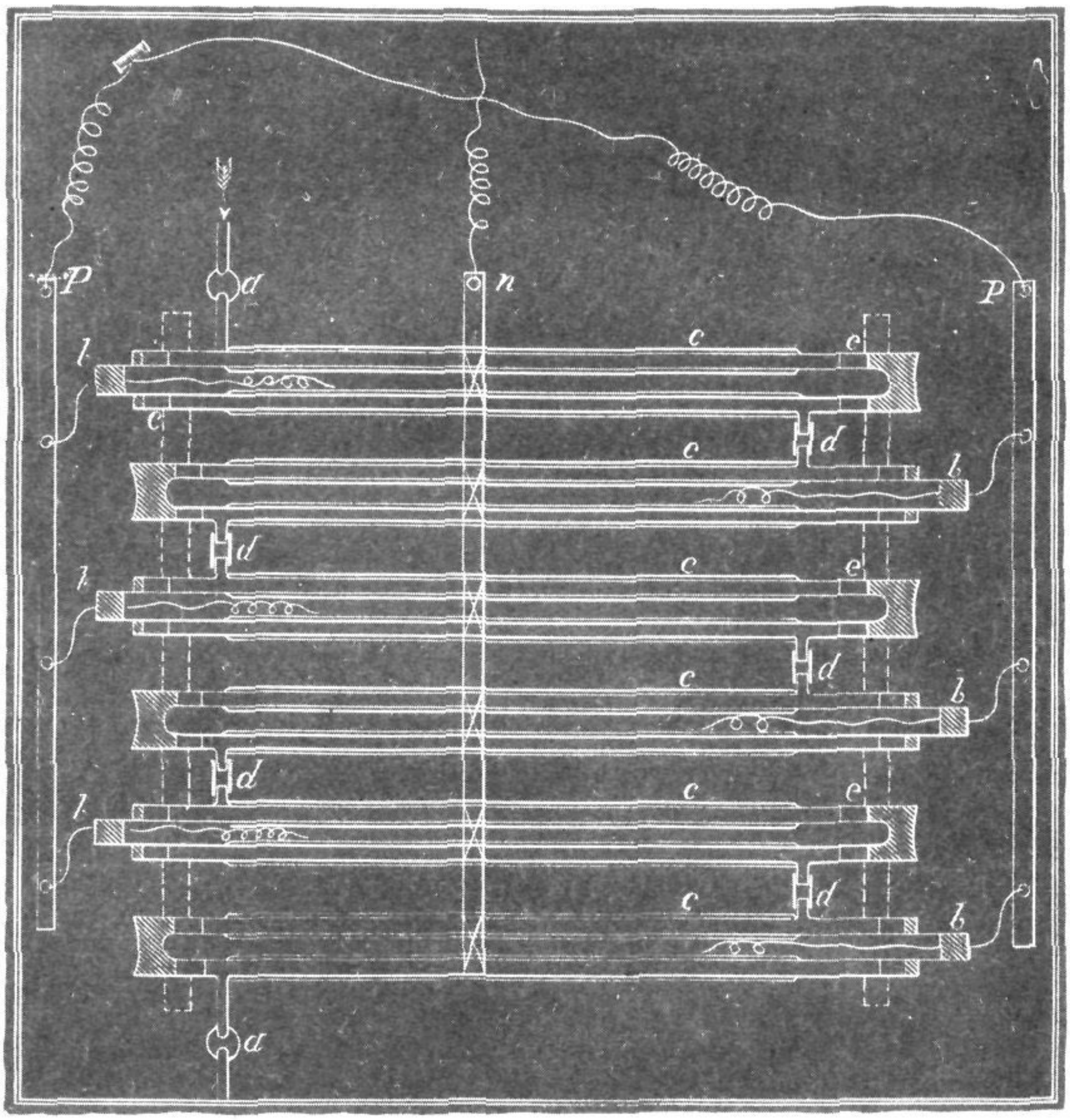
Each element is made of a tube of thin, hard glass, 60 cm long, and 21 mm inside diameter, with the inlet and outlet tubes 6 cm from each extremity. The space between these two latter tubes is coated with tinfoil. The inside tube is a little longer, one end being rounded: the other, after the interior has been coated with tinfoil, is closed with a dry cork, through which the copper connecting wire passes. The space between the rounded end of the inner tube and the outer tube, is nearly filled by a ring of glass cut from a tube of suitable bore, and the space closed by dipping in molten sealing-wax. In coupling the elements together, the exit tube of the first is joined to the inlet tube of the second, by a wrapping of strips of muslin which are bound by flower wire, and made gas-tight by a coating of molten paraffine applied with a brush. The first inlet tube of a battery, and the last exit tube, are made parts of small sulphuric acid wash-bottles, by means of which the rubber or kerite connections, with the other parts of the apparatus, are protected from backward diffusion of the ozonised gas on the one hand, and a convenient attachment is made upon the other.

Result.—With a battery of three elements: time, 30 minutes; oxygen used, 1 liter; ozone obtained, 22.8 mgms.

With a battery of six elements: time, 30 minutes; oxygen used, 1 liter; ozone obtained, 51.74 mgms.

Repeated (after an interval, but with same number of elements).—Oxygen used, 1 liter; ozone obtained, 49.5 mgms. With two batteries, twelve elements in all: spark-length, 45 mm; time, 30 minutes; temp., 24°; oxygen used, 1 liter; ozone obtained, 69.93 mgms.

In this shape, the apparatus proving adequate to perform the work required, it was used almost daily for three months, the average yield



Description.

aa	Small sulphuric acid wash-bottles.
bb	Corks dipped in melted sealing-wax
cc	Outside coating of tinfoil.
dd	Connections of paraffined cotton cloth.
ee	Rings of glass.
pp	Copper strips connecting with inner coatings and one pole.
n	Copper strip fastened to all the outer coatings and the other pole.

of ozone, with the battery in good condition, being 72 mgms per liter, or about 5 per cent.

To obtain the best results with such a battery, the following precautions should be observed :

1st. The connection at *dd* should preferably be ground, and the other joints be made by fusion.

2d. The number of ozonising elements used should be proportioned to the strength of the coil, the maximum effect being obtained when the whole interior is luminous, but without sparks, in a darkened room.

3d. The feeble inductorium should be replaced by one giving a large number as well as a great length of sparks.

4th. The exterior foil should be covered with an outer enveloping tube of glass.

5th. The temperature of the ozonising battery should be prevented from rising, by placing it within a refrigerating chamber, and surrounding it by dry air at 0°.

II. PREPARATION OF OZONE BY CHEMICAL METHODS.

A. Potassium Dichromate and Sulphuric Acid.

According to Weltzien,* the oxygen given off when sulphuric acid is allowed to act upon potassium dichromate, contains ozone, while, according to Marignac,† it is odorless. The statement of Weltzien does not appear probable, from the fact that no evolution of oxygen takes place until the mixture is heated. But, in order to settle the question by experiment, the following arrangement was adopted: a small tubulated retort, with dropping funnel passing through the tubulure, was connected with three Geissler washing apparatus, the first of which was empty, the second and third containing water. The third Geissler apparatus was connected with a straight drying tube, in which were placed strips of moistened iodo-cadmium-starch paper. Similar strips were coiled in small open glass tubes, which were introduced into the neck of the retort. In the earlier experiments, a mixture of three parts of the dichromate (some of Merck's chemically pure) was treated with four parts of sulphuric acid at various temperatures, from the common to the boiling point of sulphuric acid. In all cases, the test-paper in the neck of the retort was turned blue, that in the drying tube remaining colorless. The wash-water retained the chlorine which had been evolved from the chlorides contained in the dichromate, and which were the source of the apparent ozone reaction.

50 gms of Merck's potassium dichromate were then subjected to 4 successive recrystallizations, and 12 gms of the salt obtained of a

---

* Ann. Pharm., **142**, 107; Jahresb. der Chem., 1867, 128.

† Gmelin-Kraut, Handb. der anorgan. Chem., 1872, 24.

much deeper and more brilliant red color than the original preparation. On decomposing this salt in the apparatus described above, no coloration took place in the test-papers, either before or after the passage of the evolved gases through the wash-water, or whether the experiment was conducted at ordinary or higher temperatures. No ozone, therefore, is evolved from potassium dichromate when treated with sulphuric acid, at whatever temperature the experiment is conducted, the origin of the supposed ozonic reaction being the minute amounts of chlorides which are contained in all potassium dichromate, except that which has been purified by successive recrystallizations.

B. Potassium Permanganate and Sulphuric Acid.

Similar remarks apply to the supposed generation of ozone by the action of sulphuric acid upon potassium permanganate.* In a former article,† I have shown that when the precaution is taken to conduct the experiment in an apparatus like that described in the foregoing section, the wash-waters yield the chlorine reaction, while the iodo-starch test-papers placed *after* the wash-waters, are not affected. In conducting the operation great caution is requisite, because the violet vapors of permanganic acid which are set free, are liable at any time to be decomposed with excessive violence, large volumes of oxygen being liberated and dense clouds of manganese sesquioxide formed. The least impure of a number of preparations of supposed chemically pure potassium permanganate examined, contained 97.06 per cent. of the salt, the remainder being chlorate, chloride, manganic oxide and sand.

I have called attention to this error again, because the statement that ozone is generated by the action of sulphuric acid upon potassium permanganate, is not only generally made in works upon chemistry, but because chemical manuals published subsequently to the appearance of my former note, have reiterated the statement. The error is a serious one, because medical authorities have used and still use this mixture for purifying the air of hospitals, and recently some writers on sanitary science have proposed its employment on a great scale to purify the atmosphere of places infected with yellow fever. They do so on the ground that the mixture liberates *ozone.* If, as it has been supposed, the ozone is peculiarly efficacious in the destruction of disease germs, then sanitarians must obtain it by the

---

* Bottger, Journ. pr. Chem., 86, 377; Chem. News, 4, 74; Zeitsch. f. Chem. u. Phys., 3, 718.

† Proc. Amer. Chem. Soc., 2, 153.

employment of other means; if the chlorine and oxides of chlorine, which the mixture of the impure potassium permanganate usually employed with oil of vitriol, affords, are desirable, then these chlorine compounds can be more readily and cheaply obtained from other materials. We do not herein criticise the employment of potassium permanganate to oxidize putrescent and noxious organic matters, or doubt that its solution may be employed as a valuable disinfecting fluid, but desire simply to see corrected the error ingrained in works on chemistry, medicine and sanitation, that upon its admixture with an acid, ozone is given off.

C. Barium Peroxide and Sulphuric Acid.

According to the earlier publications of Houzeau,* "active oxygen" is set free by the action of concentrated sulphuric acid on barium peroxide; but later he arrived at a different opinion, regarding the liberated gas as similar to, but not identical with, ozone.† The peculiarity consisted not in its odor, which was similar to ozone, but in its producing in contact with water, a characteristic cloud. Hence it was regarded by Schoenbein ‡ and Meissner, as their so-called *antozone*. But Nasse and Engler, § after demonstrating that the antozone which is formed when ozone is decomposed in contact with water, as is the case when ozonised oxygen is passed through potassium iodide solution, is, in fact, a chemical myth, the cloud being only hydrogen peroxide diffused through a large amount of aqueous vapor, applied the same method of investigation to the case under consideration. They passed the evolved gas through U-tubes, maintained at a temperature of 20°, and on testing the product of condensation, found that it was peroxide of hydrogen. The remainder of the escaping gas was proved to contain ozone. We have repeated their work under a variety of conditions, but have nothing to add further than some determinations of the influence of temperature upon the amount of ozone generated, and a remark upon the availability of the method for any practical use.

In an experiment in which 20 gms of barium peroxide hydrate were decomposed by sulphuric acid added in small portions at a time, the retort being surrounded by ice, and the operation continued for

---

* Compt. Rend., **41**, 947.

† *Ib.*, Feb. 21, 1870.

‡ Journ. für prakt. Chem., **83**, 86.

§ Ann. der Chem. u. Pharm., **154**, 230.

30 hours, 14.29 mgms of ozone were given off. On replacing the potassium iodide solution used to absorb the ozone, by a fresh solution, and continuing the operation at the same temperature for 6 hours longer, only 0.04 mgm of ozone additional was given off. In these and the following experiments, six wash-bottles were interposed to absorb the last traces of hydrogen peroxide.

A second experiment conducted at 27°, the amount of barium peroxide being 15 gms. and the time likewise 30 hours, the amount of evolved ozone was 7.41 mgms. A final trial at 50°, with same amount of material and of equal duration, yielded but 3.88 mgms of ozone.

These results show, in a striking manner, the rapid decrease in the production of ozone with elevation of temperature, and they likewise make evident, that while we have in this purely chemical process an indubitable source of ozone, yet the amounts obtained under the most favorable circumstances are so small, that the process unfortunately cannot be utilized to any practical end.

III. HYDROGEN PEROXIDE AND SULPHURIC ACID.

That the oxygen given off on the decomposition of hydrogen peroxide by strong sulphuric acid contained ozone, was originally stated by A. Riche,* a result abundantly confirmed by our trials with the same apparatus, as that used in the experiments with barium peroxide. Since in the latter case, the evolution was greatest at the lowest temperature, the retort containing the hydrogen peroxide was surrounded by ice. The evolved gas, after repeated washing, turned not only the various iodo-ozonoscopes and Houzeau's test blue, but changed guaiacum tincture, and blackened moist silver foil as well. The same tests, I should have stated, were likewise at once affected by the ozoniferous oxygen evolved from the mixture of barium peroxide and sulphuric acid.

IV. NON-PRODUCTION OF OZONE IN THE CRYSTALLIZATION OF IODIC ACID.

It has been stated by Prof. H. H. Croft,† that air over crystallizing iodic acid becomes ozonised. In preparing the acid according to Millon's process, Prof. Croft noticed that when the acid was left

---

* Bull. Soc. Chim., 1860, 178.

† Chem. News, 25, 87; Amer. Journ. Sci., 3, 466; Canadian Journ., 13, No. 3.

to crystallize over oil of vitriol, the air in the jar (over the drying dish) had the characteristic odor and gave the usual tests of ozone. He states that the solution in every instance, was boiled down to thin syrup, so that no trace of chlorine or nitric acid could possibly have remained. The air in the jar was tested from day to day, both by the smell and the action upon iodized starch paper. Even when a few crystals began to form, no change was noticed, but when the crystallization set in fully, the evolution was most remarkable, the strong smell being quite characteristic, entirely different from that of chlorine or nitric acid.

We have repeated these experiments, and have found that the phenomena may be quite differently interpreted. After preparing the potassium iodate, by oxidation of iodine, by means of potassium chlorate and nitric acid, and expulsion, as far as possible, of free chlorine from the solution, the potassium was converted into the barium salt, and the latter washed thoroughly. This was then decomposed by an equivalent weight of sulphuric acid, and after separation from the insoluble salt, the solution of iodic acid was evaporated nearly to the point of crystallization. It was then transferred to the apparatus used in the experiments on potassium dichromate, barium peroxide, etc. The dropping funnel was now, however, replaced by a tube through which a very slow current of dessicated air was continuously aspirated. The test-papers in the space above the iodic acid turned blue even before crystallization set in. At the end of 6 hours they began to bleach, and at the expiration of 24 hours had become colorless. The test-papers exposed to the current, after its washing through the small amount of water contained in the Geissler bulbs, remained colorless throughout this and all succeeding trials. The strong odor given off from the crystallizing solution, was compared from time to time with the ozone generated by an electrical ozoniser, and was found to be essentially different in character. The crystallized iodic acid was then redissolved in the smallest possible amount of water, and recrystallized in the same manner. The test-papers were less and less affected at each recrystallization, until finally no change whatever occurred in them, either in the process of evaporation or in the act of crystallizing. The crystals were nearly colorless, with brilliant faces of considerable size. Now, when the difficulty of getting rid of every trace of extraneous matter by chemical operations, however carefully conducted, is borne in mind, it appears to me that the simplest explanation of the above phenomena is, that the apparent ozone reaction is not due to ozone produced in the act of crystallizing, which, as Prof. Croft says, is anomalous, but to a trace of chlorine or nitrous acid, or possibly some lower oxide of iodine formed in the process of manufacture, and gradually eliminated by successive recrystallizations of the acid.

V. ACTION OF OZONE UPON ORGANIC SUBSTANCES.

The principal portion of our knowledge upon this subject is derived from the extended investigations of Gorup-Besanez.* He found, as might be anticipated, that the action of ozone upon organic bodies, was far more powerful in the presence of alkalies than in their absence. In the latter case, most of the substances operated on were unaltered, as urea, alloxan, allantoin, leucin, amygdalin, cane and grape sugar, inosite, mannite, glycerine, olein, starch, fibrine, glutin, hippuric acid, purified galls, and also the organic acids free from nitrogen, like acetic, butyric, palmitic, lactic, oxalic, tartaric, malic and citric. But in the presence of alkalies, in these and other cases, a powerful action took place: urea was decomposed, with evolution of carbonic acid and ammonia; leucin yielded ammonia and valeraldehyde ; grape sugar was completely oxidized to formic and carbonic acids, as was also, although less readily, cane sugar. Volatile, fatty acids were likewise oxidized in presence of alkalies, formic acid yielding carbonic acid, acetic yielding carbonic and formic acids, and butyric acid the same. Non-volatile, fatty acids were but little affected, a small amount of carbonic acid being given off after prolonged action.

It appeared probable after the construction of an ozoniser, which renders it possible to employ large amounts of strongly ozonised oxygen (72 mgms per liter), that interesting results might be obtained by the ozonation of organic compounds. Many of the bodies experimented upon by Gorup-Besanez were, therefore, studied anew, but little was done beyond confirming his original results. The complex molecules of organic structure are broken down under the destructive action of so powerful an oxidant, and rearrange themselves either into familiar bodies belonging to simpler types, or the carbon and hydrogen atoms are eliminated in the form of carbonic acid, water and hydrogen peroxide. Absolute alcohol, for example, surrounded by ice, yields on ozonation, large volumes of carbonic acid, and formic acid, acetic acid, aldehyde and hydrogen peroxide,

---

* Ann. der Chem. u. Pharm., 118, 232, and 125, 207.

are left behind in the liquid. According to A. Boillot,* there is likewise formed a white powder, which is deposited on the evaporation of the residue in the air, and which is soluble in water and alcohol. This singular product, whatever it may be, we did not succeed in procuring. According to Gorup-Besanez, glycerine yields on ozonation in alkaline solution, carbonic, formic, propionic acids, and possibly also acrolein. In addition, we found that considerable amounts of hydrogen peroxide were formed, as well. In fact, the preparation of hydrogen peroxide by the ozonation of suitable organic bodies, may possibly afford a method of obtaining this difficultly obtainable body, more convenient than those at present in use.

New Test for Hydrogen Peroxide: In testing for hydrogen peroxide, an aqueous solution of *diastase* was used in place of malt extract. The reaction is a delicate one, and the diastase solution remains unchanged for a long time.

Ozonation of Petroleum and of Petroleum Products.

The object of this inquiry was to discover what changes could be produced in petroleum, or in the distillates from petroleum, by means of ozone, which would so alter the color, odor, volatility, inflammability or other properties, as to render the process of ozonation of importance in the arts. The hope was also entertained that bodies of definite physical character, and susceptible of crystallization, would be isolated, which would serve as starting points of interesting chemical studies.

As a preliminary experiment, some crude petroleum from the carboniferous strata of Ritchie Co., W. Virginia, of specific gravity 0.885, was treated for 17 hours with the air ozonised by the phosphorus ozonator. Its dark green color at the expiration of this interval had grown somewhat lighter, and it appeared to burn less readily. It was then connected with the electrical ozoniser, and subjected to the action of a slow current of ozonised oxygen for 5 days. The liquid portion was then poured off from the yellowish-white residue, which was afterwards dissolved in alcohol. It dissolved readily, but refused to crystallize on standing. On combination with soda, and separation from the soda salt by addition of a mineral acid, the same thick, uncrystallizable oily substance was obtained.

Another preliminary experiment was tried upon a petroleum distillate which had been preserved, exposed to diffused light in a cork-

---

* Chem. News, **27**, 256; Compt. Rend., May 5, 1873.

stoppered bottle, for 6 years. During this interval considerable sediment had been deposited, and the oil which was originally nearly colorless, had assumed a strong reddish hue. Before ozonation of the oil its specific gravity was 48° B., its flashing point 88° F., its burning point 93° F. ; after being treated with ozonised air for 12 hours these numbers were respectively 45° B., 96° F., and 123° F. Another distillate of specific gravity 51.5° B., flashing point 100.4° F., burning point 127.4° F., after similar treatment, afforded instead of the foregoing, the following results: 49.4° B., 102.2° F., and 128.3° F.

It would at first sight appear that the effect of ozonation had been to increase the specific gravity, and notably to diminish the volatility and inflammability of the petroleum distillate—results of great practical value. But it must be remembered that the volume of ozone obtained by this method of phosphorus ozonation, is but small compared with the total volume of air drawn over, about 1 cc per liter, so that similar effects might have been obtained by aspiration through the oil, of air alone. Subsequent experiments with non-ozonised air showed that this was actually the case.

A series of six petroleum distillates were then kindly furnished to the author by Mr. A. Bourgougnon, who had obtained them according to the method which he has described in the JOURNAL OF THE AMER. CHEM. SOCIETY, I, 188. They were derived from one sample of crude petroleum, and were as follows :

	PER CENTS.	TEMPERATURES [C.]	SPECIFIC GRAVITIES [15° C.]
No. I.	0 p.c. to 8 p.c.	124° to 142°	0.707 to 0.728
" II.	8 p.c. to 16 p.c.	142° to 163°	0.728 to 0.746
" III.	16 p.c. to 24 p.c.	163° to 186°	0.746 to 0.758
" IV.	24 p.c. to 32 p.c.	186° to 209°	0.758 to 0.772
" V.	32 p.c. to 39 p.c.	209° to 238°	0.772 to 0.785
" VI.	39 p.c. to 50 p.c.	238° to 283°	0.785 to 0.808

The first experiment was made with distillate No. VI., a determination of the specific gravity of which, as made by ourselves with the pycnometer, showed 0.789 at 15° C. 30 cc of this oil were treated for 80 hours with oxygen strongly ozonised by the 12-tube electrical ozoniser. At the end of this time, the oil was allowed to stand, when a heavy, yellowish, oily body subsided, which was separated mechanically from the rest of the liquid as far as possible, and left for several days to ascertain whether it would crystallize. But it would neither crystallize of itself, nor from its solutions in alcohol, ether, carbon disulphide, chloroform or benzole, in all of which it is freely soluble. After these various treatments, it still retained its original strongly acid reaction. It was then converted into a soda salt, which was likewise uncrystallizable, and from this, again, separated by a mineral acid. But the oil so obtained preserved its original characteristics, nor did it crystallize after solution in the different solvents ennmerated above. The specific gravity of the mixture of the oil and the acid product was 0.798; the density of the latter in an unmixed condition could not be successfully ascertained. Since it was found by another experiment that the density of a volume of oil equal to that used in the preceding experiment, was altered to 0.7967 by the aspiration of 100 liters of air through it, the change in density was mainly attributable to the removal of some of the more volatile constituents, and not to the action of ozone.

No. V. was then treated in the same way, and for the same length of time, 30 cc of the oil being used, and 125 liters of ozonised oxygen passed through it. When removed from the ozoniser, it manifested precisely the same characteristics as the foregoing, a heavy oil of a strongly acid reaction subsiding. But neither it, nor its soda salt, in their original condition, or after solution in various solvents, were obtained in a crystalline form.

Oil No. V. was then ozonised after mixture with caustic soda. At the close of the operation, the same heavy acid oil was separated by addition of a mineral acid, and on treatment with different solvents, behaved like the foregoing.

Finally, to determine whether all the various distillates would prove equally unsatisfactory or no, a sample of oil No. II., which contained the more volatile portions, was ozonised. As similar results were obtained, the experiments were abandoned. In all these trials, the vessel containing the oil was surrounded with ice during the process of ozonation.

VI. ON THE ACTION OF OZONE ON CARBONIC OXIDE.

A variety of considerations render it probable that ozone would act upon carbonic oxide, and raise the compound to the highest possible stage of oxidation. These considerations, and the important theoretical questions whose solutions would be affected by a positive result in the experiment, have recently been summarized in an article bearing the above title, by Professors Remsen and Southworth.* In repeating their experiments which, most unexpectedly to them, yielded

---

*Am. Journ. Sci , 3, 11, 136.

a decided and emphatic conclusion *in the negative*, I have not been influenced by any doubt as to the accuracy of their investigations, which were carried on with elaborate precautions and repeatedly verified, but I believed that long continued experimentation had put in my hands a method of procuring large volumes of oxygen, raised to a higher degree of ozonation than the ozonised gas hitherto employed, and I thought that the theoretic importance of the subject, warranted the institution of a fresh attempt to discover whether, with ozone of this character, no oxidation of carbon monoxide occured. Moreover, certain preliminary experiments had shown that carbonic oxide might undergo conversion into carbonic acid, under the same circumstances which brought about the oxidation of the oxygen molecule to the state of ozone. These were notably two : 1st. The oxidation of carbonic oxide by air over moist phosphorus at ordinary temperature, an account of which experiments, resulting in one case in the production of 14 mgms of carbonic acid, has already been published.* 2d. The simultaneous formation of carbonic acid and ozone, in a mixture of carbonic oxide and oxygen subjected to the influence of the silent electrical discharge. The carbonic oxide was washed through a series of wash-bottles containing water, caustic potash and baryta water, in the process of preparation. It was similarly washed in its transfer from the gas-holder to the gasometer, the last bottle, containing baryta water, in this case remaining pellucid. The same precaution was observed in its passage to the ozonising battery, where it was mingled with as nearly as possible an equal volume of oxygen purified in like manner, and caused to flow through the apparatus at the same rate. Two liters of the mixed gases were allowed to pass through per hour. The escaping gases were made to flow through a Geissler bulb containing baryta water, which in the final experiment was weighed, and provided with a calcium chloride guard tube, likewise weighed, before beginning of the experiment. After obtaining in several preliminary trials an abundant precipitate of barium carbonate, a quantitative determination was made with the result of showing, that after 1½ liters of carbonic oxide had been subjected in this manner to the influence of the silent discharge, in company with oxygen, 0.0271 mgms of carbonic acid had been formed.

Finally, the oxygen ozonised as in the preceding experiment to the extent of 72 mgms per liter, was mingled in excess with the carbonic oxide in a tube 1 meter in length, placed *beyond* the ozoniser. In this experiment, a very slow current flowing and continued for

---

* Journ. Am. Chem. Soc., **1**, 232.

many hours, no change whatever took place in the baryta water. In other words, oxygen containing a very large percentage of free ozone, is not capable of effecting the oxidation of carbonic oxide.

In this case, the energy of combination of the two bonds, presumably free, of the carbon monoxide molecule, appears to be of less valency than the energy with which any one atom in the ozone molecule, is retained by the other two. In the two former instances, the ozone molecules are in the process of formation, and in the preexistent stage (in which the oxygen molecule undergoes a dissociation), the liberated oxygen atom is seized upon by the unsaturated carbonic oxide.

VII. REDUCTION OF CARBONIC ACID BY PHOSPHORUS AT ORDINARY TEMPERATURES—CORRECTION OF AN ERRATUM.

In a former communication with this title, I have stated that when moist phosphorus is allowed to act upon carbonic acid at ordinary temperatures, a reduction occurs with the formation of a small amount of carbonic oxide. Moreover, that a notable amount of hydrogen phosphide is formed at the same time. On repeating the experiments, the latter statement was confirmed, but the former proves to be erroneous. The fact that hydrogen phosphide is given off, was not discovered until the first series of experiments, in which the products of the reaction were aspirated through solutions of palladium chloride, was completed. And then, while pains were taken to discover that carbonic oxide is entirely without action upon argentic nitrate, the salt employed to absorb the hydrogen phosphide, the reducing action of the latter upon the palladium solution was overlooked. In repeating the experiment, 13 sticks of phosphorus were placed in a 9-liter bottle, and partly covered with water. The bottle was then filled with carbonic acid, free from air, and after sealing, exposed to the sun-light for four days. Afterwards, the contents of the flask were aspirated through solutions of potassium iodide, argentic nitrate and palladium chloride. The first and last were unaffected; the silver solution contained a dense precipitate. The metallic silver in this precipitate amounted to 0.178 gm. The same results were obtained in diffused light, but in much smaller amount. On passing large amounts of carbonic oxide through a silver solution, no change occurred, showing that the result obtained above was entirely due to hydrogen phosphide.

My thanks are due to my assistant, Dr. Edgar Everhart, for his aid in the performance of these experiments.