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## Ozone: Its Nature, Production and Uses.

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"There is no discovery in modern chemistry that is more important than that of ozone," wrote Frémy, the French scientist, a generation ago; and to this the illustrious Bunsen joined the prediction: "When we shall be able to produce it industrially, hundreds of new applications will arise."

Recent developments in electrical science have been so sensational that the quiet emergence from the laboratory into commercial use of this new agent in industry, sanitation and therapeutics, has been unmarked by any save the few experts who have wrought the change. Our admiration has been challenged by spectacular feats in wireless telegraphy and the like; and the evolution of new manufactures, the application of perfected sanitary processes, the establishment of new therapeutic principles, made possible by the fulfillment of Bunsen's prophecy, have received a few casual notices in technical publications, which have promptly dropped into the oblivion of the files of public libraries.

*The Nature and Properties of Ozone.*—Ozone is a form of oxygen, which, by readjustment of its molecular structure, has acquired new physical and chemical properties while preserving its original elemental character. A molecule of oxygen consists of two atoms, and in physics the element is written  $O_2$ . Ozone has three atoms to the molecule and is written  $O_3$ . This extra atom endows ozone with special powers which differentiate it from ordinary oxygen. The differences have been tabulated by the French chemist, Houzeau, as follows:—

Properties of Ozone + 15°.

A gas with strong odor, and a flavor of lobster.

Properties of Oxygen + 15°.

A gas colorless, inodorous, tasteless.

Comences to decompose at about 100° C.

Strong oxidizing agent.

Decolorizes blue litmus.

Rapidly decomposes potassium iodide, liberating the iodine.

Rapidly oxidizes ammonia, and transforms it into nitric acid.

Decomposes hydrochloric acid, liberating chlorine.

Combines with phosphoretted hydrogen with emission of light.

Oxidizes silver.

Corrodes India rubber and cork.

Very stable at all temperatures.

Feeble oxidizing agent.

Without action on blue litmus.

Does not decompose potassium iodide.

Without action on ammonia.

Does not react on hydrochloric acid.

Without action on phosphoretted hydrogen.

Does not oxidize silver.

Does not corrode India rubber nor cork.

Faraday enumerated some of its powers in a lecture delivered as early as 1851 before the Royal Society, as follows:—

“Ozone destroys many hydrogenated gaseous compounds; the combinations of hydrogen and sulphur, selenium, phosphorus, iodine, arsenic and antimony are thus affected. It appears to unite chemically with olefiant gas, in the manner of chlorine.

“It instantly transforms the sulphurous and nitrous acids into sulphuric and nitric acids, and the sulphites and nitrites into sulphates and nitrates. It changes many metallic sulphurets (as those of lead and copper) into sulphates. Like chlorine, bromine and the metallic peroxides, it is a powerful electromotive substance.

“It decomposes many iodides in their solid and dissolved state; by its continued action, iodide of potassium becomes converted into iodate of potassa.

“It changes both crystallised and dissolved prussiate of potassa into red salt, potash being evolved.

“It discharges vegetable colours with a chlorine-like energy.

“It produces oxidizing effects upon most organic compounds, causing a variety of chemical changes; thus guaiacum is turned blue by it.

“From the above enumeration, it would appear that ozone is a ready and powerful oxidizer, and, in a great number of cases, acts like Thénard's peroxide of hydrogen or chlorine and bromine.”

The real character of ozone, however, was not known even to Faraday at this date, when the new gas was variously regarded

as hypo-nitric acid, volatilized metallic matter, peroxide of hydrogen, a new element, etc., etc.

Van Marum was the first to notice, in 1783, that by passing electric sparks through a tube containing oxygen, the gas acquired a distinct odor and abnormal oxidizing properties. Cruickshank, in 1801, noticed a similar smell during the electrolysis of water; and Cavallo, soon after, reported that "electrified air" had a purifying effect on animal and vegetable matter, when in a state of decomposition, and employed it as a disinfecting application to foetid ulcers. Cavallo spoke of this condition of the air as the "aura electrica." In 1826 Dr. John Davy (Lectures on Agricultural Chemistry) recognized the existence of this principle in the atmosphere, and published a formula for the preparation of chemical tests to be used in its detection, resembling that afterwards adopted by later investigators. The discovery was then allowed to lie inert until 1840, when the Swiss chemist, Schönbein, observed afresh the peculiar smell proceeding from one of the gases liberated on electrolysis of water. This he recognized as having some similarity to the "aura electrica" developed on the points of an electric machine; and he gave it the name Ozone, from the Greek verb "to smell." The discovery was communicated to the scientific world in a paper to the Munich Academy of Science, and immediately gave rise to numerous controversies concerning the nature and properties of the gas, controversies which lasted many years. Schönbein at first believed it to be a new electro-negative element belonging to the same class as chlorine and bromine. Then he thought it might be one of the constituents of nitrogen; and later he believed it to be a combination of hydrogen and oxygen; and he so wrote to Faraday. In 1845 de la Rive and Marignac asserted that, under the influence of the electric spark, dry oxygen yields ozone; therefore, ozone is nothing but oxygen brought to a peculiar state in which the gas possesses properties which it has not in its natural state. This was combatted by other scientists, including Schönbein himself, who now declared ozone to be peroxide of hydrogen. In 1849 Leuch, representing ozone as galvanized air, *Oa*, first made mention of its industrial use "as the most powerful bleaching agent." About the same time Schönbein sent to Faraday a letter written with a manganese sulphate solution, which had turned brown under the action of ozone. He

also announced the re-discovery of Dr. Davy's test to ascertain the presence of ozone by starched iodide of potassium, which is the test applied to-day. Other investigators like Baumert, Becquerel, Faraday, Dr. Hare, of Philadelphia, Frémy, Le Blanc, Andrews and Houzeau took up the subject during the next few years, gradually revealing the properties and constitution of the new gas, until, in 1856, Dr. Andrews, of Edinburgh, confirmed de la Rive and Marignac by showing that "ozone from whatever source derived is one and the same body, having identical properties and the same constitution, and is not a compound body, but oxygen in an altered or allotropic condition."

*The Production of Ozone.*—The ozone made by early investigators was generally obtained by chemical means. Numerous reactions result in the production of  $O_3$ . The most common, and that generally employed prior to the invention of means for controlling the effects of the electric discharge, was the slow oxidation of phosphorus. This is achieved by very simple means. Oxygen diluted three times with air, or ordinary atmospheric air, is drawn by aspiration across the surface of water in which sticks of phosphorus are half immersed. The resulting gas when washed is dilute ozone. At freezing point the production of ozone is nil; but between  $15^\circ$  and  $20^\circ$  C. it is very abundant. The confusing results of early experimenters with ozone were largely due to this method of production; for the ozone was never obtained pure, being more or less mixed with phosphoric acid.

Under the influence of light, and in contact with air, turpentine is oxidized and gives off feeble quantities of ozone, with formation of acids and resinous matters. Other hydrocarbons, coal-tar, various essential oils as those of eucalyptus, lavender, citron, etc., possess analogous properties.

Troost and Hautefeuille report having produced ozone by heating oxygen to  $1400^\circ$  C. to  $2200^\circ$  C. in a porcelain tube; and the statement has been repeated by almost every writer on the subject. It is certain that their observations were defective. It might be inferred *a priori* that, at such temperatures as those stated, any ozone formed would be instantaneously destroyed so as to render its detection impossible. This inference has been confirmed by Mr. J. K. Clement who has made a series of careful experiments in this direction at high temperatures. His results are published in *Annalen der Phys.*, IV, Folge, Vol. 14, 1904.

page 334. He conducted a stream of pure oxygen over the surface of an incandescent Nernst filament, so that it was heated to about  $2200^{\circ}$  C., while, when streaming away, it was quickly cooled. He could not detect any formation of ozone, nor was any found at the temperature of the arc lamp, about  $3000^{\circ}$  C. Whenever there were traces of nitrogen present,  $\text{NO}_2$  was formed, which, in its reactions, is very similar to ozone; and it seems to be due to this fact that the former investigators thought that ozone had been formed. Clement also gives the results of extended researches on the speed of disintegration of ozone. On the basis of a formula of van't Hoff which can be applied to this case, he finds that at  $1,000^{\circ}$  C. the content of ozone decreases in 0.0007 second from 1 per cent. to .001 per cent; this means that if ozone is really formed at a temperature of  $2200^{\circ}$  C. or more, it must disintegrate almost instantaneously when cooled even very quickly.

O. Loew, in New York, in 1870, "blew a strong current of air through a tube into the flame of a Bunsen burner and collected the air in a beaker glass or balloon." "I was thus able," he says, "in a few seconds to collect enough ozone to readily identify it by its intense odor and the common tests." This is another case of inaccurate observation.

Dr. J. K. Boeke, passing oxygen through the luminous flame of a Bunsen burner, found that the peculiar odor and the property of coloring the iodine starch test which were acquired, were due to the production of a compound of oxygen and nitrogen, probably the dinitric trioxide or nitric dioxide.

Oxygen is transformed into ozone under the influence of various radio-active bodies. This suggests a relationship with the chemical rays of the spectrum. If radium is enclosed in a tube filled with oxygen, ozone is formed inside the tube; but if the radio-active substance is sealed in a separate vessel no action takes place on oxygen brought within the influence of the rays proceeding from it. From this fact M. and Mde. Curie came to a notable conclusion, viz., that the transformation of oxygen into ozone required the expenditure of active energy, and that the production of ozone under the direct rays of radium proved that these radiations represented a continuous liberation of energy.

A further deduction may be made: the walls of an ordinary

tube do not permit the passage of ultra-violet rays; therefore there is no action on the surrounding gas. A quartz tube, which is pervious to the ultra-violet rays, would probably yield other results.

Ozone may be produced by numerous chemical reactions, as, for example, that of monohydrated sulphuric acid on bioxide of barium. At a temperature below  $75^{\circ}$  C. there is produced at the same time hydrogen peroxide.

Kindred results are obtainable with the peroxides of zinc and magnesium on sulphuric acid and with the alkaline peroxides of sodium and potassium. Ozone probably plays some part in the bleaching properties exhibited by these compounds in industrial uses. Permanganate of potash lends itself to similar reactions, but its manipulation requires care to avoid dangerous explosions. The persulphates of potassium, sodium, barium, ammonium, etc., may be decomposed with liberation of  $O_3$ , a fact utilized in various industrial applications.

Of all chemical reactions by which ozone is produced, that of fluorine in water is the most promising, an ozone-concentration in oxygen of upwards of 14 per cent. having been obtained in half an hour. If fluorine can ever be made cheaply, its use in the production of ozone may become important by reason of the purity and richness of the gas made possible by its means.

Ozone is also produced by the decomposition of water by the electric current. This, indeed, led to its re-discovery by Schönbein. The process is aided by adding acid to the electrolyte. The electrolysis of acidulated solutions of potassium permanganate yields more ozone than does the electrolysis of acidulated water; but neither process has any commercial interest or value in comparison with the perfected electrical methods in use, now to be described. The highest yield of ozone reported of electrolytic processes is 3 grams per K. W. hour of energy expended.

The neutralization of two opposite charges of electricity known as an electric discharge, produces a variety of effects when it takes place through a separating body of oxygen or atmospheric air. These effects are luminous, heating, chemical, mechanical and magnetic. Most of them do not concern us here. In ozone production it is the chemical action which is sought; and the luminous, heating and other effects are accidental and often undesirable accompaniments.

A discharge may take place in any of several forms, chiefly, the arc, the spark and the glow. The arc-discharge is accompanied by the production of light, intense heat and energetic chemical action, especially on the nitrogen of the air, which, in the presence of moisture, it converts into nitrous and nitric oxides. The spark, or disruptive discharge, has similar chemical and heating properties, but gives out less light. The glow or silent discharge has little light, less heat and, in air, acts almost exclusively on its oxygen. Only when moisture is present



Fig. 1. Showing a small arc-discharge.

does it act upon nitrogen, and then only in a very small degree as compared with the other forms of discharge.

Figure 1 is a reproduction of a small arc from an alternating current transformer. It may assume a length of several feet, is characterized by a humming sound, a flame-like shape ever changing, and, as already stated, produces an intense heat. It is a continuous discharge of great current strength, and hence of great danger to the life of the apparatus.

Figure 2 is a spark discharge. It is a yellow-white, zigzag, loud snapping, oscillatory discharge. Figure 3 is a photograph

taken of 10 consecutive sparks from a static machine, as shown in Figure 2.

Figure 4 is a spark from a Rumpkorff induction coil operated by a high frequency interrupter. It is a mixture of the spark and violet brush discharge previously spoken of as the glow.

Figure 5 is the glow or silent discharge. It is characterized by a dark blue violet color. It is a convective discharge, unidirectional from positive to negative.

Figure 6 is the same kind of a discharge proceeding from the negative pole of a static machine. It may be noted that this form of discharge, whether proceeding from the positive or the negative pole, assumes an essentially cone-like shape with a hollow interior. Recognition of this fact has recently wrought important changes in the art of ozone production. This violet-colored discharge is the only one by which ozone may be continuously produced with any practical degree of purity.

The theory has recently been advanced, and is now gaining pretty general acceptance, that the formation of ozone by the brush or silent discharge is caused, not by any direct electrical action on the oxygen itself, but is simply a photo-chemical effect, due to the ultra-violet rays accompanying such discharges.

This theory, which seems destined to revolutionize our conceptions of ozone-formation, originated with the discovery of Lenard, who noticed that if the light from a spark gap was allowed to pass through quartz plate, which is transparent to ultra-violet rays, and to impinge on oxygen, ozone was generated. If, however, a substance impervious to ultra-violet light was interposed, no such action took place. Goldstein followed up the discovery by showing that the ozone odor existed on the outside of Geissler tubes through which a discharge was passing, only, however, if the tubes were partly of quartz. Warburg then announced that ultra-violet light and cathode rays accompanied the discharge in a Siemens tube; and with the assistance of Regener he showed by volumetric tests that, in addition to the ozonizing action of the rays, a deozonizing action was at work, and that the relative rapidity of the two processes was fixed. Fischer and Braehmer advanced the discovery a step, when experimenting with a quartz mercury-vapor lamp rich in ultra-violet rays, they found the chief factors determining the process to be the temperature of the gas, the light intensity of the lamp, the rapidity



of the stream of oxygen and its purity. In their experiments the temperature of the lamp, without cooling, went to  $270^{\circ}$  C., at which of course ozone does not exist; but by lowering the tem-

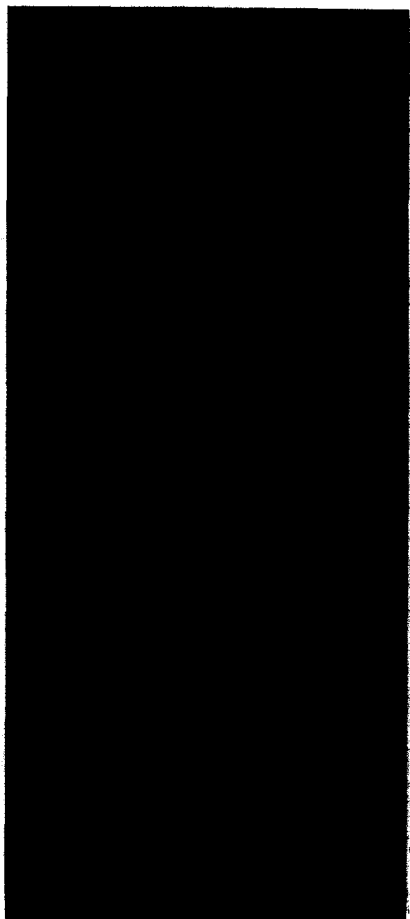


Fig. 2. A spark-discharge.

perature, the yield of ozone underwent a gradual increase. By maintaining the low temperature and increasing the intensity of the light, higher yields of ozone resulted. As the concentration increased, the yield diminished. Thus:

Per Cent. O <sub>3</sub> .	Milligrams O <sub>3</sub> .
0.192.....	0.571
0.201.....	0.593
0.234.....	0.540
0.230.....	0.528
0.249.....	0.382
0.259.....	0.382

By doubling the current the ozone generated was also nearly doubled.

This interesting theory has received collateral support from the investigations of Franz Richarz and Rudolph Schenck, who have pointed out the analogy between radio-activity and the behavior of ozone. They have shown that freshly prepared ozone, or ozone that is being decomposed under the influence of de-ozonizing agents, accelerates the condensation of water vapor. The presence of gaseous ions to which this phenomenon points, is further indicated by the considerable conductivity exhibited by ozone. In respect to this ability to produce gaseous ions, ozone is similar to radium and other radio-active substances. Further, a current of ozonized oxygen is said to cause a zinc sulphide screen to floresce, although barium platinocyanide and zinc oxide are unaffected. Red phosphorus, inert in oxygen, shows luminescence in ozone. Another point of analogy is the fact that radium salts and ozone both decompose with considerable development of heat.

In its simplest form an ozonizer consists of two metallic bodies separated from each other by a short gap, across which a current of electricity may be passed, in the form of a blue-flaming discharge, from one metallic body or electrode to the other. The electrification of the air in the path of the discharge produces the molecular changes involved in the conversion of O<sub>2</sub> into O<sub>3</sub>.

This so-called silent or ozone-making discharge may be produced in several different ways. The earliest mechanism employed for this purpose was a static machine. This also gave off sparks, which, as stated above, in moist air, resulted in the formation of nitrous products which, mixed with the ozone, led to confusion in the minds of early investigators as to the real nature of the gas. A current from a battery of cells may be passed through an induction coil furnished with an interrupter;

and this will give a small but steady and efficient ozone-making discharge. The direct current from a dynamo may also be used if passed through a similar coil. It is, however, the alternating current from a dynamo of high periodicity, stepped up to several

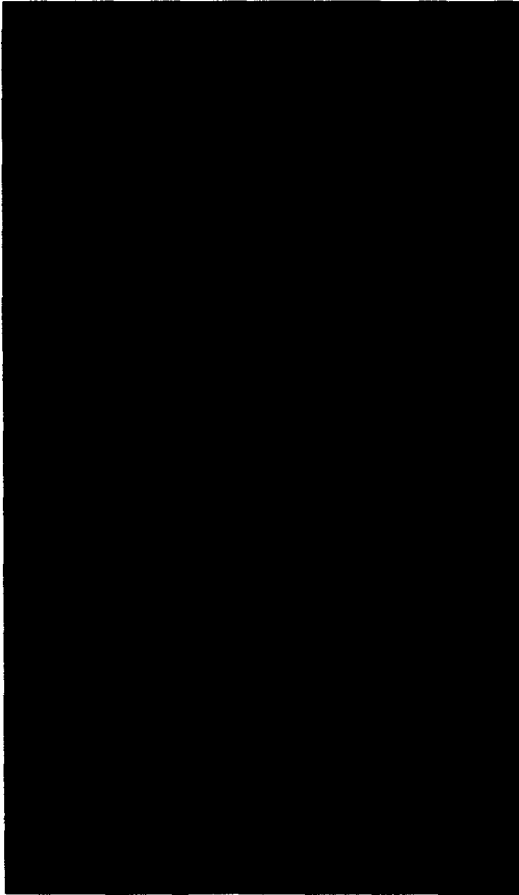


Fig. 3. Sparks from a Static Machine.

thousand volts, which offers the best means of obtaining the silent discharge; and this is the means in general commercial use to-day. Such an apparatus, however, may give any one of the three kinds of discharge described. The arc discharge by its intense heat destroys the apparatus, while the spark discharge

transforms the nitrogen of the air, mixes it with the transformed oxygen and gives impure ozone. Means must, therefore, be taken to prevent these undesirable forms of discharge, and to limit the apparatus to the production of the silent effluvium which transforms the oxygen of the air into its allotropic condition. To attain these ends the inventive faculties of all the investigators in this field have been directed for many years.

It was early discovered in the art that when a non-conducting substance like glass, mica or vulcanite, was placed between the poles of an electric machine, across the path of the current, the formation of sparks and arcs was prevented, and the current assumed the form of a silent blue discharge, which produced large quantities of ozone, varying in strength and amount with the tension and flow of the electric current. As this tension, or mechanical stress, requisite to overcome the resistance of the air as well as of the dielectric was necessarily very great, it frequently happened that the interposing glass or mica body was fractured under the strain, and before the current could be turned off an arc was formed which destroyed the mechanism. Efforts were therefore made to eliminate the dielectric; and many years of experiment and large sums of money have been expended in devising means to this end.

As regards the various yields of existing types of ozonizers, the differences in methods of testing render comparisons unreliable; and, until a uniform method is applied to determine the ozone-content of a given body of gas, no exact comparison can be made between the efficiency of the different types of apparatus now in use.

The Siemens & Halske ozonizer, with dielectrics, is reported to yield 20 to 30 grams per K.W. hour. Elworthy claims 60 to 70 grams from a machine of similar construction; but no data are available as to the richness in ozone of this product. Otto has published figures showing yields of 20 to 118 grams per K.W. hour, the former where the concentration was .852 grams per cubic meter of air, and the latter where it was only .542. Vosmaer with a concentration of 1.5 obtained a yield of 12 to 16 grams. The de Fries apparatus produces about 20 grams with a concentration of 1.0. Generally speaking, 20 grams has hitherto been considered a fair output if the air treated contains one gram and upwards of ozone per cubic meter.

A very noteworthy increase in the efficiency of ozonizers has recently resulted from a simple observation made by the author. Reference to the photographs of the silent discharges printed on pages 369 and 371 shows that these are cone-shaped funnels. They may be conceived as hollow cones of light. In all ozonizers



Fig. 4. Spark from an Induction Coil.

hitherto devised, the air is directed against, or around, these cones of light in a plane at right angles to them. Now it is a well known fact that when electricity is discharged from a point, the surrounding particles of air are electrified, and, being of the

same electrical sign, repulsion takes place. The currents of air repelled from the points of a discharging electric machine may be felt by the hand, or seen in the deflected flame of a candle held close to them. The well known electrical toy, called Hamilton's Mill, rotates because of this repulsion of the electrified air from the discharging points. With these facts in mind, it is obvious that air, when passed into the influence of a discharge at right angles to its path, is immediately thrust away from it, and any effect which the discharge may have on it is but momentary. This is an obvious disadvantage where it is sought to bring about that molecular readjustment in the particles of air submitted to electrification which accompanies their conversion into ozone.

To overcome these disadvantages the writer has devised a perforated electrode, and so arranged the air supply that it passes through the perforations in fine streams directly into the hollow cores of the discharges taking place on its surface. In this way the air is forced to travel first upwards with the discharge, while completely surrounded by it, and then forced through the luminous walls of the discharge. This brings every particle of the air into intimate contact with the discharge. The first tests of the apparatus gave 80 grams of ozone of a high concentration. The principle, thus proved so revolutionary, has been recognized as novel in the art by the patent offices of America and Europe.

An extension of this principle, which logically follows, is that by which the treated air is instantly led away from the de-ozonizing effects of the heat of contiguous discharges by withdrawal through the perforations of an opposing electrode. In this way air first passes directly into the core of a discharge taking place from one electrode, which, for convenience, may be called the anode, and is thence led directly into the core of a second discharge taking place from the opposing electrode or cathode, and so passes at once out of the influence of the discharges through the cathodic perforations. Of course, this can only be done when no dielectric is placed between the dischargers; and arcing and sparking must then be prevented by employing the usual resistance in the circuit between the source of energy and the discharge.

*Ozone in Water Purification.*—Considerable difference of opinion exists among experimenters concerning the minimum

concentration of ozone requisite for the effective sterilization of water. Tests have been made in Europe with concentrations as low as 0.5 gram per cubic meter of air and as high as 15 grams. In each case satisfactory results have been achieved, as shown by bacteriological tests. Indeed, as low as 0.3 was found effective by Professor Van Ermengem in tests made at Brussels. At Gennekin, Schneller has successfully used concentrations as low as .537. At Rotterdam, Van Delder, using the Vosmaer system, obtained satisfactory results with an average concentration of .8;



Fig. 5. Silent-discharge from positive pole of a Static Machine.

and Professor Proskauer, at Berlin, found .9 to 1.8 efficient. The following is an extract from the report of tests of the de Fries plant near Paris made by the official authorities of that city:—

Concentration.	Air per M <sub>3</sub> of water in cubic-meters.	Total ozone per cubic meter of water.	Bacteria Before ozon- ization.	After ozon- ization.	In the collecting tank.
1.6	1.383	2.216	800	2	4
1.04		2.035	850	3-4	
.98	2.077	1.352	2682	3	

.88	1.537	2.04	3732	7	
1.	1.003	1.	2886	9	
.835	1.003	0.693	2886	45	
1.12	1.037	1.61	4445	14	9
1.43	0.831	1.188	145	2	1

At Weisbaden and Paderborn, Germany, the Siemens & Halske apparatus in use there show the following results:—

Concentration in grams of ozone per cubic meter of air.	Number of germs per c.c.	
	Raw Water.	Ozonized Water.
1.4	39,000	8
1.7	26,000	12
1.6	55,000	5

At Philadelphia, during a protracted series of tests during the year 1905, the following results were achieved with low concentrations:—

Concen- tration.	Oxygen consumed.		Air in cubic feet.	Water treated. Gallons.	Bacteria.	
	Before.	After.			Before Ozon- ization.	After Ozon- ization.
.7	1.34	.37	4950	12800	12500	19
.64	.74	.57	5020	37500	4600	200
.68	1.01	.97	4800	37000	600	60
.35	1.06	.83	4840	35400	160	11
.49	1.77	1.03	5010	20200	75	10
.6			4930	20000	5400	15
.78			3045	25700	170000	42
.83			3080	30500	130000	70
.87			4196	28200	80000	34
.47			4196	31800	1200	20
.62			3113	30650	73000	250
.91			2775	29100	1800	9

The quantity of ozone absorbed varies with the amount of organic matter contained in the water. In distilled water ozone is but slightly soluble. Nor does the number of bacilli present in water make any perceptible difference in the amount of ozone absorbed; for however great their number may be, they represent an infinitesimal weight of organized matter to be consumed. Otto finds the ozone absorption of waters treated by him to vary between 0.5 gram and 0.8 per cubic meter of water treated, and asserts that these figures are corroborated by tests made by Dr. Erlwein at Weisbaden. Similarly, at St. Maur, Mr. Van der Made, engineer to the Sanador Co., told the writer he had found



that about half a gram of ozone is absorbed in the sterilization of a cubic meter of river Marne water after rough filtration.

The unutilized ozone is withdrawn from the surface of the sterilized water by Otto, de Fries and Siemens & Halske, and passed in continuous, successive cycles through the ozonizer and sterilizer. In this way they claim to save about two-thirds of the ozone produced. In the Howard-Bridge method the unabsorbed ozone is drawn from the treated water by the suction action of another current of water running rapidly down a U-shaped tube, sunk deeply into the ground. Here it is all used up in the preliminary oxidation of organic matter, so that when fresh ozone is added to this water the ozone is free to act with its primal-



Fig. 6. Spark-discharge from negative pole of a Static Machine.

strength upon the bacteria. In the Vosmaer system the excess of ozone is allowed to escape into the air.

A number of mechanical means have been devised for mixing the sterilizing gas with the water under treatment. The one most generally used consists of a tower, sometimes filled with stones or other inert matters over which the water trickles and meets the ozonizing gas forced into the tower at the bottom. This is the column invented by Gay-Lussac and called by his name. It was used by de Meritens, the pioneer in ozone sterilization, and adopted by Siemens & Halske in their installations at

Weisbaden and Martinikenfelde near Berlin. It is a simple and efficient means of mixing the sterilizing gas and water. Analyses by Dr. Erlwein of the water before and after purification, covering a period of several days, yield the following reports:—

Bacteria per c.c. before Purification.			Bacteria per c.c. after Purification.		
Maximum.	Minimum.	Average.	Maximum.	Minimum.	Average.
200,000	2,300	80,000	34	0	8

All pathogenic germs were destroyed. The amount of ozone used per cubic meter of water treated was 1.3 grams.

According to Dr. Erlwein, the cost of this process per cubic meter of water (264.17 American gallons) for a plant treating about 250 cubic meters per hour is 2 pfennigs or half a cent.

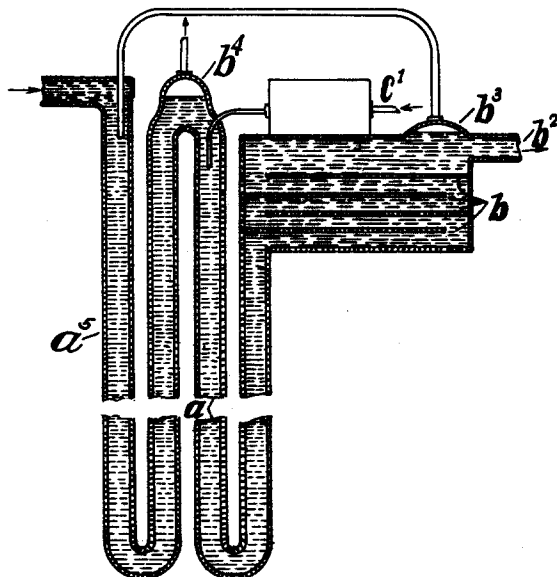
In American equivalents this is at the rate of \$18.92 per million gallons in a plant capable of treating about 60,000 gallons of water an hour. Dr. Erlwein estimates that for a similar plant of 10,000,000 gallons a day capacity, the cost of operation would be about \$7.00 per million gallons.

In the de Fries system the water and ozonized air are mixed in vertical cast iron cylinders enamelled inside. The water and air are introduced at the bottom and leave the apparatus at the top. The cylinders are divided into compartments by horizontal celluloid trays perforated with numerous small holes. On passing through these perforations the water and air are brought into close contact.

The operation of these and other systems involves the use of an air compressor for forcing the ozonized air into the column of water. As seen in Dr. Jackson's report on the Vosmaer tests, this required 4.4 H.P. hours for the treatment of 25,650 gallons. This is at the rate of about 160 H.P. hours or 110 K.W. hours per million gallons treated. In addition to this expenditure of energy, there are other disadvantages inseparable from this method of mixing the air and water. Ozone has such active oxidizing properties that ordinary lubricants cannot be used in the cylinder of an air compressor. The rings of the piston must, therefore, fit so tightly that if air is passed through the cylinder containing the least moisture, the machine either works with great difficulty and loss of power, owing to the swelling of the piston rings, or else stops entirely.

This difficulty is overcome, and a large part of the cost of

operating an air compressor is saved, by the Howard-Bridge process of causing the suction action of the water under treatment to draw into itself the ozonized air required for its purification. This principle is roughly shown in the accompanying drawing, which also illustrates the further advantage already mentioned, in that the excess of ozone which remains unabsorbed, and which in some systems is run to waste, is here utilized in the prelimin-



Raw water enters the pipe  $a^5$  drawing, by suction, unabsorbed ozone from  $b^3$ .

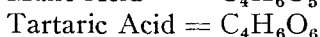
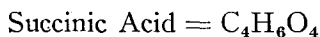
The waste gases escape at  $b^4$ . The current of water in  $a$  sucks fresh ozone into itself from the ozonizer  $c$ ; and after passing around the baffle plates in  $b$ , the purified water escapes at  $b^2$ .

ary treatment of the water. By this system municipal water supplies can be sterilized at one-half the cost of slow sand-filtration, which never wholly removes bacteria.

*The Industrial Uses of Ozone.*—The difficulty of obtaining ozone continuously and economically, and of practical strength, has prevented its general adoption in those industrial arts to which it was found by early investigators to be theoretically applicable. Now that this has been overcome, and the gas can be produced in large quantities at slight cost, its application to

numerous manufacturing processes will probably no longer be delayed.

There are some compounds in nature and in intermediate stages of manufacturing that are comparatively worthless, which, if a single atom of oxygen were added to their molecules, would be transformed into products of greater value. Here is a theoretical illustration: Succinic acid is formed of four molecules of carbon, six of hydrogen, and four of oxygen. Add a molecule of oxygen, and malic acid results. Add still another and tartaric acid is produced. Thus:—



Ozone readily yields this additional molecule of oxygen to other elements or compounds, and this faculty may be utilized to add to their commercial value. Oil of cloves, for instance, has little value in comparison with the extract of vanilla bean; yet by ozonization it is converted into substance which for all practical purposes has taken the place of the natural extract, once so costly that it was stored in steel vaults. The writer was told by one of the inventors of this process that the entire cost of vanillin is only half the amount of the duty with which the Government of the United States has protected this infant industry. Vanillin, thus produced, is used for flavoring confectionery and ice cream from California to Maine.

Professor C. Harries, who has done excellent work in this new field of research, shows that "experimental results in ozonization lead to the conclusion that all organic compounds containing an ethylene linkage (double bond) add one molecule of ozone, giving rise to a new class of substances termed ozonides." "This method of work," he adds, "has already proved its value in permitting the comparatively easy preparation, in fairly large quantities, of many substances which were hitherto unknown, or could only be obtained with the greatest difficulty."

Sulphuric acid, which is the basis of many chemical industries, is made by simply ozonizing water containing sulphur. Whether this method can compete with existing processes, in which sulphuric acid is often a by-product, can only be determined by trial on a commercial scale.

One of the least expected applications of ozone is in the extracting of gold from its ores. This forms the subject of a serious paper by de la Coux in *Génie Civil*, February 14th, 1903, who says: "In treating auriferous minerals by solutions of hydrochloric acid submitted to the action of ozone, we have been able to obtain a rapid dissolution of the gold. There may be here," he adds, "a process capable of application in the treatment of auriferous minerals."

Peroxide of nitrogen is being made every day in flour mills in England by electric discharges. This is effected by subjecting ozonized air to a sparking discharge, which modifies the nitrogen of the air, and causes it to combine chemically with  $O_3$  formed during the first part of the process.

The action of ozone on chromium is to convert it into chromic acid, which is extensively used in various industries, especially in tanning. The preparations of chromium sold to tanners bring a high price; and it is not unlikely that their manufacture can be cheapened by the new oxidizing agent.

Permanganic acid is formed from the prolonged ozonization of certain salts of manganese, which, contrary to the usual reaction, here lose a part of their oxygen. This may have no commercial value as yet; but the reactions of ozone on manganese are so numerous and interesting as to have excited some chemists to enthusiastic search for new combinations of the metal which may be found profitable. Oxides of zinc and lead are easily produced by means of ozone, but, perhaps, not so cheaply as by the electrolytic process accidentally discovered by the writer and brought to commercial completeness by Mr. Carlton Ellis. Metals, with the exception of aluminum, platinum, gold and perhaps one or two others of the very rarest of them, are readily oxidized by ozone, especially in presence of water. Here is a large field, as yet unexplored by the seeker for new industrial products.

In organic chemistry a wide vista of new industrial effects is opened through the agency of the new gas. Otto, to whom we owe so much of our knowledge of ozone and its properties, has produced formic acid and formic aldehyde from methane or marsh gas. Here we have the basis of a new tanning agent and a powerful disinfectant created, as it were, from nothing. By ozone iodoform has also been made by Otto from iodide of

potassium and alcohol, and the process is commercially practicable.

The bleaching and refining of mineral oils was one of the first industrial uses to which ozone was applied; but the cost of the gas prevented its development. This may now be changed. Otto has prepared from petroleum an ozonized jelly having strong antiseptic, parasiticial and disinfectant properties, which he calls *Petrole-Ozoné*.

According to various experimenters, Mare, Ney and others quoted by de la Coux, camphor has been made by ozonizing turpentine; and the process gives promise of having commercial value.

Numerous methods have been devised, and patents taken out, for the bleaching and purifying of sugar and syrups by ozone; but these have hitherto failed owing to the difficulty of producing the gas. In these processes ozonization is generally assisted by electrolysis; and some striking results of the double action thus obtained are published by de la Coux. These are too long to reproduce here, but they may be summarized as follows:—

	Decoloration and increase in purity,		
	By ozone.	Per cent. By electrolysis.	By ozone and electrolysis.
Decoloration .....	35	75	95
Purity .....	8.5	21	36
Saline coefficient.....	10	27	137
Organic coefficient.....	14	31	47

The Philadelphia ozonizing plant has been investigated by the experts of one of the principal refining companies in the United States, but the results of their tests have not been made known.

The bleaching properties of ozone have been applied industrially to the whitening of wax, gum lacquer, ivory, bone, feathers and various other things, with more or less success. In the manufacture of linoleum it has been found of special advantage in that the oils successively applied to the cloth are quickly oxidized, so that the capacity of the factory is increased, while the incidental bleaching of the oils results in a brighter and cleaner-looking product. Similar results have followed its use in oxidizing the varnish on "patent leather," glazed kid and the like.

In the manufacture of starch ozone has been utilized as a

bleaching agent, and has led to an incidental product intermediate between starch and dextrine which, it is stated, is taking the place of gum arabic in the textile industries. Two large plants are said to be in successful operation in Germany, one at Kryitz and the other at Fuerstenwalde. This illustrates the unseen possibilities offered to investigators by the new oxidizing gas. So far as the writer knows, ozone has not been used in the manufacture of glucose. It is possible that its use would so modify the residues of the sulphuric acid employed in its manufacture, as to rid it of its injurious properties when used as a food.

In this connection Dr. Fröhlich, of Messrs. Siemens & Halske, in illustrating the bleaching properties of ozone, states that 20 grams of ozone per H.P. hour "will bleach 110 pounds of linen as well as grass bleaching during three days; it will in presence of chlorine, bleach and refine 88 pounds of potato starch to such a degree that the color becomes a clear white and the bad odor and taste are removed; if this is roasted and ozonization is continued a product resembling gum arabic is obtained; 20 grams of ozone being sufficient for 66 pounds of this product."

For the use of the tanner an excellent substitute for degreas, an expensive softener of which the supply is constantly dwindling in proportion to the demand, has been produced by ozone from inexpensive oils. Here is a chance for the creation of a new and profitable industry.

Roscoe is said to have produced aniline from alcohol years ago; and the researches of Otto have shown, close to this field, a wide range of unexplored territory awaiting commercial development. In the synthetic production of indigo ozone may have an important role; as it has been found to possess in the preparation of artificial perfumes.

In a single month in 1903, the Société Française de l'Industrie Chimique produced 22,000 kilograms of vanillin by means of ozone, which at 35 to 45 francs has taken the place of a product that in 1895 was worth 800 francs. The German firms previously making vanillin synthetically are said, by de la Coux, to have closed their factories, and now buy their supplies in France. The method employed in France and at Niagara Falls is patented, and has yielded its owners enormous profits.

Other unexpected uses for ozone have been found in the hardening and ripening of wood for special purposes, such as musical

instruments, and, in striking contrast, in the stimulation of silk worms. In Paris, the linen from hospitals is disinfected by ozone and a large laundry in the St. Honoré market has long used the gas in this way. Other uses that have been suggested for it is the purification of illumination gas, the improving of cigars and tobacco—of which it is stated “the aroma and finesse are increased,” the removal of undesirable odors from raw coffee, and the destruction of the phylloxera. These more or less doubtful suggestions may be omitted, and the actual applications already enumerated, will sufficiently indicate the wide and diversified range of the industrial uses to which this powerful oxidizing agent may possibly be applied.

*Ozone in Therapeutics.*—In 1887 Dr. Donatien Labbé, using a Houzeau vacuum tube, produced pure ozone by the silent discharge. This he found he could inhale in doses which had previously been considered injurious; and he thereupon commenced a series of experiments on tuberculous and anemic patients which for the first time fully established the high therapeutic value of the gas. In 1889 Dr. Huguet de Vars installed several ozonic sanitariums in Paris and in the south of France, where he is said to have cured his patients by means of ozone in inhaling rooms. In 1891 Dr. Labbé presented the results of his several years' experiments in the ozone treatment of tuberculosis, etc., in a paper read before the French Academy of Sciences. The curative effects set forth in this paper produced a profound impression on the medical world. Ozonizing apparatus were installed in several French hospitals; and in May, 1892, at the Lariboisière the wounds of the victims of the dynamite explosion at Véry's restaurant were bathed with ozonized water.

Upon the nutritive functions ozone inhalations have a stimulating effect. Perisalsis is markedly quickened, so much so that the characteristic griping sensations following the use of an energetic cathartic are sometimes experienced after a short inhalation. There is increased elimination of urea and phosphoric acid, which indicates a corresponding stimulation of the kidneys. Improved appetite accompanies and succeeds a prolonged series of ozone inhalations, and the fact, reported by nearly all investigators, that the iron constituents of the blood are increased, shows improved nutrition. Since the iron is not conveyed into the blood by the inhalations, it must necessarily be derived from



the food ; and this indicates a more efficient working of the entire nutritive system.

The physiological changes thus indicated show that ozone may be advantageously used to correct the conditions producing anemia ; while the increased elimination of urea and phosphoric acid found by Dr. Peyrou and confirmed by Drs. Labbé, Oudin and Caritzalis, may be considered as indicating possible beneficial effects of ozone in gout, rheumatism, diabetes, etc.

On the circulatory system ozone again acts as a stimulant, and patients generally show the effect of this by heightened facial color. A slight dizziness sometimes follows its inhalation, indicating increased capillary pressure. The writer has found that headaches due to night-work are relieved after inhaling the gas for fifteen or twenty minutes. This stimulation joined to the increased richness of the blood in oxyhemoglobine—that is, in its oxygen carrying properties—may account for the many cures reported of troubles due to defective circulation and suboxidation.

On the blood current itself the oxidizing properties of ozone have been observed as distinctly as in the case of other liquids. Specific blood poisons are reported to be eliminated with remarkable rapidity. Scrofulous and even syphilitic toxines are said to be especially amenable to this form of treatment, when they have been found to yield to no sort of drug medication. If this is so, there is no reason why other toxines like that of tetanus, ptomaine poisons, malaria and the virus of rabies, may not be oxidized into innocuous forms, and eliminated from the blood by the usual channels. It is said by de la Coux that ozone “is indicated in the treatment of cancer and other infectious maladies ; and many physicians are actively employing ozone in the treatment of these diseases in the medical institutes of France.” If this is so, it is unfortunate that reports of their treatment of cancer should not have been published to the world.

The increased action of the heart and the peristaltic movement of the bowels, just spoken of, indicate that ozone inhalations have a direct influence on the nervous system. This is said to be especially marked when neurasthenic patients are submitted to a course of treatment.

The bactericidal action of ozone is so pronounced that it is not surprising to find it especially effective in diseases of microbic

origin. In tuberculosis, catarrh, influenza, grippe, bronchitis, whooping cough, croup and other affections of the respiratory organs due to microbic invasion, the bactericidal properties of ozone are said to act with almost miraculous promptness. And not only does the gas act as a direct microbicide, but it has an indirect bactericidal action as a result of the modifications it is said to produce in the tissues forming the media on which the bacteria lodge and propagate—modifications which render these media unfavorable to the development of the bacteria. This, if true, is a physiological modification of the highest importance in therapeutics; and the claim seems to be based on a reasonable explanation. It is this: ozone modifies the constitution of the blood and of the intra-cavitary fluids by rendering them more acid than before; and Dr. Oudin claims that it does this in strong proportions. Now it is well known to biologists that bacteria will only grow in alkaline media. The least acidity kills them. Even a neutral culture of bouillon inhibits the growth of these organisms. Thus ozone not only destroys the bacteria infecting the tissues with which it comes in contact, but it produces in the tissues themselves a physiological condition hostile to other germs which may afterwards find lodgment on them.

Another factor may possibly here come into play. Modern research tends to prove that infectious diseases are not caused directly by the action of bacteria themselves upon the tissues, but by the production of soluble poisons of the nature of alkaloids. This theory has so far advanced beyond the realm of conjecture as to be generally accepted as a final explanation of the symptoms of infectious disease. By ozonization the alkalinity of these toxins is probably neutralized, and so they are rendered inert. That this takes place in laboratory tests has been abundantly demonstrated; and the results reported by physicians of actual experiences seem to indicate that kindred effects take place physiologically. If this should prove to be the case, the therapeutic value of ozone will have a scientific basis of fact that will compel its recognition by pathologists everywhere, and ensure its general adoption in the treatment of all diseases due to the invasion and activity of bacteria.

When we recall the fact that over forty per cent. of deaths are caused by diseases having a microbic origin, and therefore due to infected air, food or water, to which the sterilizing action of

ozone may serve as a preventive; when we recall another long list of diseases having their cause in malnutrition, imperfect circulation and defective nervous conditions, capable of amelioration in ways indicated above, it would seem that ozone presents itself as the most efficient, most readily accessible and easily administered therapeutic agent ever discovered. It is not possible to send all consumptives to the mountains, nor all anemic children to the seaside; but it is possible to create an atmosphere in any home that shall contain all the healing and health-giving properties of mountain air and sea breezes. And if, as it is reasonably claimed, typhoid fever can be practically eliminated from the death list, and the white plague of consumption cured, two of the greatest sources of suffering and sorrow will have been removed from civilized life.

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#### FREIGHT CARS DELIVERED ON STREET RAILROADS.

The possibilities of the electric street railroad for freight purposes are demonstrated in the announcement of the New York Hudson River & Hartford Railroad that Providence merchants and manufacturers whose establishments are not located directly upon the line of steam roads will be given the opportunity to have freight delivered directly to their doors in the cars in which it has been hauled to the city by the steam lines. The company has now acquired the electric street railroad system of the city of Providence and its suburbs. It already controlled all the steam lines radiating from the city. The gauge of the tracks of the two systems is the same. All that will be necessary will be to replace existing rails in the street with those having the deeper grooves necessary to take the wider flanges of the wheels of the rolling stock of the steam lines. Electric locomotives will then haul freight cars from the tracks of the steam lines through the streets to the doors or yards of shippers; and, of course, freight will be collected in the same manner, giving to the manufacturer or merchant as economical conveniences in shipping as those possessed by establishments having spur tracks from the steam railroads. This traffic will be carried on in the night, when the street lines have comparatively little passenger service, and consequently no inconvenience will be caused to the public.

The advantages of such a system of freight delivery and collection are apparent. The merchant will, of course, have to pay some extra charge for delivery, covering transportation over the street lines, and the manufacturer will doubtless have to put in a spur track from the street in order that cars may be delivered into his yard. But against these costs is that of carting goods to and from a freight depot, which, it is stated, is greater than the rates that the railroad will charge for delivery by its street line.—*Iron Age*.