

## THE FORMATION OF OZONE BY SILENT DISCHARGE.

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THE different methods of the formation of ozone by means of a silent electric discharge through air or oxygen have been investigated by various writers. The formation of ozone by means of a brush discharge from sharp points has been exhaustively studied by Professor Warburg and others in his laboratory.<sup>1</sup> The yield per kilowatt hour by this method was comparatively small, never reaching that obtained by the use of a dielectric between the electrodes.

A. W. Gray<sup>2</sup> using a modified form of Siemens type of ozonizer and an influence machine, found that the amount of ozone per coulomb increased as a linear function of potential difference. It would seem from his results that the amount of ozone produced was proportional to the energy consumed in the apparatus.

A. W. Ewell,<sup>3</sup> using an ozonizer with parallel plate conductors one of which was covered with a sheet of glass, and an alternating current of 6,000 to 30,000 volts, found the amount of ozone produced per coulomb to be a function of current density through the gas, reaching a maximum and then rapidly falling off with the increase of the current. This fact was explained by him as due to the deozonizing effect of the current pointed out by Warburg.<sup>4</sup> No direct relation can be obtained from his results between the energy consumed in the ozonizer and the amount of ozone produced by the discharge.

APPARATUS.<sup>5</sup>

A cylindrical glass tube 3.5 cm. in length and 3.25 cm. in radius was fitted with a square brass plate at one end and a glass plate at

<sup>1</sup>Verhandl. d. Deutschen Phys. Gesellschaft., 22, p. 382, 1903. Preuss. Akad. Wiss. Berlin Sitz. Ber., 46, pp. 1011-1015. Annalen der Phys., 17, 1905, pp. 1-30, etc.

<sup>2</sup>Phys. Rev., Nov., 1904, pp. 347-368.

<sup>3</sup>Phys. Rev., 22, 1906, pp. 232-244.

<sup>4</sup>Ann. der Phys., 9, p. 788, 1902.

<sup>5</sup>This apparatus, which is not essentially different from the one used by Ewell, was constructed by the writer before he had seen the results of Ewell's investigation, the article having somehow escaped his notice.

the other, which, when bolted together by means of brass rods passing through the corners and sealed with wax at the outer edge of the cylinder, formed a small air-tight chamber. A glass disk *a*, Fig. 1, 3 cm. in radius was mounted on one of these plates and carried one of the electrodes. A similar disk *b* parallel to the first one,

attached to a movable brass rod *c* passing through the center of the brass plate, carried the other electrode. The brass rod *c* was provided with a screw drive and a graduated screw-head *d* by means of which the distance between the electrodes could be varied and accurately determined. The electrodes were tin-

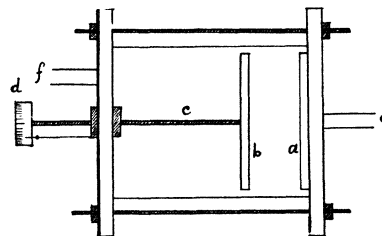


Fig. 1.

foil disks 2.5 cm. in radius, one of which was always covered with a disk of glass or mica 3 cm. in radius and of various thicknesses, cemented to the electrode by means of shellac solution.

A glass tube *e* passing through the center of the glass plate and cemented to it with shellac, was ground to fit a hole at the center of the glass disk *a* carrying the stationary electrode. The air entered the chamber through a brass tube *f* and after passing radially through the space between the two electrodes, where the discharge took place when the ozonizer was in action, left through the glass tube *e* at the center.

The volume of the air drawn through was measured by a gas meter in the circuit. It was dried by passing through concentrated sulphuric acid and a long glass tube filled with alternate layers of glass-wool and fresh phosphorus pentoxide. Another glass tube filled with cotton-wool served to retain any particles that might be carried by the air just before it entered the ozonizer (see Fig. 2). On leaving the ozonizer the air passed through two wash-bottles containing pure distilled water to take up any oxides of nitrogen, then through two more such bottles containing potassium iodide solution (about 0.5 gm. KI in 500 c.c. of water) and through a flask of 2.5 liters capacity, to equalize sudden changes in pressure, to the aspirator. The wash-bottles had ground glass stoppers and in

making the connections great care was taken to reduce to a minimum the contact of ozonized air with any oxidizable substances.

An alternating current of 60 cycles and 110 volts was stepped up by means of a transformer to the desired voltage, which was measured by means of an electrostatic voltmeter constructed for this purpose and calibrated by means of a Kelvin multicellular voltmeter. The effective value of the current was determined by reading the fall of potential across a non-inductive carbon film resistance (20,000–80,000 ohms) by means of a Kelvin voltmeter.

The amount of ozone produced by the discharge was measured in the following way. The aspirator was adjusted until it gave a

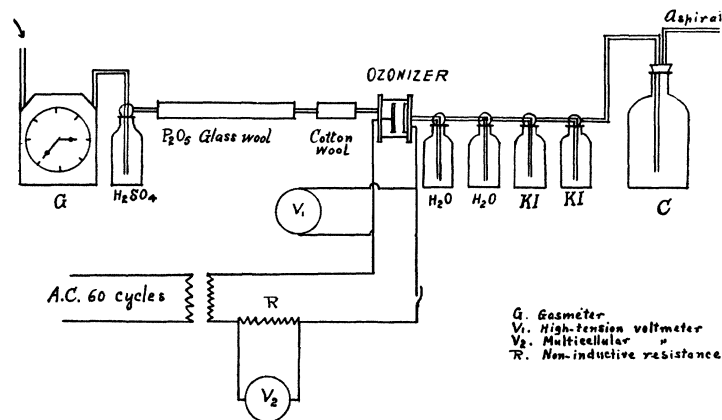


Fig. 2.

desired air current of approximately constant velocity.<sup>1</sup> The current was turned on for one minute and then cut off. When enough air had passed through to replace the air in the apparatus, the wash-bottles containing the iodide solution were disconnected, acidified and the liberated iodine determined by titrating with fresh thio-sulphate solution.

The titrated solutions were kept for one or two hours to test for any recoloration, the absence of which proved<sup>2</sup> that all the oxides of nitrogen had been absorbed before the ozonized air reached the iodide solutions.

<sup>1</sup>Small variations in the velocity of the air current made no appreciable difference in the production of ozone.

<sup>2</sup>Ann. der Phys., 17, 1905, p. 22.

Ewell concludes from his investigation that the amount of ozone produced per coulomb depends upon the current density. But since the current per square centimeter passing through the gas for a given voltage and air space depends also upon the capacity of the ozonizer, it would be of interest to note the effect of varying the capacity on the yield of ozone per coulomb. This was done both by varying the thickness of the dielectric between the electrodes and the air space between them. The results of these variations are given below.

#### VARIATION OF AIR SPACE.

To determine the effect of varying the air space on the yield of ozone per coulomb the following measurements were taken. Tables I. and II. were obtained by using a mica disk 0.2 mm. in thickness,

TABLE I.

*Dielectric, mica, 0.2 mm.  $d=0.15$  mm.*

No.	$V$	$i \times 10^6$	$O \times 10^6$	$Y \times 10^3$
1	1,380	194	62	5.54
2	1,850	355	155	7.27
3	2,760	584	341	9.70
4	3,270	740	418	9.40
5	4,750	1,090	620	9.50
6	5,350	1,220	728	9.90

TABLE II.

*Dielectric, mica, 0.2 mm.  $d=1.0$  mm.*

No.	$V$	$i \times 10^6$	$O \times 10^6$	$Y \times 10^3$
1	2,300	165	201	20.3
2	2,660	335	526	26.2
3	3,050	426	651	25.5
4	3,390	489	929	31.7
5	4,520	745	1,510	32.9
6	5,400	1,020	2,030	32.7

and III., IV. and V. with a glass disk 1 mm. in thickness. These disks were always cemented on the same electrode. Velocity of the air current was 1.2 liters per minute.

In these tables  $d$  is the air space in millimeters,  $V$  is the difference

of potential in volts,  $i$  the current in amperes,  $O$  the mass of ozone produced in grams per minute, and  $Y$  the yield per coulomb in grams. In Tables III., IV. and V. the voltage is not given as in some of the readings it was beyond the range of the voltmeter used.

TABLE III.

*Dielectric, glass, 1.0 mm.  $d=0.6$  mm.*

No.	$i \times 10^6$	$O \times 10^6$	$Y \times 10^3$
1	150	198	22.0
2	206	305	24.6
3	281	442	26.2
4	370	602	27.1
5	470	808	28.6
6	572	1,070	31.1
7	640	1,220	31.8

TABLE IV.

*Dielectric, glass, 1.0 mm.  $d=1.6$  mm.*

No.	$i \times 10^6$	$O \times 10^6$	$Y \times 10^3$
1	196	352	29.9
2	228	527	38.5
3	290	718	41.0
4	360	938	43.4
5	385	1,055	45.6
6	442	1,235	46.4
7	518	1,470	47.1
8	588	1,730	49.0

TABLE V.

*Dielectric, glass 1.0 mm.  $d=3.2$  mm.*

No.	$i \times 10^6$	$O \times 10^6$	$Y \times 10^3$
1	255	835	54.6
2	297	1,010	59.3
3	375	1,360	60.6
4	400	1,440	60.4
5	445	1,540	55.0
6	493	1,760	59.4

The examination of these figures at once shows that the yield per coulomb is greatly increased with the increase in air space and

hence decrease in capacity. For example, when mica is the dielectric, an increase of air space from 0.15 mm. to 1 mm. increases the yield more than three times, while in the case of the glass disk increasing the air space from 0.6 mm. to 3.2 mm. more than doubles the yield per coulomb.

To test if an increase in capacity by simply increasing the area of conducting surface would produce the converse effect, an ozonizer was constructed of six rectangular glass plates  $5 \times 6.7$  cm. and about 1 mm. thickness and on one side of each of these, rectangular pieces of tin foil  $3 \times 5.5$  cm. were pasted. The plates were arranged in parallel with about 1 mm. of air space between, through which the air current was made to pass, the rest of the arrangement being the same as before.

The measurements are given in Table VI. Comparing these with the figures of Tables III., IV. and V., in which glass of the same thickness was used as the dielectric, it will be readily seen that the maximum yield in this case is always smaller than any one of them although the air space is greater than one and less than the other two.

TABLE VI.

*Six plates. Dielectric, glass, 1.0 mm.  $d = 1$  mm.*

No.	$V$	$i \times 10^5$	$O \times 10^5$	$I' \times 10^3$
1	2,230	243	87	6.08
2	2,460	333	338	18.30
3	2,620	460	654	23.7
4	3,150	691	1,005	25.2
5	3,460	770	1,265	27.4
6	4,140	916	1,500	27.2
7	4,640	1,150	1,920	27.8
8	5,400	1,460	2,490	28.4

In the curves plotted in Fig. 3 and Fig. 4 the abscissæ are the values of current in  $10^{-4}$  amperes and the ordinates ozone produced per minute in  $10^{-4}$  grams.

It will be seen that except at the start all the curves are very nearly straight lines, showing that at those parts the mass of ozone produced in each is almost a simple linear function of the current, independent of the voltage, although the amount produced by the

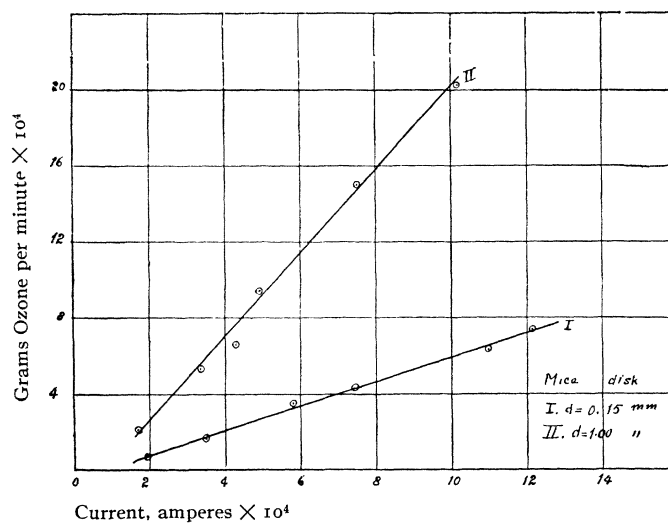


Fig. 3.

same current is different in different cases depending upon the constants of the arrangement such as air space, capacity, etc., and is greatest where the capacity is smallest.

In Fig. 5 curves are plotted to show the relation between the yield

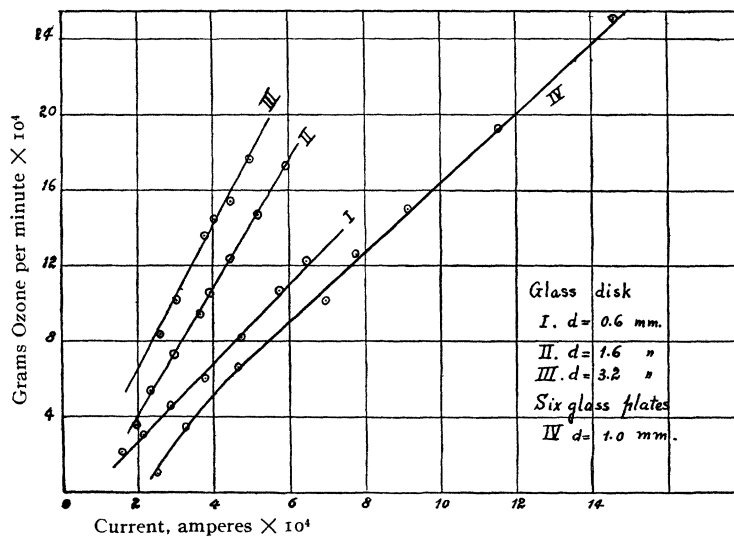


Fig. 4.

per coulomb and the voltage. The abscissæ are the difference of potential in volts and the ordinates the mass of ozone per coulomb in milligrams. Curves I. and II. are taken from readings in Tables I. and II., while curve III. is from Table VI. The curves all indicate a more or less steep rise at the start, but soon tend to become parallel to the axis of abscissæ, showing that beyond a certain point the additional increase in voltage has very little effect on the yield per coulomb. The maximum yield and the value of the voltage at which this maximum is reached, however, is very different in different curves.

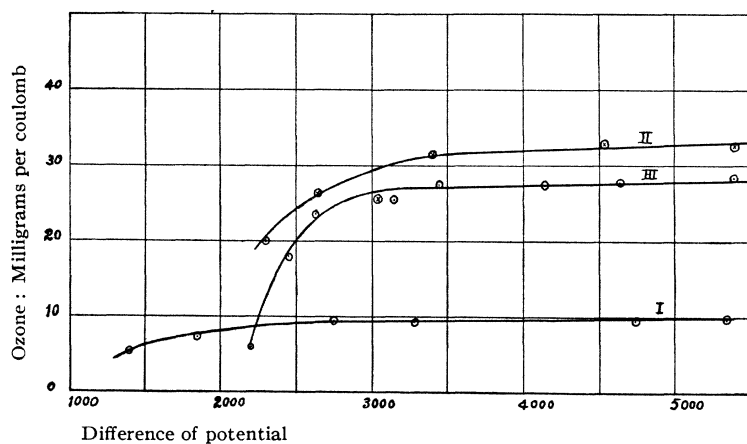


Fig. 5.

#### VARIATION OF THE THICKNESS OF THE DIELECTRIC.

The effect of variation in capacity by simply varying the thickness of the dielectric plate, keeping everything else unchanged was also examined. Three discs of the same radius but of different thicknesses were used for this purpose. No. 1 was of mica .04 mm. in thickness, no. 2 also mica .20 mm. in thickness, while no. 3 was of glass 1 mm. in thickness.

The readings were taken in as nearly similar conditions as possible. The results are given in Tables VII. and VIII.

These figures show that for the same air space and current density the yield of ozone per coulomb for different thicknesses of the dielectric is in the direct order of the thickness and consequently



TABLE VII.

 $d = 0.6 \text{ mm.}$ 

No.	Dielectric.	$V$	$i \times 10^6$	$O \times 10^6$	$F \times 10^3$
1	mica .04 mm.	1,950	450	390	16.7
2	" "	2,050	580	643	18.5
3	" "	2,250	810	935	19.7
4	" "	2,570	1,230	1,850	25.1
5	mica .20 mm.	2,530	420	643	25.5
6	" "	2,900	504	838	27.8
7	" "	3,700	679	1,010	26.8
8	" "	4,750	988	1,770	29.6
9	" "	5,500	1,180	2,180	30.8
10	glass 1 mm.		390	605	25.8
11	" "		458	877	31.9
12	" "		611	1,210	33.0

TABLE VIII.

 $d = 1 \text{ mm.}$ 

No.	Dielectric.	$V$	$i \times 10^6$	$O \times 10^6$	$F \times 10^3$
1	mica .04 mm.	2,800	550	916	27.8
2	" "	3,050	840	1,750	34.8
3	" "	3,450	1,470	3,060	34.7
4	mica .20 mm.	3,550	550	1,270	38.4
5	" "	4,880	840	2,240	44.5
6	" "	6,850	1,470	3,590	40.7

in the inverse order of the capacity, although the effect in this case is not so marked as in the case of increased air space.

The results already obtained show that the quantity of ozone produced in an ozonizer for a given current is closely related to the capacity of the ozonizer, and hence to the energy consumed in the circuit. The increase in the yield per coulomb by decreasing the capacity does not necessarily mean an increased efficiency, since the voltage necessary to give a certain current in the gas is much higher in the latter case than in the former. The power factor also cannot be neglected, which would be different in different cases.

An effort to determine the power factor experimentally by placing in the circuit a condenser of known capacity and measuring the partial voltages across the terminals of the ozonizer, and of the condenser, and also the total voltage in the circuit, although giving

fairly good results for very small air spaces failed to give correct values when the air-space was increased. It was found later<sup>1</sup> that in such cases the discharge is oscillatory, and more or less irregular. There is also considerable rectification of the current which was tested by means of a D.C. galvanometer in series.

For this reason the power consumed in the ozonizer was determined by deducting the transformer losses from the readings of a wattmeter placed in the primary circuit of the transformer.

In Table IX. some readings are given to compare the efficiency of such ozonizers as are described in this paper. Readings were taken for one pair of electrodes with two different thicknesses (.05 mm. and .20 mm.) of mica between and also ten pairs of rectangular electrodes mounted on glass, with mica plates .05 mm. in thickness and an air space of .5 mm. between each pair. The readings show an increase in efficiency with increased capacity.

In the table  $V$  is the difference of potential in volts,  $i$  the current in amperes,  $W$  the product of  $V$  and  $i$ ,  $W'$  the power consumed in the ozonizer in watts,  $O$  the mass of ozone produced per minute in grams and  $E$  the yield of ozone per kilowatt hour in grams.

TABLE IX.

*Air space between plates 1 mm. Gas velocity .95 liter per minute. Thickness of mica plate .05 mm.*

$V$	$i \times 10^6$	$W$	$W'$	$O \times 10^6$	$E$
3,350	955	3.20	.85	957	67.5
3,550	1,200	4.25	1.2	1,490	74.5
3,700	1,500	5.54	1.8	1,950	65.0
4,030	2,200	8.87	3.0	2,770	55.4

*Thickness of mica .20 mm.*

4,470	630	2.81	1.0	990	59.4
4,700	806	3.7	1.3	1,090	50.3
4,900	896	4.4	1.5	1,220	48.7

*Ten rectangular plates. Air space between plates .5 mm. Gas velocity 2.85 liters per minute.*

1,620	1,435	2.32	1.0	1,667	100.0
1,650	1,790	2.96	1.4	2,058	88.2
1,700	2,270	3.86	2.0	2,820	84.6
1,730	2,540	4.36	2.5	3,341	80.2

<sup>1</sup>See the writer's article "The Formation of Ozone by Silent Discharge," above p. 117, Fig. 2.

The results of this investigation may be summarized as follows:

1. In all cases studied by the writer the quantity of ozone produced in a given ozonizer was found to be, over quite a large range, almost directly proportional to the current, *after a full steady discharge is established*, and practically independent of the voltage. The phenomenon cannot be explained by the increased ozone density or by the deozonizing effect of the current, as these were varied in many different ways and yet the law seems to hold good in general.
2. A given current passing through a given volume of air does not produce the same amount of ozone in different ozonizers. Other things remaining the same the yield per coulomb increases with decrease of capacity.
3. The efficiency of the ozonizers such as described in this paper was found to increase with increase in capacity.
4. No definite voltage seems to be necessary for the transformation of oxygen into ozone.<sup>1</sup>

#### DISCUSSION.

Warburg has advanced the theory<sup>2</sup> that the formation of ozone is a photochemical reaction, being due to the action of ultra-violet and cathodic rays on oxygen. In a later article by him and G. Leithauser<sup>3</sup> the author adds that the rapidly moving electrons may have the same effect on the gas as rays of small wave-length.

Although certain elementary substances are converted into their allotropic modifications by the action of light, such transformations are found to take place with *evolution* of heat as, for example, in the transformation of yellow into red phosphorus, or of monoclinic into rhombic sulphur, giving rise to more stable forms. But as the formation of ozone is accompanied by an *absorption* of energy it is clear that it cannot be classified under the changes of this kind.

A molecule of ozone is found to consist of three atoms of oxygen. Its formation from molecular oxygen necessitates the dissociation of these molecules into their atoms, from which groups of three atoms may be formed. It does not seem probable that such dis-

<sup>1</sup>By suitable arrangement it was possible to produce ozone at 800 volts, and probably this value can be brought down still lower.

<sup>2</sup>Preuss. Akad. Wiss. Sitz. Ber., 46, p. 1011, Nov., 1903.

<sup>3</sup>Ann. der Phys., 20, pp. 751-758, 1906.

sociation can be brought about to any great extent by the *direct* action of ultra-violet light, on the gas. J. J. Thomson has found<sup>1</sup> that ionization produced in air by ultra-violet light is very small. and E. Bloch,<sup>2</sup> repeating Lenard's experiments, came to the conclusion that the ionization reported by him was produced by the light waves striking solid particles in suspension, since when the gas was carefully filtered through cotton wool no appreciable ionization was produced in it. Therefore it appears from these facts that the dissociation is produced by the ions or electrons carrying the discharge which break up the molecules of oxygen into their atoms, rearrangement of these atoms in groups of three giving rise to ozone.

Most of the results obtained during this investigation can be explained on this hypothesis. It has been shown that the amount of ozone produced by a given current through a given volume of air is not, in general, a function of the *current* alone, but also of the *voltage*, within certain limits. Since the velocity of the ions is determined, when everything else remains constant, by the strength of the field in the air space, the greater this force the greater the velocity, and hence the number of dissociations produced by each ion passing through the gas. In other words, assuming a constant source of ionization the current passing through the gas would be proportional to the average velocity of the ions, whereas the kinetic energy of each moving ion would be proportional to the square of this velocity. And if this energy is absorbed by the gas in producing dissociations in it, we would expect to find an increase in the amount of ozone produced per coulomb with the higher voltage.

This relation, however, would not hold indefinitely, since if the air space is small the ions may acquire such a velocity that only a fraction of their kinetic energy will be absorbed in producing dissociations, the remaining part being transformed into heat or other forms of radiant energy at the surface of the opposite plate.

The curves given in Fig. 5, where the mass of ozone per coulomb is plotted with the voltage, confirm this view. In each case the curves show a more or less rapid rise with the voltage at the start but soon approach a constant value. The voltage at which this

<sup>1</sup>Camb. Phil. Soc. Proc., p. 417, 1908.

<sup>2</sup>Comptes Rendus, 147, p. 892, 1908.

critical point is reached is seen to be different in different cases being smaller where the air space is smaller, and probably represents the conditions at which a full steady discharge is established.

It was also found that the efficiency of ozonizers increased with increase of capacity.<sup>1</sup> On examining the oscillographic curves of the discharge current<sup>2</sup> it will be seen that when the capacity is small the curves show an oscillatory discharge like a spark discharge of very large period. As the capacity is increased the curves become smoother and more regular. It is well known that sparks produce little ozone and decompose rapidly what is formed. Therefore it would be natural to expect a higher efficiency with smoother discharges.

In concluding this paper the writer wishes to acknowledge his indebtedness to Professor A. W. Goodspeed for kindly placing at his disposal all the facilities of the Randal Morgan Laboratory of Physics and to Dr. R. H. Hough for many valuable suggestions and criticisms during the course of this investigation.

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<sup>1</sup>This agrees with the experimental results, and also with those of Ewell's investigation who recommends a thin sheet of insulator of high dielectric strength between the plates and also a small air space, for greater efficiency, both of which would give an increased capacity.

<sup>2</sup>See the writer's article, "Some Observations on the Silent Discharge," p. 117.