ON THE PRODUCTION OF OZONE IN THE SIEMENS GENERATOR; AND ON AN IMPROVED CONSTRUCTION OF THIS APPARATUS.

By Arthur W. Gray.

1. The writer has described elsewhere[1] some preliminary experiments which he made to compare the quantity of electricity passed through the oxygen in a Siemens ozone generator with the mass of the ozone formed. As was there mentioned, two main sources of error were present, whose effect on the results could not then be estimated, conduction of electricity along the glass surfaces of the generator and failure of the total charge to pass through the galvanometer. In the determinations described in the present paper both of these difficulties were avoided and in addition other improvements conducive to accuracy were introduced. These included a greatly improved key[2] for automatically sending a single charge or discharge through the galvanometer while the generator continued to be charged and discharged in rapid succession, an automatic potential regulator,[3] the use of more concentrated oxygen freed with greater care from water vapor, carbon dioxid, and organic impurities, and the substitution of Schönbein's method of determining the mass of ozone formed by absorbing with potassium iodid and titrating with sodium thiosulfate for Thénard's method of absorbing with sodium arsenit and titrating with iodin.

Greater accuracy was also secured by employing the expression used in calculating the quantity of electricity sent through the gas in a form independent of the shape and dimensions of the generator, so that all the quantities involved could be determined by purely electrical measurements.

In addition to investigating the formation of ozone from concen-

[1] A. W. Gray, Sitzungsber. d. k. Akad. d. Wissensch. zu Berlin, p. 1016, 1903; Ann. d. Phys., 13, p. 477, 1904.

[2] A. W. Gray, Phys. Rev., Vol. XIX., p. 293.

[3] A. W. Gray, Phys. Rev., Vol. XIX., p. 344.

trated and dry oxygen, and the capacity of the generator at various electrical potentials, experiments were made to determine in a general way the influence of water-vapor, air, and the lengthening, the duration of the charging current (*i. e.*, reducing the current strength) by the insertion of a very high resistance in the circuit.

Brief Outline of the Method of Investigation.

2. A Toepler-Holtz machine driven by an electric motor served as the source of electricity. One pole was earthed while the other was connected with a large Leyden battery and a Braun electrometer. The potential was maintained uniform by means of a specially designed point overflow to earth. While the outer electrode of the generator always remained earthed, the inner one was connected alternately with the Leyden battery and with the earth. From time to time the quantity of electricity used in charging or discharging the generator was measured. To accomplish this the writer constructed an automatic commutator and galvanometer key. By depressing a lever attached to this a *single* charge was caused to pass from the outer electrode through a ballistic galvanometer instead of direct to earth, while the charging and discharging continued in rapid succession without interruption. By depressing a second lever the current on discharging could be measured at will.

On leaving the generator the ozonized gas passed through a three-way cock lubricated with concentrated sulfuric acid and through either one of two ozone-absorbing solutions into the atmosphere. The first was merely to prevent the ozone from escaping into the room, the second for determining the amount formed during an experiment.

The number of times the electricity passed through the gas was recorded by a specially constructed rotation counter attached to the charging and discharging commutator.

In order to make a determination the electrical machine and the commutator were set in operation, the potential adjusted to the desired value, the current of gas allowed to flow through the first solution, and the counting device set at zero. After a few trial galvanometer deflections showed that the electrical part of the apparatus was working uniformly, the three-way cock was turned to divert the gas stream into the second solution and the counting device was set in operation. From time to time the quantity of electricity used in charging the generator was measured as described above. After 12,000 to 65,000 passages of the electricity through the gas, the number depending on the potential employed and on the other conditions of the experiment, the three-way cock was turned to its original position, the counting device thrown out of operation, and the mass of ozone produced determined by analyzing the second solution.

Calculation of the Quantity of Electricity Passed Through the Gas.

3. As ordinarily constructed, the effective part of a Siemens ozone generator consists of two coaxial cylindrical shells of glass separated by a layer of the gas to be submitted to the action of the electrical discharge — the whole forming a compound condenser of three layers. As long as the potential difference between the electrodes is insufficient to cause a conduction current through the gas, the electrostatic capacity remains constant; but when the stress becomes sufficient to break down the insulation offered by the gas, the capacity is increased by the effect of the conduction. In his previous paper[1] the writer showed how to calculate the quantity of electricity that flows through the second layer of a condenser composed of three infinitely long coaxial shells, when the potential difference between the outer surfaces is changed from any given value V to any other $V + \Delta V$; the first and third layers being assumed to insulate for all values of V, the second to insulate for low values, but to conduct partially or wholly if V exceeds a certain amount. If we substitute in the expressions there given

$$C_1 \equiv \frac{K_1 l}{2 \log_e r_1/r_0}; \qquad C_2 \equiv \frac{K_2 l}{2 \log_e r_2/r_1}; \qquad C_3 \equiv \frac{K_3 l}{2 \log_e r_3/r_2},$$

at the same time remembering that

$$\frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} = \frac{1}{C_0}$$

[1] A. W. Gray, Ann. d. Phys., 13, p. 477, 1904.

and

$$\frac{1}{C_1}+\frac{1}{C_3}=\frac{1}{C_\infty},$$

it follows that

$$\frac{1}{C_2}=\frac{1}{C_0}-\frac{1}{C_\infty},$$

or

$$C_2=\frac{C_0 C_\infty}{C_\infty - C_0}.$$

Substituting this value in equation (5), p. 480, gives

$$Q_2=\frac{C_\infty(Q - C_0 \cdot \Delta V)}{C_\infty - C_0} \equiv \frac{C_\infty}{C_\infty - C_0}(C_v - C_0)\Delta V.$$

Here Q is the quantity of electricity that flows to or from the outer electrodes of the condenser, Q_2 the quantity that flows through the middle layer, C_0 the electrostatic capacity when the middle layer insulates, C_v when it conducts partially, and C_∞ when it conducts completely. In this expression all the quantities occurring can be measured electrically; and since it contains no dimensions, it is not restricted in its application to the case of coaxial cylinders, but applies to a condenser of any form whatever. It is also to be noted that the expression remains the same whether the magnitudes occurring in it are measured in C.G.S. electrostatic units, in C.G.S. electromagnetic units, or in coulombs, farads, and volts.

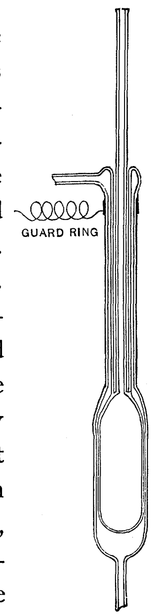
Improved Construction of the Siemens Type of Ozone Generator.

4. The ozone generator used in the writer's preliminary work was of the usual construction with only a very short length of glass surface separating the walls bounding the gas space, so that it seemed not at all improbable that a portion of the electricity in passing from one side to the other took this path instead of going *through the gas*. As this portion would be measured by the galvanometer, although ineffective in producing ozone, the values obtained for the mass of ozone per coulomb sent through the gas would be too low. A similar error would be caused if the surface separating the electrodes of the generator failed to insulate sufficiently. The

conduction here could be decidedly reduced by coating with fused shellac as was done then while the oxidizing action of the ozone made such an application within entirely out of the question.

To overcome these difficulties the writer constructed the generator represented in longitudinal section by Fig. 1. The effective portion that comes between the electrodes is of large diameter, with thin walls as close together as possible, and short enough to permit a flow of gas sufficiently rapid to prevent the concentration of ozone from becoming so great that the deozonizing action of the electric discharge pointed out by Warburg[1] would have an appreciable effect. The remainder of the generator is of thicker glass. Interior insulation is secured by extending the gas-space above, and by reducing the diameter there; and the flow of gas is facilitated by increasing the distance between the walls in the upper portion as well as by providing a considerable space at the bottom. That the insulation thus obtained was effective, even when considerable water-vapor was present in the oxygen, seems clearly indicated by the results obtained.[2] External surface insulation is increased by carrying the conductor to the inner electrode down through a narrow glass tube sealed into the neck as indicated. As an additional precaution a metallic guard-ring connected to earth surrounded the neck of the generator just below the gas exit. The electrodes were of silver deposited on the glass in order to avoid strains which would be caused by the employment of a liquid.

Fig. 1.



Great care was given to the construction of the generator in order to get the walls bounding the narrow part of the gas space as nearly parallel as possible. The interior was also carefully cleaned by boiling concentrated acids in it for about half an hour. The length of the uniform narrow portion was a little over 5 cm. and the mean radii (determined by weighing with mercury) were : $r_0 = 1.138$ cm.; $r_1 = 1.222$ cm.; $r_2 = 1.284$ cm.; $r_3 = 1.366$ cm. More accurate

[1] E. Warburg, Sitzungsber. d. k. Akad. d. Wissensch. zu Berlin, p. 712, 1900 ; Ann. d. Phys. 9, p. 788, 1902.

[2] See 12 and 21.

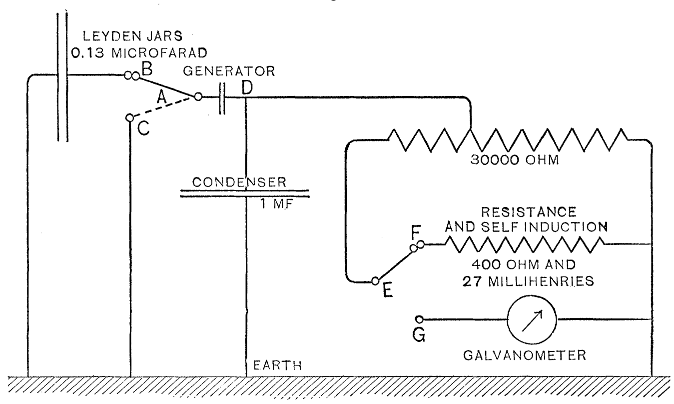
special determinations of the mean thickness of the gas layer gave $r_2 - r_1 = 0.064$ cm. with a probable error of less than 0.001 cm.

Arrangement of the Electrical Circuit for Avoiding Leakage.

5. Owing to the great self-induction (about 27 millihenries) of the galvanometer employed, which was of the Deprez-d'Arsonval type constructed by Siemens and Halske, considerable difficulty was experienced in getting all of the current to be measured to pass through the entire length of the coil. Attempts were first made in the direction of improving the insulation of the circuit and by inserting a high resistance immediately after the generator, so as to obtain as low a potential as possible in the rest of the path through the galvanometer to earth. But when high potentials were used, the suspended coil behaved as if it were not swinging freely; instead of giving a prompt deflection, it would quiver for a few seconds, and then drift, sometimes slowly, sometimes suddenly, perhaps to the right, perhaps to the left. This behavior had also previously been observed with the similar galvanometer employed in the earlier investigation; but after removing the coil and wiping the pole pieces with the finger, the trouble, for some reason or other, apparently disappeared, so it was assumed that the coil had been catching against a bit of thread or something of the kind; but when the trouble recurred with a different instrument, its cause was searched for until found. Upon removing the brass plate across the front of the magnet and observing the coil while attempting to get a deflection, it was noticed that the coil was violently drawn aside against one of the pole-pieces and held there, while a series of small sparks appeared. Thus the difficulty was evidently due to an electrostatic charge accumulating on the insulating material of the coil on account of the great self-induction. And this effect persisted even when the resistance in series was increased to over forty megohms. Attempts to avoid the self-induction by substituting a Dubois-Rubens iorn-clad galvanometer failed because the brief but strong current changed the controlling magnetic conditions sufficiently to produce a large shifting of the resting-point after every deflection.

The difficulty was, however, finally removed completely by adopting the arrangement indicated in Fig. 2. The essential point was to place a condenser of large capacity in parallel with the galvanometer, so that the current from the generator flowed first into the condenser, which then discharged itself under very low voltage through the galvanometer at a rate governed by the self-induction in the circuit.

Fig. 2.



The motor-driven key A connected the inner electrode of the generator alternately through B with the Leyden battery, which had a capacity of about 0.13 microfarads, and through C with the earth, making about five cycles per second. At the point D in the wire leading from the outer electrode of the generator a branch lead to one terminal of a microfarad condenser, whose other terminal was connected with the earth. The wire from the generator also lead to an Ayrton shunt of 30,000 ohms, one end of which was earthed, while the other lead to the key E, which was ordinarily connected through F with a resistancc and self-induction equal to that of the galvanometer (about 400 ohms and 27 millihenries); but which could, by means of an automatic device attached to A, be connected during the course of a single charging or discharging with G, so that the current would flow through the galvanometer. With this arrangement no resistance was needed in series with the galvanometer.

Since the capacity of the generator was very small compared with the other two, and since the arrangement was in series, the total capacity of the circuit through which the generator was charged, and also of that through which it was discharged, was a trifle less than its own capacity. Also, the resistance and self-induction of these circuits, being merely that of the connecting wires, was extremely small, affording a very sudden passage of the electricity. To investigate the effect of lengthening the duration of this current (see 10), a resistance of about 42 megohms was inserted between the generator and the point *D*.

The galvanometer was calibrated by substituting for the generator an Elliott standard condenser charged with a single storage cell and removing the microfarad condenser attached at *D*. While the effect of the residual charge introduced a slight error, it was of no special consequence for the present purpose, and would have no effect whatever upon the comparisons of results made later. (9 ff.)

The length of time that the key *A* remained in contact with *B* or with *C* was about 0.047 seconds. Lengthening this by decreasing the speed at which *A* was operated made no perceivable difference in the galvanometer deflection, even when 42 megohms were in the circuit of the generator.

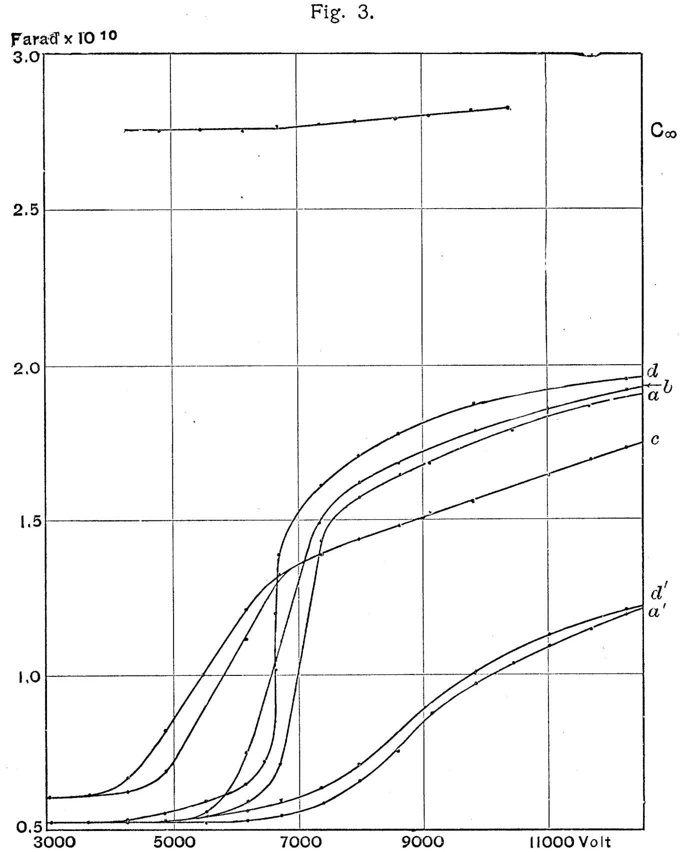
Results.

9. As the writer had observed in his preliminary experiments,[1] a flash of light occurred in the generator when it was charged *suddenly* as well as when it was discharged. Also, with dry oxygen or dry air flowing through it, the same quantity of electricity passed through the circuit on discharging as on charging; but an exception (12) to this was observed when the oxygen contained considerable water-vapor. The results of the measurements, collected in Tables I., II. and III., and represented graphically in Figs. 3, 4 and 5, show, however, not only the unreliability of the previously used method of connecting the galvanometer for the purpose of measuring the quantity of electricity passing through the circuit, but also the serious deficiency of the ordinarily constructed Siemens generator as a means both of carrying out such investigations as are here described, and of applying to the production of ozone the greatest fraction of the electricity employed.

The writer considers all of the determinations described in the present paper as reliable to within about one per cent., while in

[1] A. W. Gray, Ann. d. Phys., 13, p. 486, 1904.

Fig. 3.



many cases greater accuracy was undoubtably reached. Among the thousands of galvanometer deflections that were obtained, not a single unusual one was observed, while in the previous work abnormal ones would appear every now and then.

On account of lack of time for perfecting a means of reliably measuring potentials beyond 12,240 volts, which was the limit of the Braun electrometer employed, it is to be understood that the general statements that follow concerning the description and interpretation of the results are intended to apply only to cases where the potential is less than this value, although some of them, at least, are undoubtedly applicable beyond the range investigated.

The Capacity of the Generator at Various Potentials.

10. Table I. shows the influence of the potential and other conditions on the electrical capacity of the generator. The first column, V., gives in volts the potential difference applied between the electrodes; the other columns give the corresponding values of the capacity, $C_v \equiv Q/V$, expressed in units equal to 10^{-10} farads. The results recorded under *a* and *a′* were obtained when oxygen, more than 98 per cent. by volume pure, and given its final drying by passing over fresh phosphoric anhydrid, was passed through the generator. Those under *b* illustrate the effect of a very slight amount of water-vapor with the same oxygen, being obtained after the phosphoric anhyrid had been somewhat used up and was coated with a slight liquid film. Renewing the P_2O_5 caused the return of the values under *a*. In obtaining the results under *c* the same oxygen was again used, but the soda lime and phosphoric anhyrid were removed and the gas caused to bubble through distilled water contained in an absorption apparatus of five chambers in series, and then to pass through a considerable length of cotton wool to prevent spray from being carried along into the generator. The temperature of the water was slightly lower than that in the neighborhood of the generator, so the vapor was not quite saturated. The results for air dried with phosphoric anhydrid appear under *d* and *d′*, and those for mercury filling the gas-space under C_∞. While making the measurements for *a*, *b*, *c*, *d* and C_∞, the only resistance in the charging and discharging circuits was that of the conducting wires, whereas while obtaining the last two columns, *a′* and *d′* the duration of the electric current was considerably increased by inserting between the generator and the point *D*, Fig. 2, a resistance of about 42 megohms composed of a solution of cadmium iodid in amyl alcohol. All of these results are represented graphically in Fig. 3, each curve being designated by the letter heading the column from which it was plotted. Except for the low potentials, *a* and *a′* are the mean values taken from Tables II. and III.

During the various experiments in which oxygen was used, the pressure in the generator ranged from 76.2 to 78.4 cm. of mercury, while with air it was about 73.5 cm. A thermometer suspended about four centimeters from the generator indicated a mean temperature during any one series of measurements ranging from 15.6 to 19.7° *C*. A careful inspection of the results revealed nothing that could be traced to these slight variations of either pressure or temperature.

TABLE I.

V	a	b	c	d	C_∞	a'	d'
3070	0.522		0.609				
3660	0.524		0.615			0.519	
4250	0.525		0.62 0.66	0.53	2.76		0.528
4850	0.523		0.69 0.82	0.55	2.76	0.524	0.533
5500	0.552	0.554	0.91 1.00	0.60	2.76	0.520	0.541
6160	0.588	0.750	1.12 1.21	0.65	2.75	0.530	0.555
6430				0.72			
6600				1.20			
6710	0.717	1.112	1.32	1.40	2.77	0.540	0.600
7380	1.42	1.490	1.39	1.61	2.78	0.587	0.633
7960	1.57	1.637	1.44	1.71	2.78	0.659	0.710
8590	1.64	1.670	1.48	1.78	2.79	0.751	0.801
9220	1.68		1.53		2.80	0.877	
9810	1.76	1.790	1.55	1.87	2.82	0.966	1.002
10410	1.79				2.82	1.034	
11680	1.86		1.69			1.144	
12240	1.90	1.912	1.73	1.95		1.197	1.205

$$C_0 = 0.523. \quad C_\infty = 2.76. \quad Q = \frac{C_\infty}{C_\infty - C_0}(C_v - C_0)V = 1.23(C_v - C_0)V.$$

11. It is to be noticed that none of these curves show the discontinuity observed in the preliminary experiments; but instead, a very rapid rise between certain potentials, provided the electric current is of very short duration, the capacity soon reaching a value between three and four times what it had before the gas began to conduct. When, however, the duration of the current is increased by the insertion of a large resistance, the rise in the capacity begins at a greater potential, takes place much more slowly, and, at least within the range of the potentials here investigated, is very much less, indicating greatly reduced conductivity of the gas, and also that the minimum potential difference between the boundaries of the gas-space, which plays an important part in Warburg's theory of the Siemens generator,[1] depends on conditions other than its construction.

[1] E. Warburg, Verhandl. d. Deutschen Phys. Gesellsch., **22**: p. 382, 1903.

12. A comparison of curves *a* and *b* shows that the presence of a slight amount of water-vapor in the oxygen increases its conductivity a little, but causes the rate of most rapid rise in the capacity to be reduced somewhat. Curve *c*, however, shows some rather remarkable effects of the presence of considerable water-vapor. In column *c* of Table I. it is to be noticed that for values of V between 3,660 and 6,710 volts two values of C_v are given. Those on the left were obtained when the generator was being charged, while those on the right while it was being discharged. Each value given represents a series of consistent galvanometer deflections, and as a check, the same measurements were repeated several hours afterward with the same result of finding that between these potentials a greater deflection was obtained on discharging than on charging; while outside of this region the direction of the current seemed to make no difference.

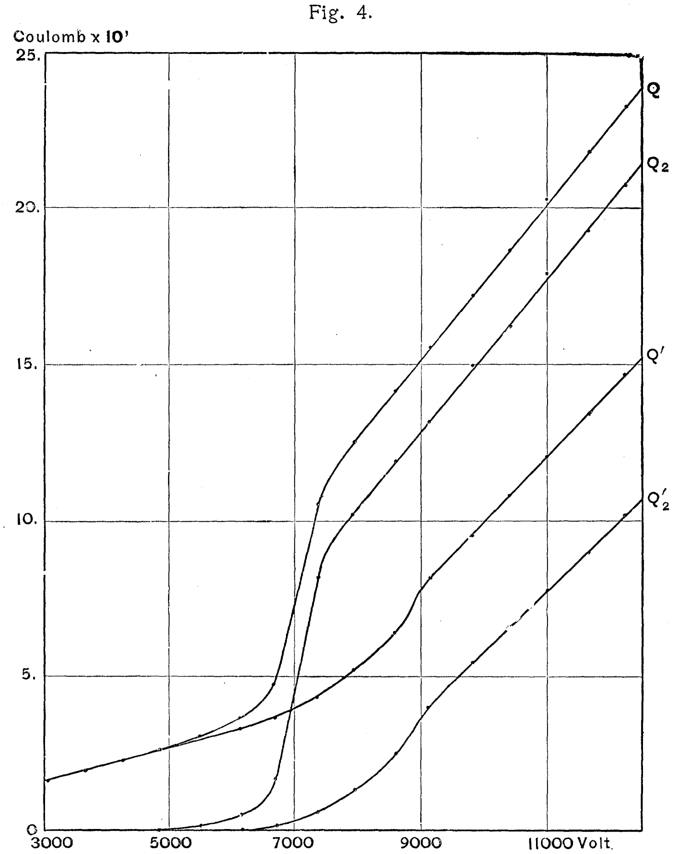
Another point exhibited by curve *c* is that while the presence of considerable water-vapor causes conduction through the gas to take place when the dry gas would insulate, and to reach a much higher value for low potentials; on the other hand, it retards conduction as soon as the potential exceeds a certain value, and from here on the increase in the capacity seems to be directly proportional to the increase in the applied potential. Just what correction may be necessary for the effect of any conduction there may have been along the internal surfaces is not apparent.

It should be remarked in passing that curve *c* is only one of a series of many similar curves representing the conditions for the same generator when water-vapor was present. In a series of twenty consecutive galvanometer deflections, the greatent deviation from the mean would be less than one half per cent.; in fact, the uniformity was greater than with dry oxygen; but an equally consistent series obtained with the same potential several hours later might differ from the first by five per cent. or even more. Just what part was played by differences in humidity, temperature, pressure, or other influencing conditions was not apparent. The results represented in curve *c* were all secured within a short space of time, and represent merely a typical case.

13. Examination of curves *d* and *d′* show that dry air begins to

conduct sooner and conducts better than oxygen; also that the difference between the air and the oxygen becomes less when the electric current is retarded by great resistance or when the potential difference applied between the electrodes of the generator is increased.

Fig. 4.



Air also shows the most rapid rise in the capacity in the neighborhood of the critical potential.

14. When the gas space was filled with mercury, the capacity remained constant up to about 7,000 volts, and then seemed to increase slowly, proportionally to the increase in the potential, at the rate of about ⅔ per cent. for every additional 1,000 volts. This is apparently due to conduction through the glass.

15. Some interesting information is imparted by Fig. 4, which presents from another point of view the results recorded in columns a (and a') of Table I. The ordinates of curves Q and Q' represent the quantities of electricity used in *charging the generator* at various potentials, those of Q_2 and Q'_2 the quantities that passed as *conduction current through the oxygen*. Q and Q_2 are from the same data as $\bar{a}$ and are taken directly from Table II.; Q' and Q'_2 correspond to $\bar{a}'$ and are from Table III.

Until reaching the critical potential at which conductivity in the gas begins Q and Q' follow the same straight line from the origin of coördinates; similarly Q_2 and Q'_2 both remain zero. In the neighborhood of the critical potential each curve suffers a rapid rise along a curved path and then continues along a straight course which is considerably steeper than before the critical potential was reached; showing that after a certain potential is attained, the increase in the quantity of electricity is directly proportional to the increase in the potential. These lines are all slightly divergent although very nearly parallel. Fig. 4 also makes clear that the lengthening the time required in charging and in discharging the generator reduces not only the *total quantity* of electricity that passes through the circuit, but also the fraction of this (Q_2/Q) that passes as *conduction current through the gas*.

Corresponding curves (not shown here) were plotted for the other cases investigated. All showed the same general characteristics exhibited in Fig. 4. The values of $\frac{dQ}{dV}$ and $\frac{dQ_2}{dV}$ after these curves become straight lines at the higher potentials are given in the following table, where the letters have the same significence as before.

	$\frac{dQ}{dV}$	$\frac{dQ_2}{dV}$
a.	2.51×10^{-10}	2.47×10^{-10} coulombs per volt.
b.	2.54 "	1.91 "
c.	2.25 "	1.72 "
d.	2.42 "	1.92 "
a'.	2.11 "	1.89 "

The Production of Ozone.

16. The results of the measurements made to determine the relation between the mass of ozone produced under given conditions

and the quantities of electricity involved are collected in Tables II. and III. Both series were obtained when commercial oxygen, more than 98 per cent. by volume pure, and passed in succession through a solution of potassium permanganate, glass beads drenched with concentrated sulfuric acid, solid potassium hydroxid, soda lime, phosphoric anhydrid, and cotton wool, flowed through the generator rapidly enough to exclude any possibility of the ozone reaching such a concentration that the deozonizing action of the silent electrical discharge would have an appreciable effect. Nor could any

TABLE II.

V	$C_v \times 10^{10}$.	$C_v - C_0 \times 10^{10}$.	$Q \times 10^7$.	$Q_2 \times 10^7$.	$M \times 10^7$.	M/Q_2.	M/Q.
5,500	0.552	0.029	3.02	0.196			
6,160	0.588	0.065	3.62	0.492			
6,710	0.717	0.194	4.81	1.60			
7,380	1.42	0.901	10.5	8.18			
7,960	1.56	1.04	12.4	10.1	1.47	0.145	0.120
"	1.58	1.06	12.6	10.3	1.43	0.138	0.114
"	1.57	1.05	12.5	10.2	1.45	0.142	0.117
8,590	1.67	1.15	14.3	12.1	1.91	0.157	0.133
"	1.61	1.08	13.8	11.5	1.74	0.152	0.126
"	1.64	1.12	14.1	11.8	1.77	0.150	0.126
"	1.65	1.12	14.1	11.8	1.78	0.151	0.126
"	1.64	1.12	14.1	11.8	1.80	0.152	0.128
9,220	1.67	1.15	15.4	13.0	2.18	0.167	0.142
"	1.69	1.17	15.6	13.2	2.11	0.160	0.136
"	1.68	1.16	15.5	13.1	2.15	0.159	0.139
9,810	1.76	1.24	17.2	14.9	2.64	0.177	0.153
"	1.75	1.23	17.2	14.8	2.58	0.174	0.150
"	1.76	1.23	17.2	14.9	2.61	0.176	0.152
10,410	1.79	1.27	18.7	16.3	2.99	0.184	0.160
"	1.78	1.26	18.6	16.2	2.99	0.185	0.161
"	1.79	1.27	18.6	16.2	2.99	0.184	0.161
11,020	1.85	1.33	20.4	18.0	3.55	0.197	0.174
"	1.83	1.31	20.3	17.8	3.50	0.197	0.173
"	1.84	1.32	20.3	17.9	3.53	0.197	0.173
11,680	1.85	1.33	21.7	19.1	3.90	0.204	0.180
"	1.85	1.33	21.7	19.1	4.06	0.212	0.187
"	1.88	1.36	22.0	19.5	4.03	0.206	0.183
"	1.86	1.34	21.8	19.2	4.00	0.208	0.184
12,240	1.90	1.38	23.3	20.8	4.62	0.222	0.198
"	1.90	1.38	23.2	20.7	4.63	0.233	0.199
"	1.90	1.37	23.2	20.7	4.57	0.221	0.197
"	1.90	1.38	23.2	20.7	4.61	0.225	0.198

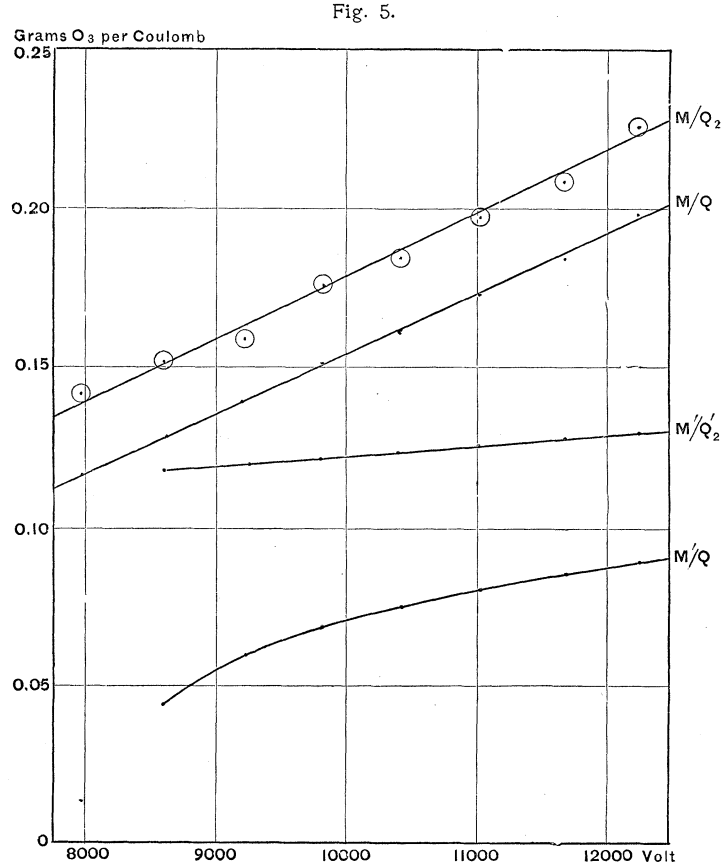
measurable quantity of ozone have escaped absorption; for, while the solution of potassium iodid contained in the first chamber of the absorption apparatus became darkly colored with the liberated iodin, that in the second chamber never exhibited more than a very faint tinge of yellow, and that in the third, fourth, and fifth remained perfectly colorless. In obtaining the results in Table II., the only resistance and self-induction in the charging and discharging circuits was that of the conducting wires, which were for the most part of polished brass about 3 mm. in diameter. Table III. gives the results secured when about 42 megohms were inserted between the generator and the point D, Fig. 2. V, C_v, Q, and Q_2 have the same significance as in 3, and are expressed in volts, farads, and coulombs respectively. The primed letters refer to Table III. M is the number of grams of ozone formed by a single passage of the electricity through the circuit. Just below each single horizontal line are given the means for the same potential of the quantities immediately above.

TABLE III.

V	$C'_v \times 10^{10}$	$C'_v - C'_0 \times 10^{10}$	$Q' \times 10^7$	$Q'_2 \times 10^7$	$M' \times 10^7$	M'/Q'_2	M'/Q'
6,160	0.530	0.007	3.26	0.053			
6,710	0.540	0.017	3.62	0.140			
7,380	0.587	0.064	4.33	0.580			
7,960	0.659	0.136	5.24	1.33			
8,590	0.756	0.233	6.49	2.46	0.292	0.119	0.0449
"	0.746	0.223	6.40	2.35	0.273	0.119	0.0435
"	0.751	0.228	6.45	2.41	0.285	0.119	0.0442
9,220	0.877	0.354	8.07	4.01	0.480	0.120	0.0595
9,810	0.966	0.443	9.47	5.33	0.650	0.122	0.0687
10,410	1.032	0.509	10.74	6.53	0.819	0.125	0.0762
"	1.022	0.499	10.64	6.40	0.778	0.122	0.0732
"	1.037	0.514	10.80	6.59	0.812	0.123	0.0752
"	1.046	0.523	10.89	6.70	0.825	0.123	0.0757
"	1.034	0.511	10.77	6.56	0.808	0.123	0.0751
11,020	1.096	0.573	12.09	7.78	0.981	0.126	0.0812
11,680	1.144	0.621	13.38	8.94	1.140	0.128	0.0854
12,240	1.197	0.674	14.67	10.15	1.296	0.128	0.0885
"	1.198	0.675	14.68	10.16	1.316	0.130	0.0897
"	1.198	0.675	14.68	10.16	1.306	0.129	0.0891

17. Inspection of the columns headed M/Q_2 (represented graphically in Fig. 5) shows beyond question that, contrary to what the

Fig. 5.



preliminary investigation seemed to indicate, the mass of ozone produced per coulomb sent through the gas increases with the potential difference applied between the electrodes of the generator, and that the increase in the former is apparently directly proportional to the increase in the latter. In addition, it is evident that the insertion of the high resistance not only decreases the quantity of electricity that passes as conduction current through the gas, but also decreases a great deal the mass of ozone produced per *coulomb of what is conducted.* And again, the presence of the resistance lessens decidedly the rate at which M/Q_2 increases with the potential. The circles around the points representing the mean values of M/Q_2 are intended to indicate approximately the degree of reliability that could be reasonably expected. Similar straight lines (not shown here) represent M/Q_2 as a function of Q_2.

18. In Fig. 5 the values of M/Q and M'/Q' are also represented. Here it is to be noticed that, in addition to what is apparent from the discussion of Fig. 4, the mass of ozone produced per coulomb of the *total quantity* of electricity used in charging the generator increases almost, if not quite, in direct proportion to the increase of the potential, provided the resistance in the circuit is negligible; but that this is not at all the case if the resistance is considerable, although proportionality is approached as the potential is increased.

19. Some experiments were made to determine the effect of considerable water-vapor on the production of ozone; but as was mentioned in 12, it was impossible to maintain constant conditions within the generator long enough so that determinations taken several hours apart could be compared with each other. However, in every one of fifteen determinations the yield of ozone per coulomb sent *through the gas* was found to be from ten to fifteen per cent. less than when well dried oxygen was employed with the same potential difference between the electrodes of the generator. And here, too, there *seemed* to be indications that, as long as the gas remained under the same conditions, the increase in the yield of ozone was directly proportional to the increase in the potential.

20. The results described in the last few paragraphs are not out of harmony with those obtained by Warburg [1] in the case of the silent electrical discharge from points. He found that the production of ozone seemed to be closely connected with the amount of illumination, and that when the positive brush discharge made its appearance, the ozone formed per coulomb increased rapidly with the current strength, although the ozone produced by the negative discharge seemed to be independent of the current. In the writer's experiments increase in potential was accompanied by increase in current. In the Siemens generator both positive and negative light are present, and it also seems reasonable to expect that the amount of illumination would be influenced by such things as the resistance

[1] E. Warburg, Sitzungsber. d. k. Akad. de Wissensch. zu Berlin, p. 1011, 1903; Ann. d. Physik., 13, p. 464, 1904.

in the circuit, the nature of the gas, and the presence of water-vapor. The Siemens generator, however, gives a much greater yield of ozone for a given quantity of electricity sent through the gas. It is possible that the great difference in current density in the two cases may have considerable influence.

Comparison with the Results of the Preliminary Experiments.

21. It remains to point out a few things which seem to offer plausible explanations for certain differences between the results here described and those of the preliminary experiments. The discrepancies appear to arise mainly from the two sources of error referred to in 1; and these errors in the earlier work were evidently much greater than was then suspected. But, in addition, inserting a high resistance while using the galvanometer[1] probably changed the conditions within the generator; and it is possible that some differences are to be referred to the reduction of the distance between the walls bounding the gas-space from 0.8 mm. to 0.64 mm.

Poor insulation along the glass surfaces would account for the irregularities and discontinuity previously observed in the neighborhood of the critical potential and would cover up slight differences in conductivity that depended on the condition of the gas used. Surface leakage would also tend to mask the increase in M/Q_2 with the potential. And good evidence of the inadequate internal insulation of the generator employed in the earlier experiments is afforded by some attempts to use moist air and oxygen, which gave values for the capacity only five or ten per cent. less than those obtained when the gas space was filled with mercury.

It is also to be noticed that the greatest value of M/Q_2 that appears in Table II. is considerably less than the smallest value to be found in the corresponding table of the writer's earlier paper. While part of this difference is possibly due to the differences in the generator referred to above, it seems much more reasonable (5) to refer the large values previously obtained to failure of a portion of the electricity to be measured to pass properly through the galvanometer.

[1] A. W. Gray, Physical Review, Vol. XIX., p. 293.

TABLE IV.

V	a	b	c	d	e	f
3,070	1,240		1,190			
3,660	1,480		1,420		1,490	
4,250	1,720		1,640 1,610	1,720		1,720
4,850	1,960		1,820 1,710	1,940	1,960	1,950
5,500	2,200	2,190	1,840 1,750	2,160	2,230	2,210
6,160	2,420	2,240	1,830 1,740	2,360	2,490	2,460
6,430				2,380		
6,600				1,870		
6,710	2,480	2,010	1,750	1,660	2,700	2,630
7,380	1,790	1,700	1,840	1,540	2,900	2,840
7,960	1,720	1,650	1,910	1,520	3,030	2,960
8,590	1,740	1,700	1,950	1,530	3,120	3,050
9,220	1,780		2,060		3,140	
9,810	1,790	1,730	2,150	1,580	3,190	3,120
10,410	1,830				3,250	
11,020	1,840	1,800	2,240		3,320	3,250
11,680	1,910		2,270		3,420	
12,240	1,910	1,890	2,290	1,800	3,470	3,440

APPLICATION OF WARBURG'S THEORY OF THE SIEMENS OZONE GENERATOR.

22. Warburg[1] has given a theory of the Siemens ozone generator in which an important part is played by what he terms the "minimum potential," that is, the potential difference between the boundaries of the gas space when conduction through the gas ceases. Designating this by $\overline{V}_2$ and using the notation employed in the present paper Warburg expresses this in the form

$$\overline{V}_2 = \frac{V}{2}\left[1 - \left(1 - \frac{C_0}{C_2}\right)\frac{C_v}{C_0}\right];$$

this can also be expressed (see p. 350) in the form

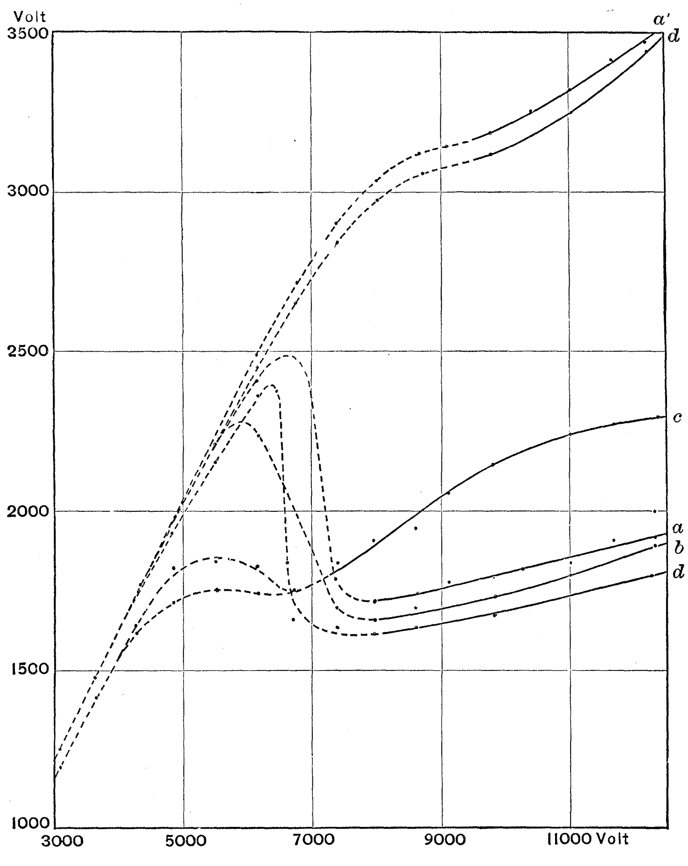
$$\overline{V}_2 = \frac{V}{2}\left(1 - \frac{C_v}{C_\infty}\right).$$

This form is much better adapted to the determination of $\overline{V}_2$ since all the quantities can be easily measured electrically, whereas in calculating C_2 from the dimensions of the generator, very slight errors in measurement have an enormous influence.

[1] E. Warburg, Verhandl. d. Deutschen Phys. Gesellsch. zu Berlin, **22**, p. 382, 1903

From the data in Table I. $\overline{V_2}$ has been calculated and recorded under corresponding headings in Table IV. Fig. 6 represents the same facts graphically, the abscissæ being V and the ordinates $\overline{V_2}$.

Fig. 6.



The maxima in the curves seem to mark the potential differences between the electrodes at which conduction through the gas begins to take place pretty generally.

Warburg also gives an expression for the potential difference, $(V_2)_0$, between the boundaries of the gas when conduction begins. It is difficult to decide what value of V should be used in this expression to calculate $(V_2)_0$ for a layer of gas 0.064 cm. thick enclosed between glass walls. According to data given by Paschen[1] the sparking potential difference between metallic spheres 1 cm. in radius and 0.064 cm. apart in ordinary air is about 3,360 volts. This value is obtained for $(V_2)_0$ when a point at about the middle of the steep descent of curve *d* in Fig. 6 is chosen as the basis of the calculation. This corresponds to the point of inflection of curve *d*, Fig. 3.

CONDITIONS FAVORABLE TO THE ECONOMICAL PRODUCTION OF OZONE.

23. From what has been brought out in this paper, it would seem of importance to those engaged in the preparation of ozone for technical purposes to secure the following conditions:

1. Good surface insulation of the generator, both internal and external, by means of some such device as described in 4.

2. Dry oxygen.

3. Charging and discharging as sudden as possible. For this reason the resistance and self-induction of the circuit should be reduced to a minimum, and it is also possible that operation by connection with a Leyden battery somewhat as described might yield better results than the ordinary method of employing an induction coil or an alternating current dynamo, as these machines could not give such a rapid change in the potential difference between the electrodes. Merely placing the generator in parallel with the spark-gap of an electrical machine, as was done by Shenstone and Priest,[2] is inefficient, because the charging takes place so slowly that no illumination,[3] and consequently no ozone,[4] is produced.

In conclusion, the writer wishes to acknowledge his obligations to Professor Warburg for his kindly interest and helpful criticisms, and also to the University of California for generous financial aid extended through the Whiting Fellowship in Physics.

BERLIN, PHYSICAL INSTITUTE OF THE UNIVERSITY,
April, 1904.

[1] Paschen, Wied. Ann., **37**, p. 79, 1889.
[2] W. A. Shenstone and M. Priest, Jour. Chem. Soc. Trans., **63**, p. 960, 1893.
[3] A. W. Gray, Ann. d. Phys., **13**, p. 486, 1904.
[4] J. J. Thomson and R. Threlfall, Proc. Roy. Soc., **40**, p. 340, 1886.