8. The method here employed, as well as the results, should prove very useful for studying salt effects in organic and biological media. It is far more sound from a kinetic or a thermodynamic point of view than the usual method which employs single electrodes and ordinary salt bridges.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

THE FORMATION OF OZONE BY CATHODE RAYS

BY ABRAHAM LINCOLN MARSHALL

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The purpose of this investigation was to secure quantitative data on a supposedly simple reaction, the production of ozone from oxygen under the influence of high velocity electrons, which could be used in the interpretation of more complicated reactions. It has been found, however, due to the secondary decomposition of the ozone formed, that an analysis of the results is far from simple. The cathode ray tube recently described by Coolidge[1] was used, which allows one to obtain an intense source of very high velocity electrons. The various controllable variables, such as duration of exposure, average velocity and number of electrons, size and shape of the reaction chamber, were studied separately.

Not much work has been reported in the literature on the chemical effects of high velocity electrons in gaseous systems. Krüger and Moeller[2] have studied the formation of ozone with very low intensity, low velocity electrons and their work has been subsequently very materially amplified by Krüger and Utesch.[3] The latter worked with a hot cathode tube as a source of electrons and used an aluminum foil, 0.011 to 0.005 mm. thick, supported on a brass plate containing 65 holes 0.8 mm. in diameter as a window through which they obtained electrons from their tube. The source of voltage was a 500-cycle, high voltage transformer with a single kenotron rectifier giving peak voltages up to 60 kv. The largest current used in the tube was 0.4 milliampere. With a tube current of 3×10^{-4} ampere, 4.5×10^{-5} ampere was incident on the aluminum foil and of this 2.0×10^{-6} ampere passed through into the reaction chamber. The maximum amount of energy entering the reaction vessel in any experiment was estimated to be 0.12 watt. In one set of experiments a vessel containing two condenser plates placed 26 mm. apart was fastened to the window end of the tube. The plates were 4 × 2.5 cm. The diameter of the cathode ray beam at the window was 19 mm. and the authors be-

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[1] (a) Coolidge, *J. Franklin Inst.*, December, 1926, p. 693; (b) *Am. J. Röntgenol. Radium Therapy*, **19**, 313 (1928).

[2] Krüger and Moeller, *Physik. Z.*, **13**, 1040 (1912).

[3] Krüger and Utesch, *Ann. Physik*, **78**, 113 (1925).

lieve that none of the primary electrons hit the condenser plates. With the tube operating, and oxygen at atmospheric pressure in the cell, voltage was applied to the condenser plates. At about 3000 volts, saturation current was reached and this current was taken as a measure of the intensity of ionization. The amount of ozone formed with the tube operating under the same conditions was determined and it was then possible to calculate the ratio of the number of molecules of ozone formed to the number of ions formed. The values obtained for this ratio range from 12 to 40. Any uncertainty in this value comes from the measurement of the saturation current, and in view of the importance of the value of this ratio in developing the theory of these reactions the measurements should be further substantiated. In their experiments oxygen was circulated through the reaction vessel at varying rates up to 15 liters per hour, and it was found that the amount of ozone formed increased up to a circulation of 10 liters per hour and then remained roughly constant. From the results it was calculated that 6–11% of the energy put into the gas was used to form ozone, from 2–4% caused ionization and the remainder heated up the gas. Their conclusion was that the formation of ozone by cathode rays was not connected with ionization of oxygen but with activation. The larger fraction of the energy absorbed from the electron stream was taken up in small amounts which produce excited oxygen molecules and these subsequently react to form ozone.

Experimental Method

The cathode ray tube was operated from a 200-kv. transformer which in turn was fed from a 1:1 transformer having a secondary insulated for 100 kv. As the case of the high voltage transformer was insulated from ground and connected to its primary and to the middle of the secondary, this method of operation enabled one to ground the anode end of the tube.[4] Since the cathode ray tube only imposes a half-wave load on the line, the inverse or non-useful voltage would normally be higher than the useful. This imposes an unnecessary strain on the tube and high voltage transformer and renders difficult a measurement of the voltage usefully employed. To obviate this difficulty, the wave form is distorted on the low voltage side of the transformer by connecting a half-wave load to the line, in the form of a mercury arc, on that half of the wave not used by the cathode ray tube. This load is made much greater than that of the tube and thus causes the inverse voltage to fall below the useful. Voltage was measured by means of a regulation sphere gap using the standard tables of the A. I. E. E. for calibration. A large ballast resistance was placed in the primary circuit of the 1:1 transformer which was connected to a 550-volt, 60-cycle supply. The ballast resistance limited the energy input if for any reason the high voltage insulation broke down.

The tube used was modified slightly from that described by Coolidge, to enable one to fasten the reaction vessel directly to the anode arm of the tube. An invar ring one inch wide was brazed onto the end of the invar sleeve which constitutes part of the anode structure of the tube. The cell was fastened to a similar ring and the two were

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[4] Ref. 1 a, p. 707.

clamped together with a rubber gasket between them. This made a gas-tight joint which could be easily assembled and aided greatly in all subsequent manipulation.

The bulb of the tube was 30.5 cm. in diameter and the tube was 89 cm., overall length. A detailed description of this particular type of tube which is the best available at present for operation in air has been given by Coolidge.[1b]

The tube and high voltage source were placed in a lead house having $^1/_8''$ to $^1/_4''$ thick walls and very thick lead glass windows. This gave complete protection from both x-rays and high voltage; the former was very necessary in an investigation of this nature where the tube was to be operated almost continuously. A remote control device was inserted in the power line supplying the high voltage transformer. Safety switches were placed on all the doors of the house so that it was impossible to come in contact with the high voltage circuit when the power was on. The filament of the cathode ray tube was operated from a storage battery in order to obtain very steady discharge currents. To avoid corona losses the battery was placed in an iron box having all the corners and edges rounded and the high voltage leads, which were kept very short, were made of 2" brass tubing with 4" spheres placed at all right angle bends.

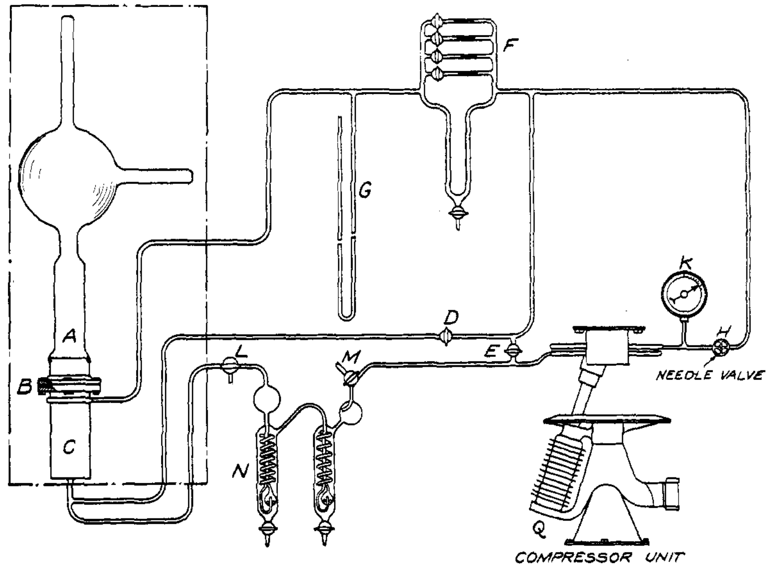


Fig. 1.

The window material employed was resistal,[1b] which is an alloy consisting of 18 parts by weight of chromium, 3 parts of silicon, 0.2 of carbon, 4–3.8 of iron and 35 of nickel. The window thickness varied from 0.50–0.57 of a mil.

A cooling coil of copper was soldered around the metal sleeve of the anode through which water was circulated. With this cooling it was possible to operate the tube continuously at 180 kv. and 1 milliampere.

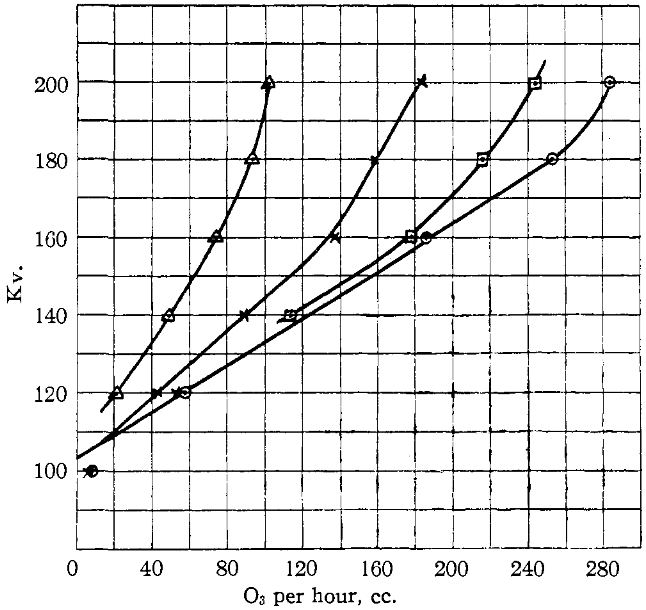
A closed system, illustrated in Fig. 1, was used at first and pure oxygen made by the electrolysis of a solution of potassium hydroxide was circulated by means of a compressor Q. The compressor unit was designed by J. G. deRemer and is described in the *Proc. Am. Soc. Mech. Eng.* for 1926. It operated on the principle of Archimedes' screw using mercury as the compressing fluid. The pump is of all steel construction and contains no stuffing-boxes, so that there is no opportunity for oxygen to be contaminated with grease or to leak from the system. The oxygen always contained traces of mercury vapor coming from the mercury in the pump and water vapor from the gas scrubbers. The high pressure side of the unit was kept at 39 lbs. above atmospheric by means of the needle valve H, the pressure being measured on the gage K. The maximum rate of flow from the compressor was 1200 liters per hour measured at one atmosphere pressure. The rate of flow through the cell C was measured on the flowmeter F and controlled by means of the by-pass D. In this it was possible to vary the rate of flow through the reaction vessel from 20 to 1200 liters per hour and keep the pressure in the cell C always at one atmosphere. After being exposed in the reaction vessel the oxygen was passed through two scrubbing bottles, N, to remove any ozone formed. These scrubbers contained an alkaline solution of potassium iodide (50 g. KI, 25 g. KOH, per liter) and ozone could not be detected in the effluent gases when circulating at 1200 liters per hour. The full flow of gas from the compressor was sent through the scrubbers in order to minimize as much as possible any momentary pressure inequalities in the system due to the method of flow through the goose-neck of the scrubber and thus ensure a steady flow of gas through the reaction vessel. After an experiment the stopcock at E was opened and then L and M were opened to the atmosphere. The solution was removed from N and replaced; pure oxygen was bubbled through to displace the air and then the wash bottles were reconnected to the system for the next experiment. These operations required from five to ten minutes so that it was quite feasible to make a large number of experiments in a day with a single filling of the whole system.

Experimental Results

Surface Effects.—A series of experiments was made to determine whether an extension of the surface exposed in the glass reaction vessel had any effect on the amount of ozone formed. A cell 87 mm. in diameter and 20 mm. long was filled with loosely packed glass wool which came in contact with the tube window. The presence of the glass wool modified greatly the method of flow of the oxygen in the cell and tended to form pockets where the gas would be moving slowly. In ten minutes with circulation at the rate of 1200 liters per hour, 180 kv. and 1 milliampere, 11.2 cc. of ozone was formed. Blank experiments without glass wool gave 21.3 and 18.7 cc. in the same time interval. The glass wool was then replaced and 10.7 cc. of ozone was formed. A number of experiments were also performed with a cell 250mm. long filled loosely with glass wool to within 50 mm. of the tube window. About 35 cc. of ozone was formed in both this experiment and the control without glass wool. A fine network of tungsten wire was used to fill the cell and this apparently produced only a very minor effect.

In order to determine whether the "resistal" window was exercising an effect on the course of the reaction, it was completely covered with a sheet of mica 0.5 mil thick which was kept in close contact with the window by a brass ring. Three consecutive experiments with oxygen circulating at 1200 liters per hour, 200 kv. and 1 milliampere gave 39.2, 38.9 and 38.1 cc. of ozone in a ten-minute interval, while a blank without the mica gave 40.4 cc. of ozone.

The nature of these results indicates that the amount of ozone formed is almost entirely independent of the nature or extent of surface exposed during raying, and the ozonization of oxygen by cathode rays is a homogeneous gas phase reaction. This does not mean, of course, that there are no complications introduced by the walls due to reflection of primary and emission of secondary electrons during bombardment.



Cell length: △, 5 mm.; ×, 24 mm.; ⊡, 56 mm.; ⊙, 247 mm. Tube current, 1 milliampere. Pressure, 1 atmosphere. Rate of circulation, 1200 liters per hour.

Fig. 2.

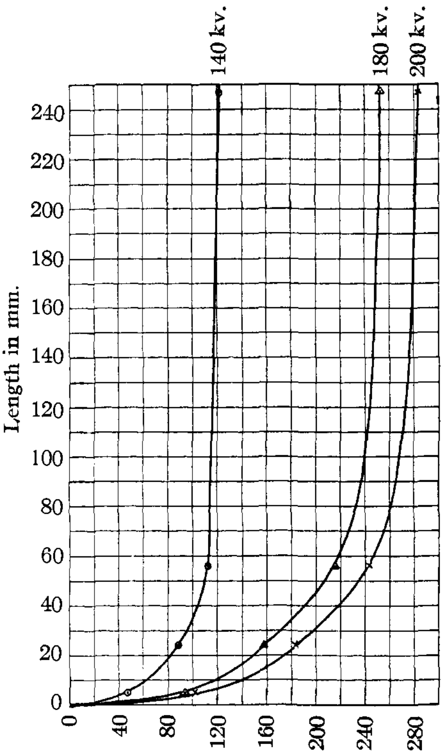
Variation in Yield with Voltage and Cell Length.—The results given in Table I for three different cells show in part the reproducibility of the results for a given set of conditions and are tabulated to show how the yield varies with the voltage applied to the tube. The rate of circulation was 1200 liters per hour with a tube current of 1 milliampere.

TABLE I

OZONE FORMED PER HOUR, CC.

Kv. (max.) applied		Cell length, cm.		
		10	25	2
200	(257, 264, 261)	261	282	177
180	(239, 234, 232)	235	242	161
160		183	198	137
140		120	132	99
120		57.8	70	49.7
100		12.7	11.4	10.7

Air was used in the 10-cm. cell in one experiment at 180 kv. and 177 cc. of ozone was formed as compared with 235 cc. with pure oxygen. The above results were all with glass cells. Fig. 2 illustrates the results of a more detailed study with copper reaction vessels varying in length from 5 to 247 mm. Copper cells were used wherever possible in all subsequent work since the glass did not stand up well under the intense bombardment and would often crack badly after only short use. In Fig. 3 the yield for a given voltage is shown as a function of the cell length. These results are for 1 milliampere tube current and oxygen circulating at 1200 liters per hour.



O_3 formed per hour, cc.

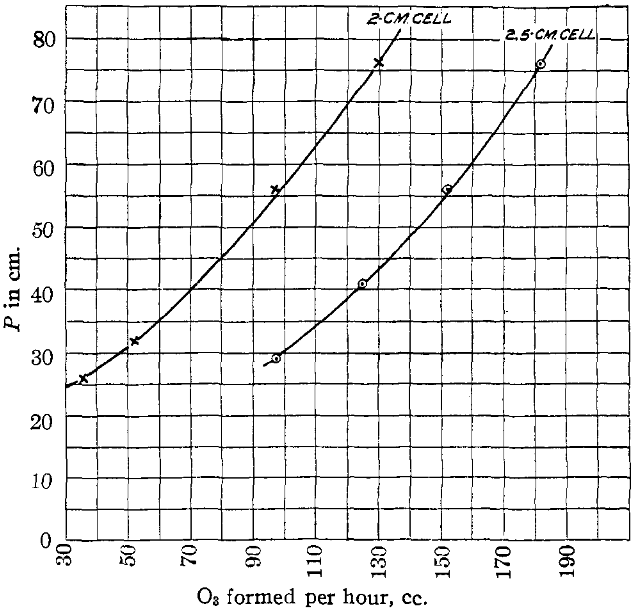
Fig. 3.

Pressure Variable.—Experiments were made with two cells on the effect on the yield of varying the oxygen pressure. The tube was operated at 180 kv., 1 milliampere and oxygen circulated at the rate of 655 liters per hour, the volume circulated being measured at the pressure under consideration. Fig. 4 illustrates the results obtained; the relationship is not a linear one and shows that at high pressures the yield for a given cell becomes independent of pressure.

Rate of Flow.—In connection with the investigation of the effect of varying the rate of flow of oxygen through the cell, a large number of preliminary experiments were made while determining the best method of carrying out the experiments. From studying these results, a purely empirical result was discovered, namely, that there appeared to be an approximately linear relationship between the logarithm of the rate of flow and the yield of ozone for a given time of raying. At low tube currents this relationship appeared to be very real over the whole range of circulation employed but deviations became large at higher currents. Fig. 5 illustrates the general trend of all these results. So far no theoretical significance has been obtained for this relationship, but it proved quite useful in the early stages of the experimental work in detecting gross errors in results obtained. A similar result was obtained when the tube current was varied.

The yield for a given rate of circulation is a linear function of the logarithm of the tube current.

In the experiments using the mercury compressor, it was noticed that a film of mercuric oxide deposited on the walls of the tubing leading away from the reaction chamber. The mercury could be removed from the gas stream by circulating through a trap immersed in carbon dioxide–ether mush. It was found that the yield of ozone was about 1 cc. greater in a fifteen minute period when the mercury was removed. Calculation showed that about 0.8 cc. of mercury vapor measured at N.T.P. would pass through the system in this period and apparently it was all oxidized.

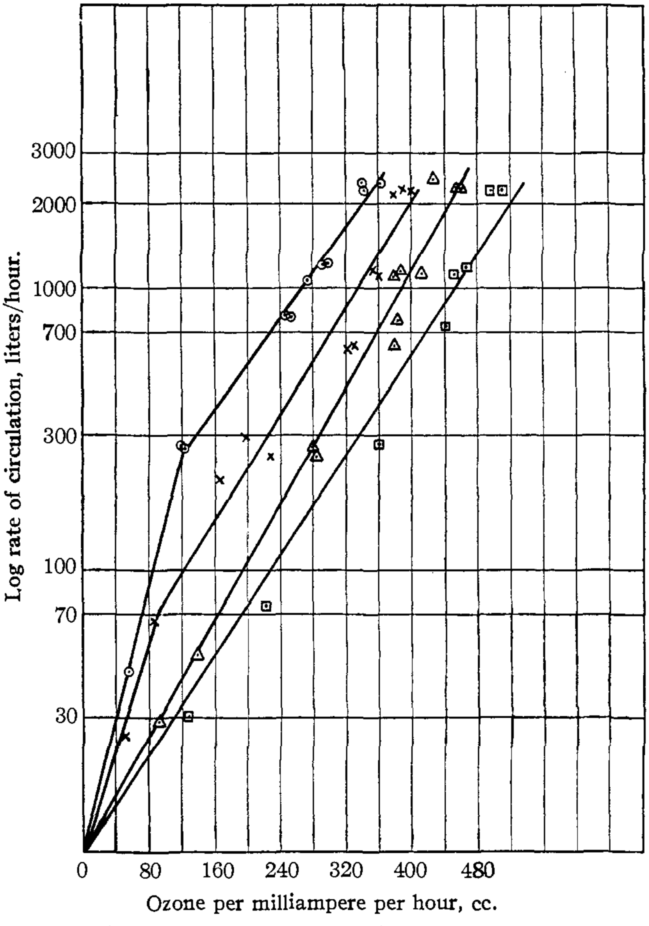


180 kv., 1 milliampere. Rate of circulation, 655 liters per hour.

Fig. 4.

At about this stage in the work a number of experiments were made with the electrolytic oxygen which we have on tap throughout the laboratory. This contains small quantities of hydrogen, nitrogen and water vapor with a trace of carbon dioxide. It was found that the results obtained with this supply of oxygen agreed very well indeed with those obtained from the specially purified gas used previously. All subsequent experiments were therefore made with oxygen from the line. In order to be able to pass oxygen through the system at rates of flow up to 2400 liters per hour and discharge the effluent gas into the atmosphere, it was necessary to operate in the cell at pressures above one atmosphere, and all subsequent experiments were carried out at a pressure of about 91 cm. of mercury.

Several thousand experiments were made with two sizes of cell, namely, 162 cc. and 1520 cc. at various currents, voltages and rates of circulation in order to obtain reliable data for quantitative treatment. The results for the 1520-cc. cell are given in Table II for a tube voltage of 180 kv. and varying currents. Each figure is the average of 4 to 5 experiments and the various experiments were made in random order to detect any source of error that might creep in during the course of a series of experiments.



Volume of cell, 162 cc.; voltage, 180 kv.; pressure, 91 cm.; current, ⊙, 1.00 ma.; ×, 0.50 ma.; △, 0.20 ma.; ⊡, 0.10 ma.

Fig. 5.

In treating these results, it will be more convenient to deal in terms of concentration of ozone and time of exposure rather than rate of flow and amount of ozone formed and these are calculated in the third and fourth columns of the table. In order to make this transformation, the assumption is made that the concentration of ozone is uniform in the cell as the gas passes through. This may be approximately correct at high rates of passage where the flow through the cell is turbulent and the gas is stirred up very rapidly. At lower rates of circulation, however, the concentration

TABLE II

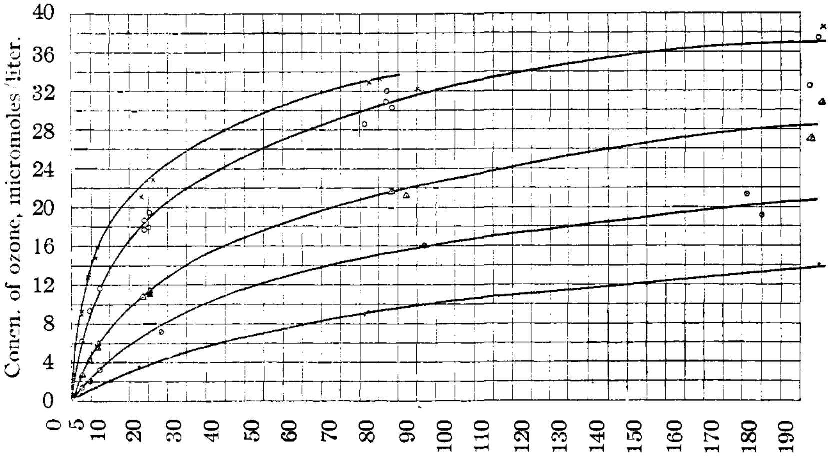
VARIATION OF OZONE YIELD WITH CIRCULATION

Circn., liters/hr.	O_3 per hour, cc.	t, sec.	Concn. ozone, micromoles/liter
1 Milliampere Current			
870	289	6.2	14.8
1210	353	4.46	13.0
2136	428	2.53	8.94
288	146	18.7	22.7
60	49.6	90.0	37.0
27.6	22.4	196	36.3
No circn.		600	37.2
No circn.		600	35.0
27.0	23.4	200	38.8
61	43.6	89	32.0
280	141	19.3	22.5
816	292	6.62	16.0
69	51.4	78	33.2
1266	363	4.26	12.8
2124	436	2.54	9.2
300	142	18	21.1
70.8	52	76	32.8
260	139	20.8	23.8
0.5 Milliampere Current			
No circn.	6.6	600	31.9
28.5	20.8	192	32.5
67	46.4	82	30.9
288	120	19	18.6
750	196	7.3	11.7
1134	237	4.83	9.35
1164	245	4.71	9.4
2100	291	2.61	6.19
798	209	6.87	11.7
270	118	20.3	19.5
66.6	47.7	82	32.0
28.3	23.7	193	37.4
No circn.		600	38.2
26.7	21.9	205	36.5
2120	294	2.58	6.19
1218	242	4.50	8.6
786	206	6.97	11.7
270	118	20.3	19.6
306	117	18.0	17.6
72	46.1	76.3	28.6
276	110	19.9	17.9
66	45	83.4	30.3
0.20 Milliampere Current			
270	69	20.3	11.4
66	32	83	21.6
26.4	18	207	30.7
No circn.		600	20.4
786	97	6.97	5.53
1122	112	4.88	4.44
2100	124	2.61	2.63
1120	112	4.89	4.47
768	103	7.13	5.99
294	71	18.6	10.8
63	30	8.7	21.2
28.2	17	194	27.1
No circn.		600	29.2
2040	124	2.68	2.72
270	67	20.3	11.1
1200	112	4.58	4.17
270	70	10.3	11.6
66	32	83.4	22.0
28.8	16	190	24.8
0.10 Milliampere Current			
744	53	7.40	3.24
1146	51.4	4.80	2.00
1920	59.8	2.86	1.39
744	52.1	7.40	3.13
258	41.3	21.3	7.15
1140	54	4.82	2.11
2075	60.5	2.65	1.30
60	21.5	92	16.0
60	21.5	92	16.0
31.2	14.8	176	21.3
30.5	13.0	180	19.1
No circn.		600	25.3
No circn.		600	22.3
258	41.9	21.3	7.24
780	54.7	7.06	3.12
1170	61.8	4.69	2.36
1968	66.5	2.79	1.51

Table II (*Concluded*)

Circn., liters/hr.	O_3 per hour, cc.	t, sec.	Concn. ozone, micro-moles/-liter	Concn., liters/hr.	O_3 per hour, cc.	t, sec.	Concn. ozone, micro-moles/-liter
1164	59.5	4.73	2.28	72	13.8	76.4	8.9
1950	66.2	2.82	1.51	70.8	14.6	77.6	9.2
				27	8.5	203	14.0
0.05 Milliampere Current				310	24	17.7	3.5
2100	30.9	2.61	0.66	1110	29.6	4.95	1.19
1130	28.2	4.85	1.11	2100	33.3	2.62	0.71
840	25.2	6.55	1.34	870	28.6	6.32	1.46
300	24.9	18.0	3.7	294	24	18.3	3.65

may vary greatly from point to point through the cell. The entering gas contains no ozone and meets the highest electron density at the window of the tube. At the exit the ozone concentration is high and the rate of production much lower. The concentration should be much more uniform in a short cell than in a long one. The time is taken as the average time that a molecule is present in the cell; if there is any tendency to form pockets in the cell when the gas is moving more slowly, the calculated time will be incorrect and again the factor will be more important at the slower rates of flow.



1520-cc. cell. 180 kv. ×, 1.00 ma.; ⊙, 0.50 ma.; △, 0.20 ma.; ⊖, 0.10 ma.; ●, 0.05 ma.

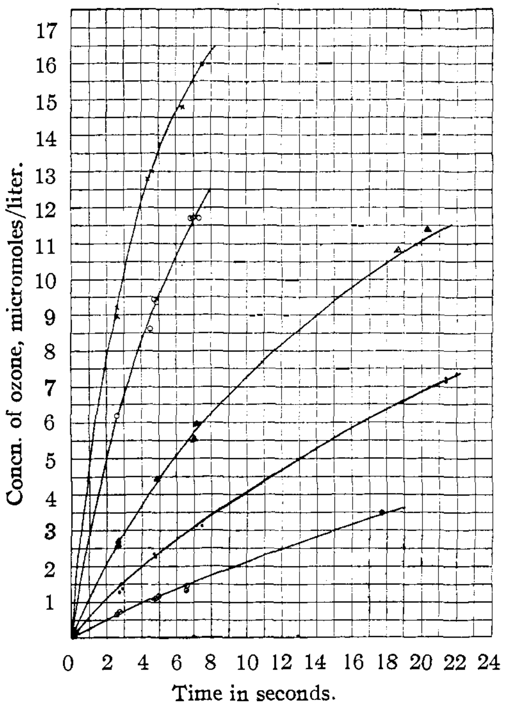
Fig. 6.

$$C_{O_3} \text{ (in micromoles per liter)} = \frac{\text{Cc. of ozone formed in } t \text{ minutes}}{\text{rate of flow in liters/hour}} \times \frac{60}{t} \times \frac{1}{22{,}400}$$

$$t \text{ in seconds} = \frac{3600 \times \text{volume of cell in liters}}{\text{rate of flow in liters/hour}}$$

where t is time of exposure.

Some of the results which have been obtained are presented graphically in Figs. 6, 7 and 8. One at once observes that the rate of increase of concentration with time is decreasing rapidly and that a steady state is soon reached. The concentration of ozone in the steady state is about 1 molecule of ozone to 1700 of oxygen. At first sight it did not appear probable that ozone at such a low concentration was being decomposed as fast as it was formed and an alternative explanation was advanced: an intermediate product is formed initially by the cathode rays and is able to break down in two ways—either reverting to oxygen or forming ozone. A study of the reaction between hydrogen and oxygen, however, gave definite evidence in support of the instability of ozone at this low concentration. This will be reported in a subsequent paper.



1520-cc. cell. 180 kv. ×, 1.00 ma.; ○, 0.50 ma.; △, 0.20 ma.; ●, 0.10 ma.; ⊖, 0.05 ma.

Fig. 7.

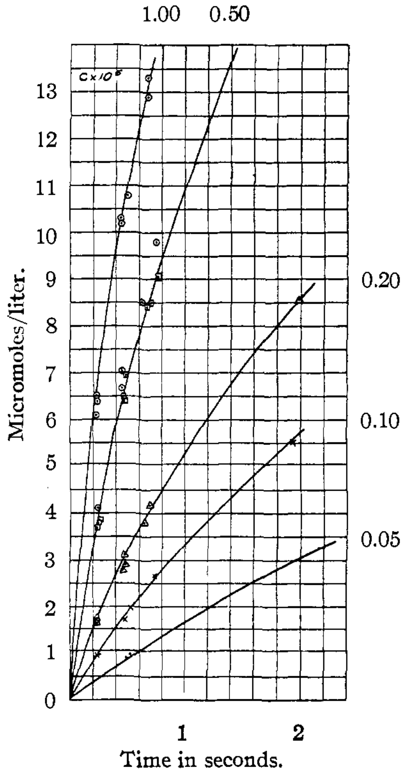


Fig. 8.—Volume, 162 cc.

Warburg[5] and Warburg and Leithäuser[6] have studied the rate of formation of ozone in the silent discharge by both static and dynamic methods. In this case also the rate of formation of ozone falls off rapidly with in-

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[5] Warburg, *Ann. Physik*, [4] **9**, 781 (1902).

[6] Warburg and Leithäuser, *ibid.*, [4] **28**, 24 (1909).

creased time of exposure. Table II illustrates some of the results which they obtained with a glass ozonizer having electrodes 1.4 mm. apart and operating on 50 cycles with a current of 1.15 milliamperes. The pressure was 764 mm. and the temperature 19.5°.

TABLE III

PRODUCTION OF OZONE BY SILENT DISCHARGE

Concn. O_3, mml./liter	341	513	660	689	907	1176	1381	1514	1785
O_3, cc. at N.T.P. per ma./hr. obs.	204	202	195	193	186	175	172	168	159
O_3, cc. at N.T.P. per ma./hr. calcd.	207	202	197	196	189	180	173	168	159

The calculated yield of ozone at zero concentration was 218 cc. per milliampere hour and the concentration of ozone in the steady state which was obtained by a separate experiment in a static system was 3720 micromoles per liter. The striking part of these results as compared with those obtained with cathode rays is the much greater concentrations of ozone obtained. In this case one molecule in twelve is converted to ozone in the steady state, where with cathode rays the concentration was one in seventeen hundred. There is a very marked increase indeed in the stability of ozone in silent discharge as compared with the cathode ray stream.

They have discussed their results theoretically on the basis of an equation involving both formation and decomposition of ozone and have obtained good quantitative agreement with experiment. The amount of ozone formed in time *dt* is proportional to the current *I* and to the oxygen concentration. The amount of ozone decomposed is taken as proportional to the current and the ozone concentration

$$\frac{\mathrm{d}(n_{O_3})}{\mathrm{d}t} = I(k_1c_{O_2} - k_2c_{O_3})$$

where n_{O_3} is the number of molecules of ozone formed in time d*t*. If there is no ozone present the rate of formation is given by

$$\frac{\mathrm{d}(n_{O_3})}{\mathrm{d}t} = k_1Ic_{O_2}$$

and the amount of ozone formed per ampere hour is

$$A_0 = \frac{\mathrm{d}(n_{O_3})}{I\mathrm{d}t} = k_1c'_{O_2}$$

where c'_{O_2} is the initial concentration of oxygen and $c'_{O_2} - c_{O_2} = 3/2c_{O_3}$.

$$\frac{\mathrm{d}(n_{O_3})}{I\mathrm{d}t} = A_0 - k_1(c'_{O_2} - c_{O_2}) - k_2c_{O_3}$$

The concentration of ozone in the steady state is given by

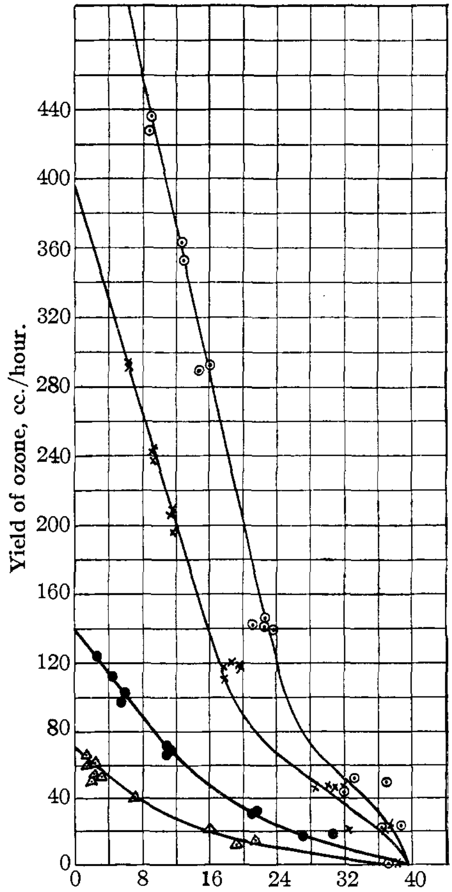
$$A_0 = (3/2\,k_1 + k_2)c'_{O_3}$$

Hence the concentration in the steady state is independent within certain limits at least of the current. The current strength determines the velocity at which equilibrium is attained, but not the equilibrium concentration.

$$
\begin{aligned}
A &= \frac{d(n_{O_3})}{I dt} = A_0 - k_1(c'_{O_2} - c_{O_2}) - k_2 c_{O_3} \\
&= A_0 1 - \left\{ \frac{c_{O_3}}{A_0} (3/2\, k_1 + k_2) \right\} \\
&= A_0 \left(1 - \frac{c_{O_3}}{c'_{O_3}} \right)
\end{aligned}
$$

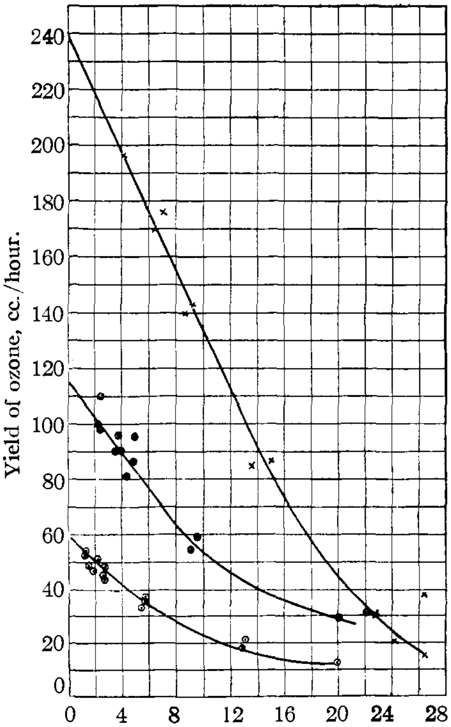
A_0 and A are the moles of ozone formed per ampere hour at $t = 0$ and $t = t$.

From this result, it is evident that the yield of ozone should be a linear function of the concentration of ozone in the gas. The results given in Table II and Figs. 6, 7 and 8 and also others obtained with 130 kv. applied to the tube have been treated in this way in Figs. 9–12. One notices at once that at the higher concentrations of ozone, which represent experimentally the slower rates of flow, the linear relationship breaks down and the yield approaches zero



180 kv., 1520 cc. volume. ⊙, 1.00 ma.; ×, 0.50 ma.; ●, 0.20 ma.; △, 0.10 ma.

Fig. 9.



130 kv., 1520 cc. volume. ×, 1.00 ma.; ●, 0.50 ma.; ⊙, 0.20 ma.

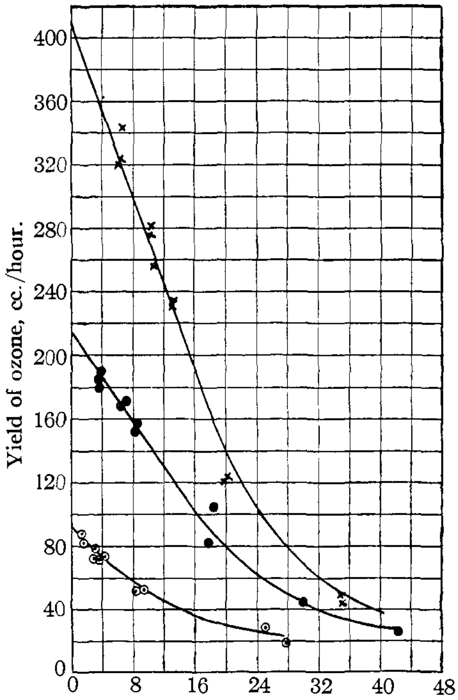
Fig. 10.

more slowly than predicted. This may be due in part to the fact that the values calculated for the concentration are much more inaccurate at the higher concentrations. These portions of the curve have not been treated theoretically since the variation in concentration of ozone throughout the cell is unknown and the radiation density is so far from uniform.

There are two methods available for determining the maximum yield of ozone for a given voltage and tube current. One can draw tangents to the curves in Figs. 5 and 8 at zero time. These give a measure of the actual rate of ozone production when none is present to be decomposed. The other method is to extrapolate the straight lines of Figs. 9–12 to zero concentration of ozone.

The results obtained by the use of these two methods with the data given in Fig. 7 are tabulated in Table IV.

The result for 0.50 milliampere is apparently too large; the discrepancy was not noticed at the time and it has not been possible to recheck this value. When one attempts to draw tangents to the curves at the origin one soon realizes that the results in Cols. 2 and 3 are well within the experimental error and that the extrapolation method is more likely to give a reliable result.



180 kv., 162 cc. volume. ×, 1.00 ma.; ●, 0.50 ma.; ⊙, 0.20 ma.

Fig. 11.

Table IV

Maximum Rate of Ozone Formation

Curr., milliampere	Yield from tangents in Fig. 7	Yield from extrapolation in Fig. 9	Yield per milliampere
1.00	746	640	640
0.50	422	382	764
.20	135	139	695
.10	73.5	70	700
.05	37	..	740

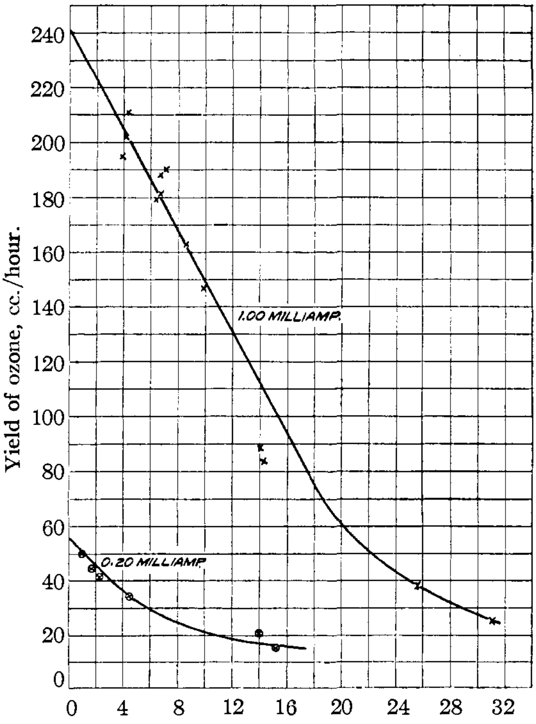
A similar set of results has been obtained with the data from the 163-cc. cell and these are given in Table V.

TABLE V

MAXIMUM RATE OF OZONE FORMATION

Current, milliampere	Yield from tangents in Fig. 8	Yield from extrapolation in Fig. 11	Yield per milliampere
1.00	392	407	407
0.50	202	215	430
.20	91	92	460
.10	49	49	490
.05	24	24	480

The rate of formation of ozone, expressed in micromoles per second, for various times of exposure has been plotted in Fig. 13 as a function of the tube current. For zero time the rate is a linear function of the tube current within the experimental error, but for all actual experiments it deviates from this ideal result due to secondary decomposition of ozone, the deviation being greater the longer the time of exposure and the greater the electron density.



Concn. of ozone in micromoles/liter.

130 kv., 162 cc. volume.

Fig. 12.

A series of experiments was carried out with a large spherical reaction vessel of twelve liters capacity in an attempt to find out what additional effect would be obtained by allowing the electrons to scatter laterally; it was also hoped to obtain more exact data on the concentration of ozone in the steady state. The results are given in Table VI; the voltage used was 180 kv. and the current 0.80 milliampere.

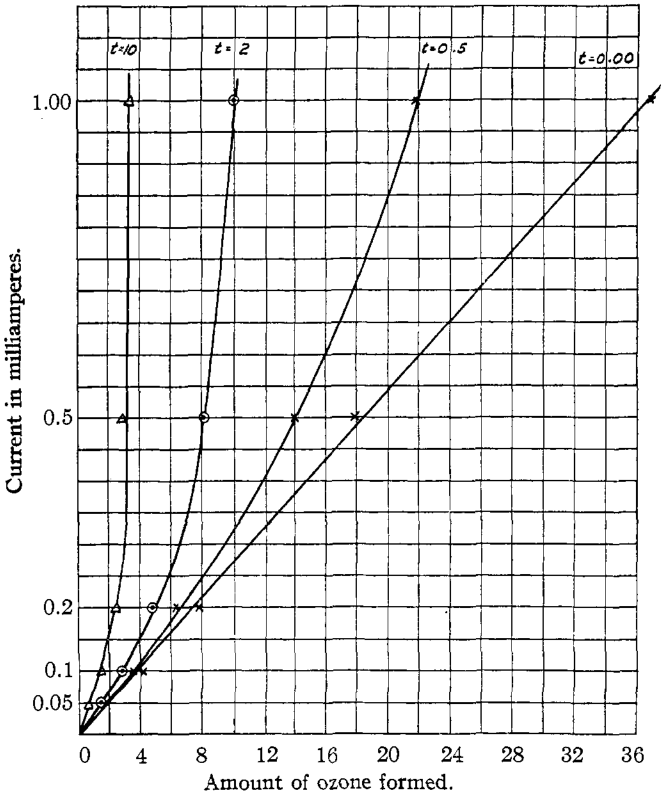


Fig. 13.—All calculated on the basis of one second.

TABLE VI

FORMATION OF OZONE WITH 12-LITER VESSEL

Rate of circulation	O_3 formed per hour, cc.	Time, sec.	Concn. of ozone, micromoles/-liter	$c \times 10^6$ (corr.)
2400	378	18	7.04	7.0
1350	293	32	9.7	9.4
660	183	65.5	12.4	11.7
300	128	144	19.0	16.8
75	69	580	41	26.4
Static	..	300	21.5	..
Static	..	600	26.4	..
Static	..	900	26.4	..
Static	..	1800	26.4	..

The calculated concentrations given in Col. 4 are too large, due to the experimental conditions. The oxygen in this case is passing through a vessel of 12 liters capacity. After the exposure the vessel is still filled with partially rayed oxygen, which, however, has been rayed during the period of the exposure; the amount of gas rayed is thus greater than that passing through the cell during the duration of the experiment. In the case where oxygen was circulating at 75 liters per hour one knows from the static experiments that the ozone concentration is 26.4×10^{-6} mole per liter and this enables one to calculate the actual concentration in all the experiments. When these results are plotted with the ozone yield as a function of its concentration and extrapolated to zero concentration, the maximum yield is found to be 660 cc. per hour for 0.8 milliampere or 825 cc. per hour per milliampere. This result is to be compared with the value of 640–700 cc. of ozone obtained with the cylindrical cell of 1520-cc. volume and 410–490 cc. obtained with the 162-cc. cell. It appears that approximately half of the energy in the electron stream can be expended in a cell 26 mm. deep and 89 mm. in diameter as measured by its ability to produce ozone. Of course, there is considerable reflection of electrons from the walls of the cell, which helps to increase the yield, and the fraction might be much lower if the walls were completely transparent to electrons.

Experiments with an Applied Electric Field

In discussing the work of Krüger and Utesch, the main criticism was launched against their method of determining ionization. If their result is valid and there are as many as 40 molecules of ozone formed per ion, then the conclusions of Lind[7] on the mechanism of these reaction is incorrect. The ozonization of oxygen is a reaction which proceeds with a free energy increase and it would be impossible for one ion to initiate a chain of reactions producing many molecules of ozone. An attempt was made to see if it is possible to obtain saturation currents under somewhat similar experimental conditions to those used by Krüger and Utesch. A copper plate with a slit 1 cm. wide by 5 cm. long was fastened over the window of the tube. This permitted about 20% of those electrons to enter the gas which would have entered in the absence of the shield. Two condenser plates 6 cm. × 8 cm. were placed in the reaction vessel so that they were symmetrically mounted with respect to the slit. The upper edges of the plates were 3 cm. distant from the window of the tube. They were placed either 2.4 cm. or 6.3 cm. apart.

A 10-kw., 60,000-volt DC outfit consisting of transformer, full wave rectifier and condensers was used as a source of voltage; the mid-point of the condenser bank was grounded so that the voltage drop between the window and each of the plates in the reaction vessel was the same.

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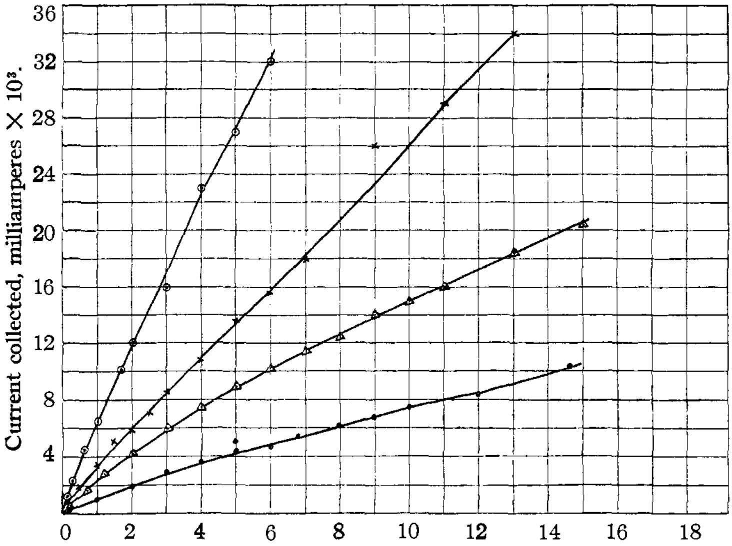
[7] Lind, "Chemical Effects of Alpha Particles," The Chemical Catalog Co., Inc., New York, 1928.

Experiments were first made with and without the field applied, circulating oxygen through the cell and determining the amount of ozone formed. With 180 kv. and 0.50 milliampere, two experiments without applied field gave 46.5 and 55.5 cc. of ozone formed per hour. With the plates 5 cm. apart, 16 kv. applied and a current of 1.3 milliamperes flowing in the ionization chamber, 69 cc. of ozone was formed. With the plates 2 cm. apart, 16 kv. applied and 2.6 milliamperes flowing, 205 cc. of ozone was formed.

A second set of experiments was made with much lower power. The tube was operated at 106 kv. with a current of 0.10 milliampere. A blank experiment without applied field gave 1.6 cc. of ozone formed per hour. With the electrodes 2 cm. apart and 16 kv. applied, a current of 0.11–0.14 milliampere was collected and 3.4 cc. of ozone was formed. The electrodes were than placed 5 cm. apart, 24.5 kv. applied, the same current collected and the same yield obtained. When a voltage gradient as high as 8 kv. per cm. is applied, it is evident that a considerable increase in ionization is obtained, as measured by ozone production; about 3000 volts per cm. is the highest which can be used without causing an increase in the ozone yield. In terms of saturation current phenomena, 3000 volts per cm. should produce saturation and higher voltage should cause increased ionization due to the kinetic energy of the ions becoming sufficient to ionize the gas molecules by impact.

Krüger and Utesch estimated that the maximum current which they had entering their reaction chamber was 2×10^{-6} ampere. The yields of ozone reported in their experiments where ionization was studied varied from 0.3 to 66 cc. of ozone per hour. These are of the same magnitude as those reported above. In Fig. 14 the currents collected in the ionization chamber are plotted as a function of the applied voltage. There is no indication whatever of a saturation current; the curves in some cases were continued up to 40 kv. and were perfectly continuous. In one case with 0.010 milliampere, the yield of ozone would have been of the order of 0.10–0.20 cc. per hour. With 83 kv. applied to the tube, the current collected at 15 kv. was less than 0.0001 milliampere; at 90 kv. applied to the cathode ray tube, it amounted to 0.0013 milliampere, but here also there was no indication of saturation being attained.

The experiments reported above differ, however, in one respect from those of Krüger and Utesch; they used 500-cycle power to operate their cathode ray tube while 60-cycle power was used in this investigation. It is difficult to see how this could affect the current collected in the ionization chamber. The average velocities of the electrons were approximately the same in the two cases. In order to be certain that the absence of a saturation current was not due to some ionization being produced outside the region of the applied field from which an increasing number of ions was drawn as the field increased, the ionization chamber was re-designed. The copper plate over the window of the tube was covered with mica, the condenser plates were moved up in the cell until their upper edges touched this mica and they were enclosed in a mica box. In this way all the ionization occurred in the space between the plates.. Within the experimental error, the results were the same as those already described. These results render the values for the ratio of molecules produced to ions collected, as reported by Krüger and Utesch, very doubtful and the real value for this quantity will remain an open question until a more reliable method is devised for measuring the rate of ion production at high intensities of ionization.



Tube current—with plates 2.4 cm. apart: ⊙, 0.10 ma.; ×, 0.03 ma.; △, 0.01 ma.—with plates 6.3 cm. apart: ●, 0.01 ma.

Fig. 14.

Summary

A cathode ray tube installation has been described which can be conveniently used for studying the effects of high velocity electrons on pure and mixed gases.

The tube can be operated continuously with a current of 0.0010 ampere and 200 kv.

A detailed study has been made of the ozonization of oxygen. The reaction has been shown to occur wholly in the gas phase and to be uninfluenced by the nature of the walls of the containing vessel.

Fifty per cent. of the reaction takes place in a volume within 2 cm. of the

tube window, although the cathode rays have a range of 20 cm. under these conditions. This corresponds to the roughly exponential manner in which the energy of the beam falls off as one proceeds away from the window of the tube.

Ozone is both formed and decomposed under the influence of cathode rays. With continued raying a steady state is reached with an ozone concentration of 1 molecule to 1700 of oxygen. This concentration is independent of the tube current. This value compares with the concentration of 1 in 12 obtained with the silent discharge. Cathode rays have a much greater decomposing action than the silent discharge.

The maximum yield of ozone is 825 cc. of gas, measured under standard conditions and obtained with a tube current of 0.0010 ampere at 180 kv.

It has not been possible to check the results of Krüger and Utesch, who determined the amount of ionization by a saturation current method. Saturation was never observed in any of the experiments—the current in the ionization chamber increasing regularly as the applied field increased.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

COMBINATION OF HYDROGEN AND OXYGEN UNDER THE INFLUENCE OF CATHODE RAYS

BY ABRAHAM LINCOLN MARSHALL

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The reaction between hydrogen and oxygen presented itself as the simplest oxidation reaction occurring in the gas phase which could be investigated. Hinshelwood and Thompson[1] have shown that it is possible to study a homogeneous thermal reaction between these substances in the range 550–600° with velocities increasing in rate up to explosions. It is well known that when flames of hydrogen and oxygen impinge on a cold surface hydrogen peroxide can be detected as one of the products of reaction. Marshall[2] has found that in the case of the photochemical reaction sensitized by mercury vapor the reaction proceeds by way of the peroxide stage and that this product can be obtained in the pure state. Scheuer[3] has studied the combination of hydrogen and oxygen (electrolytic gas) under the influence of α-particles and in all cases reported hydrogen peroxide as one of the products of the reaction, amounting in one case to 16% of the combined hydrogen.

In a previous paper[4] on the ozonization of oxygen the cathode ray tube

[1] Hinshelwood and Thompson, *Proc. Roy. Soc.*, **118**, 170 (1928).

[2] Marshall, *J. Phys. Chem.*, **30**, 1078 (1926).

[3] Scheuer, *Compt. rend.*, **159**, 423 (1914).

[4] Marshall, THIS JOURNAL, **49**, 2763 (1927).