[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE CHEMICAL EFFECTS OF CATHODE RAYS ON OXYGEN, AIR, NITRIC OXIDE AND CARBON DIOXIDE

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The problem of chemical reaction can be studied to advantage through ionic gas phase reactions. The most important progress in this field has been made by Lind,[1] using α-particles, but large quantities of radium are necessary for measurable quantities of chemical products. The limitations are even more severe for β- and γ-rays, and Errera and Henri[2] obtained traces of material only after exposures of about fifty hours to the β- and γ-rays from 500 mg. of radium.

The electrical discharge offers another method for producing ionization and chemical reaction in gases but the phenomena are complicated. In this Laboratory the effect of the electrodes has been studied first by increasing the electrode area[3] and then by reducing it to a minimum.[4] Attempts were made, also, to study reactions brought about by electron bombardment in the absence of electrodes.[5]

Krueger and Utesch[6] studied the formation of ozone by Lenard rays in a small apparatus and reported 20 to 40 molecules of ozone for each ion pair.

The development of the Coolidge cathode ray tube[7] marks an important advance in this field for it is now possible to pass electrons at a high voltage through a window and into a reaction chamber to give a sufficient quantity of product for chemical analysis. The authors are greatly indebted to Dr. W. D. Coolidge of the General Electric Company for the cathode ray tube used in this work.

In this communication a series of gas reactions is reported, comprising the action of cathode rays on oxygen, air, nitric oxide and carbon dioxide. The extent of each reaction was determined by chemical analysis. It was impossible to measure directly the number of ions formed in the gas and the M/N ratios (that is, number of molecules $\div$ number of pairs of ions) could not be determined, but the yields were computed in terms of the number of molecules per electron passing through the cathode ray tube,

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[1] Lind, "Chemical Effects of Alpha Particles," 2d ed., Chemical Catalog Co., New York, 1928.

[2] Errera and Henri, *J. Phys. Radium*, **7**, 225 (1926).

[3] Newsome, THIS JOURNAL, **48**, 2035 (1926).

[4] Hunt, *ibid.*, in press.

[5] Hunt, "Thesis," University of Wisconsin, 1926.

[6] Krueger and Utesch, *Ann. Physik*, **78**, 114 (1925).

[7] Coolidge, *J. Franklin Inst.*, **202**, 693 (1926).

giving what may be called an *M/C* ratio. This ratio was then compared for a given reaction under different conditions, and for different reactions under the same conditions. This *M/C* ratio was often of the order of one hundred times the *M/N* ratio.

Apparatus

The Coolidge cathode ray tube is shown at "a" in Fig. 1 and it has been described in detail by Dr. Coolidge.[7] The cathode end is similar to that of the Coolidge x-ray tube with a heated tungsten filament in the focusing cup. The electrons travel from the filament under a high potential gradient to the anode and pass through the thin nickel window (0.0012 cm. thick). The window is supported by a grid so that it can stand a full atmosphere's pressure. A copper tube protects the glass of the anode arm from the electrons. An invar tube holding the grid is sealed to the tube by a metal-to-glass seal.

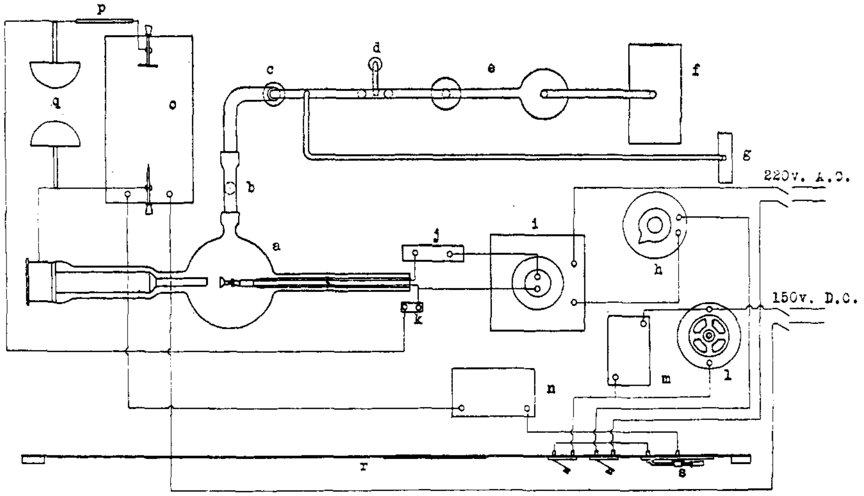

Fig. 1.—Schematic diagram of apparatus for Coolidge electron tube.

The tube was evacuated with a mercury pump, e, backed by an oil pump, ı, and a liquid-air trap, c, was used to prevent diffusion of mercury vapor into the tube. A vacuum of less than 10^{-6} mm. could be obtained, but when the tube was operating the pressure increased to about 3×10^{-5} mm. The McLeod gage is shown at g.

The construction of the tube is such that potentials up to 200,000 volts can be applied to its terminals and a space current of several milliamperes can be sent through the tube if it is operated intermittently.

A Weston induction coil, o, capable of giving a heavy spark of over 50 cm. between dull points was used as the source of the high voltage. It was operated on direct current with a mercury turbine interrupter, l, giving about sixty breaks per second. The voltage was determined from the sparking distance between 25-cm. brass hemispheres, q, using the tables of Peek[8] for spheres of this size.

The filament current was supplied by a step down insulation transformer, i. The space current or electron emission was regulated with an adjustable self-inductance,

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[8] Peek, "Dielectric Phenomena at High Voltage," 1921, p. 90.

h, in the primary circuit of the filament current transformer. The space current was measured with a calibrated ammeter, k, having a range from 0 to 2 milliamperes.

The heat generated in the window was so great that the current could be turned on only about one-fourth of the time, and an automobile timer, n, was used as an intermittent contact in the circuit of the primary.

A lead screen, r, 2 by 1.5 meters and 3 mm. thick, protected the operator from the x-rays. A window of lead glass 6 mm. thick, permitted a view of the apparatus and readings of the meter were taken with the aid of a telescope.

A condenser, m; a charcoal tube, b; a resistance, p and an ammeter, j, for the filament current made up the rest of the equipment.

Since there was danger of corroding the nickel window of the cathode ray tube with the gases used in the experiments, the reaction cells were not attached to the cathode-ray tube. This arrangement had the disadvantage that the electrons had to pass through two windows and a short air space but it made the manipulation of the cells much easier and increased the life of the nickel window. Only two windows have been necessary while the tube has been in practically constant use for two years. The reaction cells were made of soft glass tubes 7.5 cm. in diameter and of two lengths, 22 and 34 cm. Side arms with stopcocks were provided for sweeping out the gases. One end of the cell was sealed off and the other end was closed with a thin window of cellophane (a commercial product of cellulose xanthate), aluminum or mica. The cellophane and the aluminum were 0.02 mm. thick and the mica was 0.01 mm. thick. The windows were attached with the help of paraffin and a brass ring. None of the windows reduced the range of the electrons in air more than a few centimeters and the slight differences in the absorption of the different windows did not affect the results appreciably.

Range and Absorption of Cathode Rays

The maximum range of the cathode rays was determined by the red fluorescence of lime, which could be distinguished from the weak green fluorescence caused by x-rays. Fig. 2 shows the relation of the maximum range of the voltage. By extrapolating back to zero range, one finds that it takes 70 kilovolts (peak voltage) to take the electrons through a nickel window 0.013 mm. thick. Application of Thomson's[9] formula, $V_0^2 - V_x^2 = bx$, gives a value of 3.85×10^{12} for the absorption coefficient, b, for nickel. In this formula V_0 is the voltage at the start of the path and V_x is the velocity of the electron expressed in volts after the electron has traversed the distance, x. Dividing this coefficient by the density of nickel, a value of 4.32×10^{11} is obtained for the mass absorption coefficient of the nickel window and this value is very close to the mass absorption coefficient obtained by Terrill[10] for aluminum, copper and gold.

The maximum voltage as determined by the spark gap was used in these computations since it determines the maximum range of the electrons.

Although the maximum range for 185 kv. electrons was found to be about 50 cm., the number of electrons which reach this distance is very

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[9] J. J. Thomson, "The Conduction of Electricity Through Gases," University Press, Cambridge, 1911, p. 378.

[10] Terrill, *Phys. Rev.*, **22**, 101 (1923).

small. The velocity of electrons falls off in such a manner that the decrease in the fourth power of the velocities is proportional to the distance, but the number of electrons crossing a unit area decreases exponentially with the distance at a rapid rate. Accordingly it is possible to use reaction cells shorter than 50 cm. Experiments showed that for *short* exposures there was no detectable difference in the yields with reaction cells of 22 cm. or 34 cm.

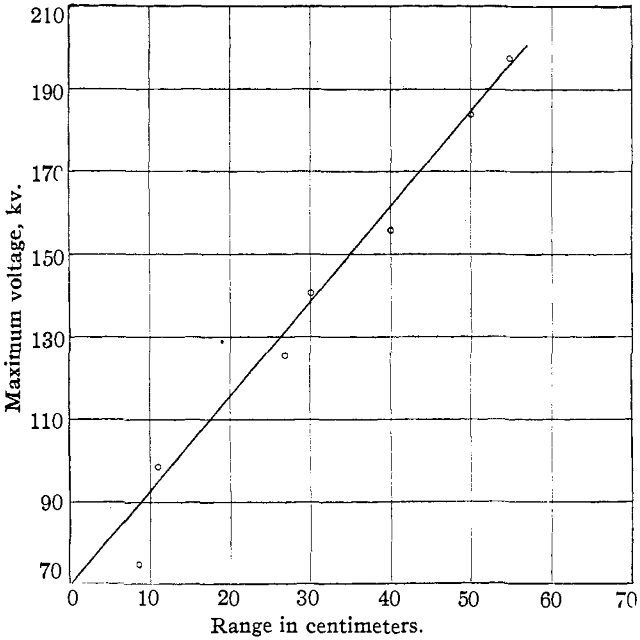


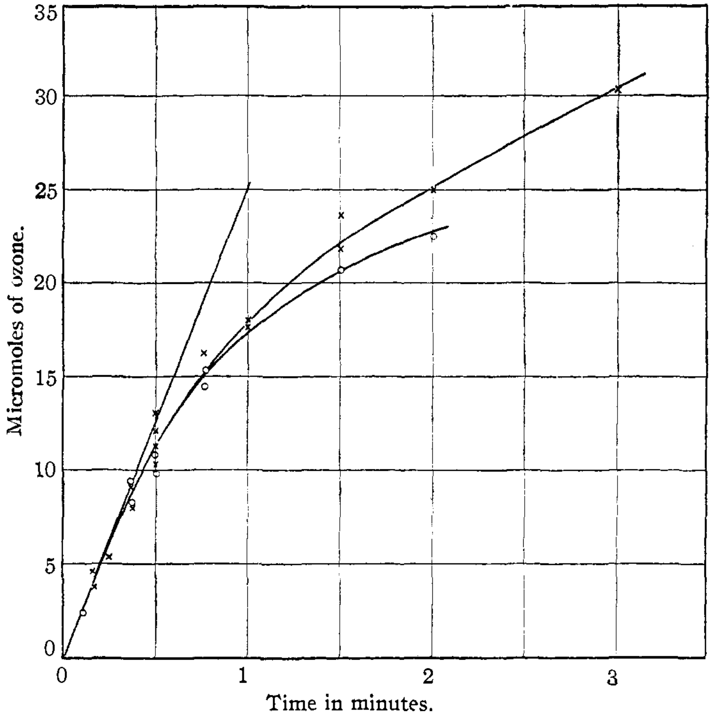
Fig. 2.—Range of electrons as measured by the fluorescence of lime in total darkness.

Action of Cathode Rays on Different Gases

Oxygen.—The action of cathode rays on oxygen was studied intensively because ozone, which is the only product, can be determined accurately in small amounts and because an extensive study of ozone formation in the electrical discharge has been made in this Laboratory. The reaction is not as simple as could be desired, however, because the decomposition of ozone very soon affects the yields.

In carrying out these experiments, the reaction cells were filled by sweeping through a rapid stream of oxygen from a tank for an hour or more and then placing the reaction cell in front of the window of the cathode-ray tube. Unless otherwise noted, the distance from the reaction cell to the window of the cathode-ray tube was 2 to 3 mm. The oxygen was then exposed to the cathode rays for the desired time, after which the ozone was determined by sweeping the gas through two bottles containing neutral 5% potassium iodide solutions. The iodine was titrated with 0.005 *N* sodium thiosulfate, 1 cc. of which is equivalent to 2.5 micromoles of ozone.

All the factors which might affect the yield were studied. It was found that for short exposures the yield was a function of the voltage of the cathode-rays, the space current, the time of treatment, the distance from the cathode-ray tube to the reaction cell and the source of the oxygen. The surface of the reaction cells, whether of glass or paraffin, had little effect and no appreciable difference in yield could be detected when using mica, aluminum or cellophane windows for the reaction cells. The yields were not appreciably influenced by the speed of the mercury turbine interrupter, the speed of the intermittent switch, the time the ozone remained in the reaction cell (except after several hours) or the moisture content of the gas.



O, Short reaction cells; X, long reaction cells.

Fig. 3.—Ozone yield from oxygen (0.4 ma.; 185 kv.).

The results of a typical series of experiments are shown in Table I and Fig. 3. In this series the influence of time was studied while the space current and voltage were kept constant.

With exposure of less than a minute the yields do not depend on the length (volume) of the tube. In all cases, time was given for diffusion so that the concentration would be nearly uniform throughout the chamber. The exposures were intermittent so that the total time of the exposure was ten to thirty times as long as the net exposure. The experiments marked "b" and "c" show that there is very little difference in the ozone yield when a 90-second exposure is spread over a period of one hour with the shorter tube or spread over a period of two hours with the longer tube. The experiments marked "a" show that only about a third of the

TABLE I

OZONE YIELD IN OXYGEN AS A FUNCTION OF TIME

Space current = 1 mil. amp. Voltage = 185 Kv.

Tube length, cm.	Time, sec.	Yield, micro-moles	Tube length, cm.	Time, sec.	Yield, micro-moles	Tube length, cm.	Time, sec.	Yield, micro-moles
22	7.5	2.4	22	30	10.8	34	60	18.0
34	10	3.8	34	30	11.2	22	90	20.8[b]
34	10	4.6	34	30	6.8[a]	34	90	21.9[c]
34	15	5.5	22	30	7.8[a]	22	120	22.5
34	22	8.0	34	30	12	34	120	25.0
22	22.5	9.5	22	45	15.5	34	150	31
22	22.5	8.0	34	45	16.4	22	150	23.5
22	30	9.8	22	45	14.5	34	180	30.5
34	30	13.2	34	60	18.0			

[a] Ozone stood in reaction cell overnight before analysis.

[b] Exposure extended over one hour.

[c] Exposure extended over two hours.

ozone decomposes on standing overnight, so that only a negligible amount can decompose thermally during an ordinary experiment.

The curves of Fig. 3 show that the rate of ozone formation soon falls off markedly, because the ozone is decomposed as well as produced by the cathode rays. The shorter tube with the smaller volume gives a higher concentration of ozone and hence a greater rate of decomposition. This condition gives a lower yield of ozone but the difference is not apparent until after fairly long exposures have built up appreciable concentrations of ozone. The important thing from a theoretical standpoint is not the actual ozone yield for any given exposure but the true rate of formation, that is, the yield that would be obtained if none of the ozone was decomposed. These values can be obtained by taking the tangents to the yield–time curves at zero time, since under these conditions there is no ozone to decompose. On account of the rather large percentage error at the low concentrations the curve and its tangent cannot be drawn with precision but the values are probably accurate to within 10%.

The initial rate of ozone formation, given by the tangent at zero time, is 25 micromoles of ozone per minute with a space current of 0.4 mil. amp. and a potential of 185 kv.; 25 micromoles contains 1.51×10^{19} molecules ($25 \times 10^{-6} \times 6.06 \times 10^{23}$) and 0.4 milliampere for one minute gives 1.5×10^{17} electrons ($0.4 \times 10^{-3} \times 60 \div 1.59 \times 10^{-19}$) and the M/C ratio is, therefore, 100. In other words, 100 molecules of ozone are formed for every electron that crosses the cathode-ray tube.

The influence of the space current is shown in Fig. 4, with the time kept constant at one-half minute and the voltage kept constant at 185 kv. The curve shows that in these short exposures the yield is directly proportional to the space current. This series was made under slightly different conditions than in the preceding series, so that the absolute values of the two series cannot be compared directly.

Figure 5 shows how the ozone yields change with time, when higher currents and longer exposures than those given in Fig. 3 are used. Each point shown on the curves is the average of from two to ten determinations. The long exposures had to be extended over several hours to allow time for diffusion. The short reaction cells gave yields (not shown in Fig. 5) considerably lower than the yields in the large cells because the concentration was higher and the decomposition was greater. It may be noted that with long exposures the ozone yield is not proportional to the space current through the tube.

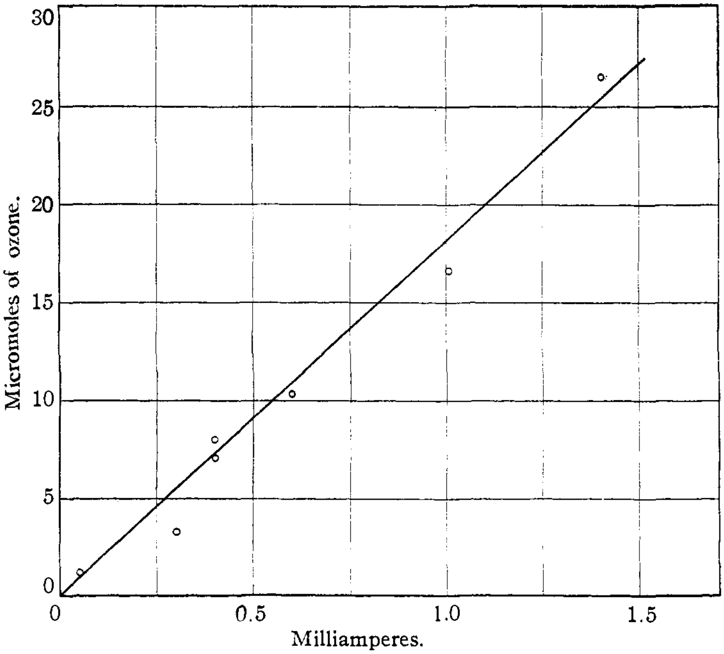


Fig. 4.—Ozone yield from oxygen with various space currents (voltage, 185 kv., time of exposure, 0.5 min.).

The curve for 1 mil. amp. space current seems to be approaching an asymptote at a yield somewhere near 75 micromoles of ozone. Since the reaction cell was 7.5 cm. in diameter and 34 cm. long, this yield corresponds to an ozone concentration of about 0.1%.

The ozone yields obtained with different voltages were studied next. All of these experiments were made with a tank of oxygen which gave low yields, probably due to an oxidizable impurity, but the relative values for the different voltages are comparable. The initial rates of ozone formation as determined by the tangents at zero time are given in Table II, together with the *M/C* ratios.

TABLE II

EFFECT OF VOLTAGE ON THE INITIAL RATE OF OZONE FORMATION

Voltage, kilovolts	140	162	185	200
Rate of O_3 formation, micromoles per min	3.2	12	19	27
M/C	12.6	48	76	107

Another factor which affected the ozone yield was the distance between the window of the reaction chamber and the window of the cathode-ray tube. A series of experiments made to test this factor showed that the yield was reduced by about one-half whenever the distance between the reaction cell and the cathode-ray tube was increased by 3.5 cm.

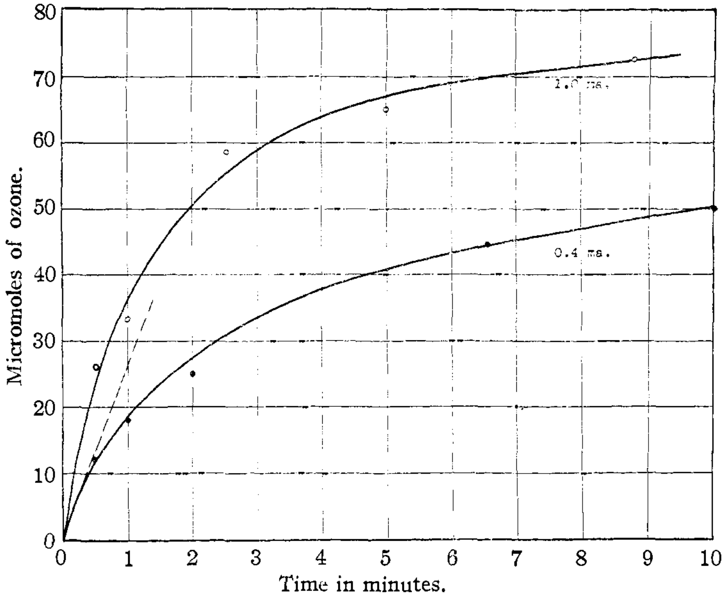


Fig. 5.—Ozone formation in oxygen (large reaction cells, 185 kv.).

Air.—When the cathode rays pass through air, they form not only ozone but also nitrogen oxides which can be determined by absorption in standard alkali before absorbing the ozone in the potassium iodide.

In carrying out these experiments the reaction cell was first filled with carbon dioxide-free, dry air, taken from outdoors to avoid the possible catalytic effect of impurities which might be present in the air of the laboratory. After treating the air with the cathode rays, the air in the cell was sucked out through a bottle of 0.01 *N* sodium hydroxide and two bottles of potassium iodide. Any nitric oxide formed by the cathode rays was oxidized by the ozone to nitrogen pentoxide and absorbed in the alkaline solution. The excess of sodium hydroxide was titrated with standard acid and each cc. of 0.01 *N* sodium hydroxide neutralized by the gases from the reaction chamber was equivalent to 5 micromoles of nitrogen pentoxide or 10 micromoles of nitric oxide.

Figure 6 gives the ozone yields for the large and small reaction cells with 185 kv. At zero time with 1 mil. amp. the yield is 26 micromoles of ozone per minute and the initial rate of ozone formation with 0.4 mil. amp. is 11 micromoles per minute. These data give an M/C ratio of 44, which is about half the M/C ratio in pure oxygen. The initial rates of formation are proportional to the space current but the direct proportionality does not hold for the longer exposures which involve the decomposition of ozone.

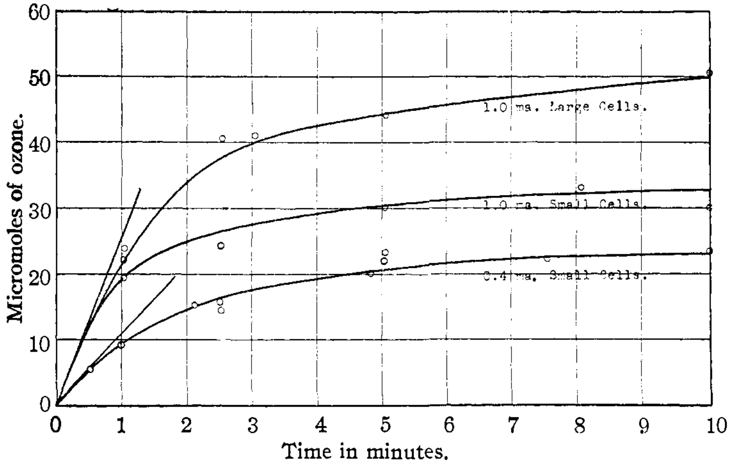
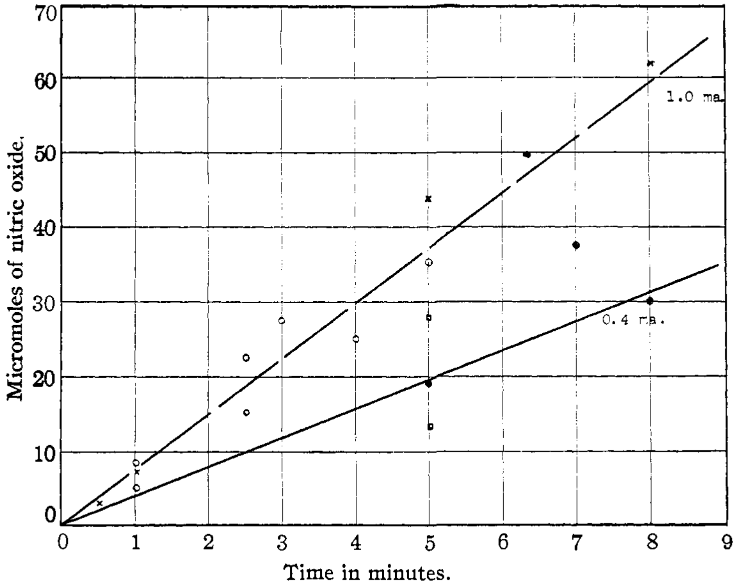


Fig. 6.—Ozone yields with air, (185 kv.).



O,⊕—Large cells; X,□—small cells.

Fig. 7.—Nitric oxide yield with air, (185 kv.).

The nitric oxide yields, expressed in terms of micromoles of nitric oxide, are shown in Fig. 7. While the ozone curves of Fig. 6 soon flatten out on account of the decomposition of ozone, the curves for the nitric oxide show no tendency to reach an equilibrium. There were rather wide variations in the nitric oxide yields, indicating that some unknown factor was affecting the yields, but the rate of formation may be taken as about 8 micromoles per minute with 1.0 mil. amp. and 4 micromoles per minute with 0.4 mil. amp. These data give an M/C ratio of 13.5 and 16.0, or an average value of about 15 molecules per electron.

The large and small cells gave the same yields within the limit of accuracy of the experiments, a result which is in accord with the fact that the rate of formation does not decrease at the higher concentrations (Fig. 7). It is probable that the nitrogen pentoxide formed from the nitric oxide is decomposed by the electron bombardment but that it is reoxidized by the excess of ozone. No attempt was made to test for nitrous oxide.

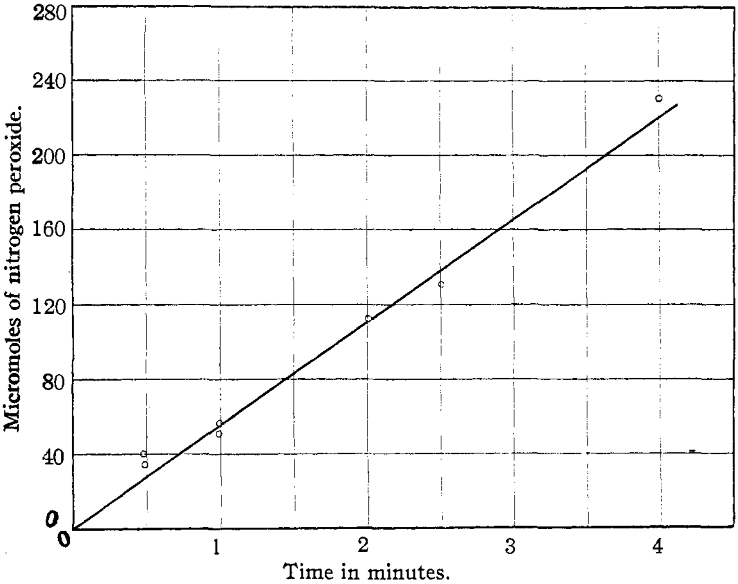


Fig. 8.—Decomposition of nitric oxide (0.4 ma., 185 kv.).

Nitric Oxide.—The nitric oxide was prepared by the action of nitric acid (1.2 sp. gr.) on copper and purified by bubbling through concentrated sulfuric acid. Any nitrogen dioxide was absorbed by the sulfuric acid. To avoid the initial oxidation of the nitric oxide by the air in the reaction cell, the air was first swept out of the cell with nitrogen.

Decomposition of the nitric oxide involved the liberation of oxygen, which then combined with the excess nitric oxide to form nitrogen dioxide. After an exposure to the cathode rays the nitrogen dioxide was determined by sweeping the gas through sodium hydroxide with nitrogen and titrating the excess alkali with 0.1 N sulfuric acid, using methyl red as an indicator.

The reactions are taken to be

$$2NO = N_2 + O_2$$
$$O_2 + 2NO = 2NO_2$$
$$NO_2 + NO + 2NaOH = 2NaNO_2 + H_2O$$

One cc. of 0.1 *N* alkali is equivalent to 50 micromoles of nitrogen dioxide or 50 micromoles of nitric oxide decomposed.

Great care was necessary to prevent the access of air to the nitric oxide, as it would also give nitrogen dioxide. It was necessary to displace the air in the absorption bottle with nitrogen and to prevent back-diffusion of air with a second wash bottle.

The nitrogen used in these experiments contained a small amount of oxygen and blank experiments were necessary to determine the amount of nitrogen dioxide produced by this oxygen impurity. The same procedure was followed as in a regular experiment except that the nitric oxide was not exposed to the cathode rays. The four blank determinations gave 2.8, 2.9, 2.7 and 2.6 cc. of 0.1 *N* sodium hydroxide. In the last experiment (2.6 cc.) the nitric oxide remained in the cell overnight before being swept out through the alkali, and the close agreement with the other values proved that the cell was air tight and that the cellophane windows were not porous.

The influence of the time of treatment is shown in Fig. 8 and the influence of the magnitude of the space current on the decomposition was studied also. These curves show no equilibrium effect up to four minutes with 0.4 mil. amp. and 185 kv. and indicate either that nitrogen dioxide is not easily decomposed by the cathode rays or more likely that the decomposition products recombine on standing. The rate of nitric oxide decomposition is 57 micromoles per minute with 0.4 mil. amp. space current at 185 kv. and the corresponding *M/C* ratio is 230.

Carbon Dioxide.—The reaction cells were filled from a tank with carbon dioxide which had been purified by passing through concentrated sulfuric acid and chromic acid and then through phosphorus pentoxide. After treatment with the cathode rays, the gas was swept out with carbon dioxide through a 10% potassium iodide solution to remove any ozone. The exit gases passed through a tube of iodine pentoxide heated to 150° in an oil-bath, and then through 10 cc. of 10% potassium iodide solution to absorb the iodine liberated by carbon monoxide according to the reaction

$$5CO + I_2O_5 = 5CO_2 + I_2$$

The ozone and the carbon monoxide were both determined by titration with *N*/200 sodium thiosulfate.

It was necessary to make a considerable correction for the iodine carried over from the iodine pentoxide when the untreated gas was passed through.

The results were very unsatisfactory and in the first experiments appreciable but inconsistent amounts of ozone were found. The last two experiments extending over a longer period of time are thought to be more reliable. The rays were passed into the carbon dioxide for a net time of ten minutes at 200 kv. and 1.0 mil. amp. The blank correction amounted to about one-fourth of the total titration; 0.35 and 0.60 mg. of carbon monoxide were obtained. The average, 0.47 mg., corresponds to 10^{19} molecules and the current of 1.0 mil. amp. corresponds to 3.8×10^{18} electrons. The *M/C* ratio is, therefore, 3 molecules per electron crossing the tube when the maximum potential drop across the tube is 200 kv.

Calorimetric Determination of Energy of Cathode Rays

It was desired to study the relation between the energy of the cathode rays and the chemical reactions produced, but the wave form produced by the induction coil was so distorted and the loss of energy so great that the energy delivered to the reaction chamber could not be calculated from the voltage and amperage in the cathode-ray tube. A rough measurement was obtained, however, with the help of a special calorimeter placed at a position corresponding to the end of the reaction chamber. It was assumed that all the electrons which would have entered the reaction chamber were stopped by the small calorimeter and converted into heat. It was assumed also that the number of secondary electrons emitted backward was small and sufficiently constant so that no appreciable error was introduced by using copper in the calorimeter and aluminum or cellophane in the reaction cell. Experiments had shown that cellophane and aluminum windows gave the same yield.

A flat, circular chamber was made of thin copper, 7.5 cm. in diameter and 0.7 cm. thick. A horizontal glass capillary was attached to the copper chamber and the apparatus was filled with nitrobenzene and operated simultaneously as a thermometer and a calorimeter. When the cathode rays were stopped by the copper chamber, the heat generated caused the nitrobenzene to expand and move out along the capillary tube. The capillary was calibrated in terms of centigrade degrees by setting the calorimeter into a water-bath at definite temperatures. The distance traveled by the nitrobenzene in the capillary was practically a linear function of the temperature. The heat capacity of the copper was 4.08 and that of the nitrobenzene 6.97, giving a total heat capacity of 11.05 calories per degree.

Heating and cooling curves were plotted and the temperature change was found to be quite uniform after a short initial period. The measurement was complicated by the fact that the framework supporting the window of the cathode-ray tube became hot after a while and radiated heat to the calorimeter, necessitating a somewhat arbitrary correction amounting usually to between 10 and 20% of the total value.

The results are summarized in Table III.

TABLE III

ENERGY OF CATHODE RAYS RECEIVED BY CALORIMETER

Dist. from window to calorim., cm.	Max. voltage, kv.	Current, mil. amp.	Temp. rise in calorim. per min., °C.	Energy rec'd. with intermit. curr., cal./min.	Energy received if current were continuous, cal./min.
0.5	200	1.0	1.50	16.5	66.0
2.0	200	1.0	0.76	8.4	33.6
2.0	200	1.0	.90	10.0	40.0
2.0	200	0.5	.43	4.8	19.2
2.0	200	0.5	.42	4.6	18.4
2.0	185	1.0	.49	5.4	21.6
2.0	185	1.0	.49	5.4	21.6
2.0	185	0.5	.25	2.7	10.8
2.0	162	1.0	.35	3.8	15.2

The energy actually measured per minute while the tube was in operation is given in the next to the last column and these values are multiplied by 4 to give the figures of the last column. The current was on for about $^1/_8$ second and off $^3/_8$ second to keep the window cool, so it was flowing for only one-fourth of the actual time of an exposure.

The results are quite consistent, the temperature rise for 1.0 mil. amp. being twice as great as the rise for 0.5 mil. amp., but the constant error due to the thermal radiation from the window of the tube may be fairly large.

The greatest energy, amounting to 66 calories per minute, was introduced when the calorimeter was half a centimeter from the window. The measurements at 2 cm. are more valuable for the calculations because the absorption by the cellophane window of the reaction chamber was found to be equivalent to 2 cm. of air.

The average value at 2 cm. with 1 mil. amp. and 200 kv. was 36.8 cal. per minute; and at 185 kv. it was 21.5.

The energy registered by the calorimeter is very much smaller than the product of the maximum voltage and the current measured in the cathode-ray tube. At 200 kv. it is 1.3%, and at 185 kv. it is 0.8%. The chief reason for the low percentage lies in the fact that the *maximum* voltage of the induction coil as registered by the spark gap is much greater than the voltage during the rest of the period. Furthermore, the energy reaching the calorimeter or the reaction chamber was less than that in the cathode-ray tube because some of the electrons were stopped by the grid and the window and some were deflected to one side by air molecules before reaching the chamber. The loss of energy was assumed to be the same in both the chemical measurements with the chamber and the energy measurements with the calorimeter.

Conclusions

For the sake of comparison, representative data on the different gases are collected in Table IV.

TABLE IV

SUMMARY OF EFFECTS OF CATHODE RAYS ON VARIOUS GASES

Reaction	Voltage, kv.	Curr., mil. amp.	Micro-moles per min.	M/C	Cal. per min.	Cal. per mole
$O_2 \longrightarrow O_3$	185	0.4	25	100	8.6	3.4×10^5
Air $\longrightarrow O_3$	185	.4	11	44	8.6	7.8×10^5
Air $\longrightarrow$ NO	185	.4	4	14	8.6	22×10^5
NO $\longrightarrow O_2$	185	.4	57	230	8.6	1.5×10^5
$CO_2 \longrightarrow$ CO	200	1.0	2	3	37	180×10^5

In Col. 1 is given the reaction which was measured chemically and in Col. 2 the maximum voltage across the tube as measured with a spark gap. Col. 3 gives the space current or electron current across the tube. Col. 4 contains the yields in micromoles per minute as obtained by chemical analysis. In cases where known secondary reactions occurred corrections were made. In Col. 5 are found the M/C values or the ratio of the number of molecules of product to the number of electrons passing across the cathode-ray tube. The actual number of electrons entering the reaction chamber is less than C and undetermined in this research, but it is directly proportional to C because the conditions were alike in all the experiments. In the next to the last column the energy of the cathode rays entering the reaction chamber is recorded in calories per minute. The values were obtained by stopping the electrons with a calorimeter. In the last column is given the energy of the cathode rays in calories necessary to give a gram molecule of the product.

An examination of Table IV shows that of these reactions the decomposition of nitric oxide proceeds the most readily and the decomposition of carbon dioxide proceeds the least readily. After the decomposition of nitric oxide, the formation of ozone from oxygen proceeds most easily, followed by the formation of ozone from air, and nitric oxide from air. All these reactions are endothermic reactions but there seems to be no simple connection between the response to cathode rays and the heat of formation, or the free energy of the different gases.

The chemical action of the cathode rays appears rather inefficient in the systems studied. In some cases the efficiencies are low because the cathode rays are used up in producing effects which are not detected by the chemical test employed. For example, the ozone yield in air is less than the ozone yield in oxygen because in air some of the electrons are used up in making nitric oxide instead of ozone.

No direct determinations were made on the decomposition of ozone but it was found that an equilibrium existed at about 0.1% ozone under the cathode-ray bombardment. Since there were about 1000 times as many oxygen molecules as ozone molecules at equilibrium, the decomposition of ozone must be approximately 1000 times as fast as the formation, under the conditions of the experiment. The decomposition of ozone is an exothermic reaction and proceeds much more readily than the endothermic reactions which have been studied. Extensive experiments were carried out also with another exothermic reaction (the union of nitrogen and hydrogen to form ammonia) but the yields were so small and so inconsistent that the data have not been reported.

The total number of ions produced in the reaction chamber could not be determined, although attempts were made to obtain a saturation current with a 2000-volt dry battery. It is possible, however, to estimate from the energy measurements the maximum number of ions which could have been obtained. From the ionization potential of 15 volts it can be calculated that the formation of a pair of ions of molecular oxygen requires 2.4×10^{-11} ergs. The input of 8.6 calories (or 3.6×10^{8} ergs) of energy in the form of cathode rays can produce no more than $3.6 \times 10^{8} \div 2.4 \times 10^{-11}$ or $1.5 \times$

10^{19} pairs of ions. The 25 micromoles of ozone produced by the same cathode rays contain 1.5×10^{19} molecules. These calculations show that within the limits of accuracy of the thermal measurements the number of molecules is equal to the number of pairs of ions. This estimate checks with the M/N ratio for ozone obtained by Lind[11] using α-ray bombardment, but it is not in agreement with the results of Krueger and Utesch[6] in which the M/N ratio was found to be about 40. If the ionization potential of 23 volts for atomic oxygen is taken, there are 1.5 molecules for every ion pair, and if the resonance potential of 8 volts is taken, there is about one molecule of ozone for every two excited oxygen molecules.

It is to be noted that the M/C ratios discussed before are purely empirical values used for purposes of comparison of different gases under similar conditions. C represents the average number of electrons crossing the tube and it is considerably larger than the number of electrons entering the reaction chamber.

The results of this investigation indicate that the chemical behavior of high voltage electrons is essentially the same as that of α-particles. This similarity in behavior is to be expected because the greater part of the chemical action of α-particles is effected through electrons of high velocity driven out from molecules in the path of the α-particle, and these electrons are the same as the electrons shot out from the cathode-ray tube. The M/N ratio for ozone obtained in oxygen with cathode rays was calculated to be the same within the limits of experimental error as that obtained with α-particles. Moreover, the decomposition of carbon dioxide was found to be very slight and this fact checks well with the facts of radioactivity. Alpha-particles do not produce any change in this gas[12] on account of reversion of the CO_2^+ ions to CO_2. The high yield in the decomposition of nitric oxide is to be expected also, because the ionization potential is only 9 volts instead of the 15 volts for oxygen.

It might be expected that an appreciable part of the energy of the moving electron would be used up in displacing the electrons in molecules rather than in expelling them. From the close relation between ion pairs and molecules and the checks with experiments using α-particles, it appears that nearly all of the energy of the cathode ray goes to complete ionization rather than to the displacements which correspond to resonance potentials. As long as the electron has energy equal to or greater than the ionization potential, most of the effects will be ionizations.

The chemical effects produced by cathode rays of definite voltage depend on the ionization potential of the gas and on the stoichiometrical reactions which follow the ionization, and they are very similar to the chemical effects of α-particles.

[11] Ref. 1, p. 92.

[12] Ref. 1, p. 155.

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Summary

1. The chemical effects produced in gases by electrons from a Coolidge cathode-ray tube have been studied. The gases were enclosed in separate vessels not in contact with the window of the tube. The influence of time, voltage and space current has been studied.

2. Ozone was obtained from oxygen and the ozone was in turn decomposed. The rate of ozone formation was obtained by extrapolation to "zero time."

3. The chemical effects were expressed as the ratio of molecules produced per electron crossing the cathode-ray tube. These M/C ratios are as follows: nitric oxide decomposition 230, ozone from oxygen 100, ozone from air 44, nitric oxide from air 14, carbon dioxide decomposition 3.

4. The energy of the cathode rays was obtained with a small calorimeter and it varied from 3 to 16 calories per minute.

5. A calculation of the maximum number of ions was made using the energy input and the ionization potential of oxygen. This estimate gives a ratio of molecules to gas ions approximately the same as has been found with α-particles.

6. The close similarity in chemical behavior of cathode rays and α-particles has been emphasized. The yield depends on the ionization potential of the gas and the stoichiometrical reactions which follow ionization.

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THE HEAT CAPACITY AND ENTROPY OF BARIUM BROMATE FROM 16 TO 300° ABSOLUTE. THE ENTROPY OF BROMATE ION

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This work is a part of the program for the evaluation of entropy of aqueous ions as a means of facilitating the thermodynamic treatment of solutions. The general theory has been treated in previous papers by Latimer and coworkers.[1]

The present paper initiates work in the field of the halogenate ions, ClO_3^-, BrO_3^- and IO_3^-, and it is planned to use the entropy values obtained with experimental reaction heats in order to obtain the free energies of these ions. The experimental method follows the general plan of study

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[1] (a) Latimer and Buffington, This Journal, **48**, 2297 (1927); (b) Latimer, *ibid.*, **48**, 2868 (1926); (c) Latimer, *J. Phys. Chem.*, **31**, 1267 (1927); (d) Latimer and Greensfelder, This Journal, **50**, 2202 (1928); (e) Latimer and Kasper, unpublished material.