

THE JOURNAL  
OF THE  
American Chemical Society

with which has been incorporated the

American Chemical Journal  
(Founded by Ira Remsen)

---

THE OXIDATION OF CARBON MONOXIDE BY PASSAGE WITH  
OXYGEN OR AIR THROUGH THE SILENT DISCHARGE  
AND OVER OZONE DECOMPOSING CATALYSTS.<sup>1</sup>

BY ARTHUR B. RAY AND F. O. ANDEREGG.

Received January 20, 1921.

During the wartime search for means to remove the toxic gas, carbon monoxide, from air, an electrical method involving the silent discharge was considered and tried out. Although the method was not found to be of practical use, conclusions may be drawn from the results obtained which seem to justify the publication of this account.

Because of the chemical inertness of carbon monoxide, in order to bring about its combination with oxygen, either both gases must be brought into an active condition or one must be changed into an extremely active modification. The easiest way to secure this activation is by raising the temperature but it is not always desirable to work at high temperatures.

<sup>1</sup> The experimental work described in this paper was begun in July, 1917, by Ray under the direction of W. K. Lewis and R. E. Wilson as a part of the War Gas Investigations conducted by the Bureau of Mines. The work was later continued by Anderegg under the direction of Lt. Col. A. B. Lamb, C. W. S. The authors desire to acknowledge their indebtedness to these gentlemen for valuable suggestions, as well as to C. F. Harding for permission to use and to K. B. McEachron for assistance in operating the large corona tube described as Apparatus E.

This paper is published by permission of the Chief of the Chemical Warfare Service.

At ordinary temperatures there are a number of catalysts which are capable of adsorbing these gases and allowing them to react. A variety of metals and oxides of metals, as described by Lamb, Bray and Frazer,<sup>1</sup> may serve this purpose. Activation may also be produced by light as described by Chapman, Chadwick and Ramsbottom,<sup>2</sup> who subjected mixtures of oxygen and carbon monoxide with various amounts of moisture to the light from a quartz-mercury lamp. In dry mixtures the activated oxygen forms ozone chiefly, but when moisture is present the amount of carbon dioxide formed increases with the moisture. Ozone is much more unstable in the presence of moisture and apparently breaks down to form perhaps atomic oxygen which is in so active a condition that it will react with carbon monoxide in one of its states of lowest activation. Later Berthelot and Gaudechon<sup>3</sup> noted the oxidation of carbon monoxide by ultraviolet light. Under these conditions carbon dioxide and moisture tend to form traces of higher order compounds.<sup>4</sup>

Remsen and his pupils<sup>5</sup> studied the action of ozone on carbon monoxide and came to the conclusion after sufficient refinement of the experimental details that carbon monoxide is oxidized to a small extent in the presence of moist ozone. Clausmann<sup>6</sup> prepared ozone of a very high concentration (200 mg. per liter) and allowed it to react with carbon monoxide. If the gases were dry and kept in the dark only 0.88% of the carbon monoxide was oxidized in 8 days, while in the sunlight 2.83% was oxidized during the same time. If the gases contained a little moisture, at the end of 7 hours a 2.5% oxidation took place and in 24 hours 3.67%. In none of these experiments was the ozone completely decomposed. It is therefore shown that carbon monoxide is slowly oxidized in the presence of a high concentration of dry ozone, and that light and moisture accelerate the reaction indicating that decomposing ozone is the active agent.

In 1879 Berthelot<sup>7</sup> observed on passing a silent discharge through a mixture of carbon monoxide and oxygen in one of his ozonizer tubes that the change to carbon dioxide was nearly complete after the discharge had passed for a long time. The failure of Berthelot to secure complete oxidation of carbon monoxide in the silent discharge indicates that the dioxide is broken up to a slight extent. But with a concentration of carbon dioxide less than 1% its decomposition is negligible.

<sup>1</sup> Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, **12**, 213 (1920).

<sup>2</sup> Chapman, Chadwick and Ramsbottom, *J. Chem. Soc.*, **21**, 942 (1907).

<sup>3</sup> Berthelot and Gaudechon, *Compt. rend.*, **157**, 129 (1913).

<sup>4</sup> *Ibid.*, **150**, 1690 (1910).

<sup>5</sup> Remsen and Southworth, *Am. J. Sci.*, **11**, 136 (1876); *Ber.*, **8**, 1414 (1875); Remsen, *Am. Chem. J.*, **4**, 50 (1882); Remsen and Keiser, *ibid.*, **4**, 454 (1883); W. A. Jones, *ibid.*, **30**, 40 (1903); Waters, *ibid.*, **30**, 50 (1903).

<sup>6</sup> Clausmann, *Compt. rend.*, **150**, 1332 (1910).

<sup>7</sup> Berthelot, *ibid.*, **88**, 50 (1879).

### Experimental.

**Apparatus and Procedure.**—Five different sets of apparatus were used in this investigation. Apparatus A was set up at the Bureau of Mines laboratory. Apparatus B was somewhat similar to A and was used at the University of Illinois. Modifications of B are described as C and D. Finally E was the large corona apparatus in the electrical laboratory of Purdue University which is being used in experiments on the fixation of nitrogen.<sup>1</sup>

**Apparatus A** is shown in Fig. 1. The simple glass ozonizer was of the Berthelot type. Alternating current at 10,000 volts was used with the induction coil after some preliminary runs to determine the optimum working voltage.

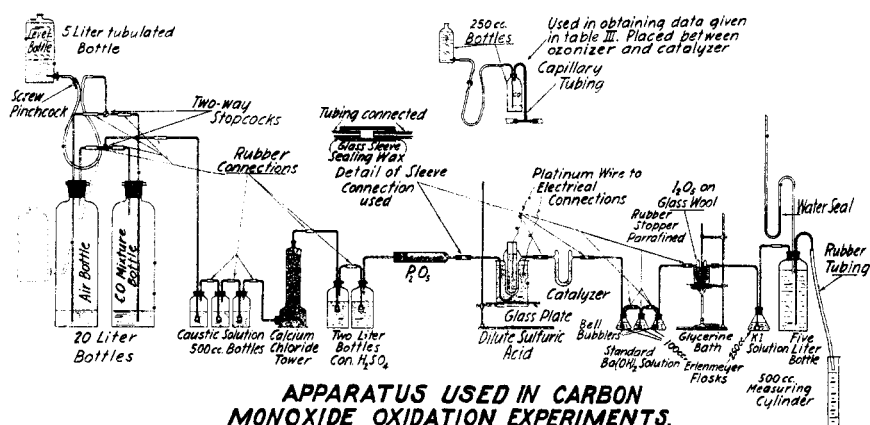


Fig. 1.

Before entering the ozonizer all gases were freed from carbon dioxide by washing with potassium hydroxide solution as proved by testing with a solution of barium hydroxide. Moisture was removed by passing through sulfuric acid wash bottles and through a 25-cm. tube half-filled with phosphorus pentoxide. Usually glass joints were fused, but a very few joints were made by slipping a larger glass tube over the ends and securing with sealing wax. After the apparatus was shown to be tight, the pressure was regulated and the carbon monoxide mixture held in a large carboy was started through at the instant electrical connection with the ozonizer was made. The rate at which the gas passed was determined by the rate at which the water in the control bottle was allowed to flow out. When the water in the measuring flask reached the 500 cc. mark the time was noted, the bottle containing the carbon monoxide mixture was cut out and the air bottle connected. The ozonizer was kept running until it was certain that all the carbon monoxide mixture had passed through. Then the electrical connection with the ozonizer was broken and the apparatus washed out with air. If the remaining carbon monoxide was being determined especial care was taken to drive over all the condensed iodine by gentle heating in a slow current of air.

**Apparatus B** was similar to the apparatus just described, with some minor modifications. The mixture of air and carbon monoxide was made up in a large carboy and for a run exactly one liter was transferred to a measuring flask set at a higher level by the

<sup>1</sup> C. F. H. Harding and K. B. McEachron, *J. Am. Inst. Elec. Eng.*, **39**, 405 (1920).

manipulation of two 3-way cocks. From this flask the mixture was forced through a U-tube containing beads and conc. sulfuric acid into the ozonizer. A trace of moisture remained in the gas. Beyond the ozonizer, by the use of stopcocks, the ozone containing gas could be passed directly to an analysis apparatus or through a tube 10 cm. long and 1 cm. in diameter filled with silvered asbestos. The ozone was not allowed to come in contact with any rubber or other organic material.

**Apparatus C** was a modification of Apparatus B obtained by silvering the outside of the inner tube of the ozonizer. Electrical contact to this silver was made by means of a platinum wire sealed through the glass. In this manner one dielectric is eliminated. The use of silver in the discharge tube was undertaken at the suggestion of A. B. Lamb in an attempt to increase the amount of atomic oxygen in the discharge.

**Apparatus D** differed from B and C only in the discharge tube which consisted of a tube 30 cm. long and 5 cm. in diameter, silvered on the inside. No glass or other dielectric was used between the outer silvered electrode and the inner which consisted of No. 18 copper wire, placed concentrically. The high voltage used in connection with Apparatus B, C and D was obtained from a transformer which changed 110 volts alternating current to 10,000 volts. This transformer was provided with a magnetic shunt containing an air gap by which the secondary voltage could be regulated. In some of the experiments with Apparatus D a Thorardson induction coil was used. This changed a 10-volt direct current to a 50,000 volts pulsating current.

**Apparatus E** had as outer, grounded electrode an aluminum tube 152 cm. long and 6 cm. internal diameter. Concentric with the outer electrode were the dielectric, a porcelain tube of 7.6 cm. inner diameter and 1.27 cm. thick, and an inner rod electrode 1.6 cm. in diameter composed of aluminum. Into a carboy enough carbon monoxide was introduced to make a 1 to 2% mixture with air. After removing a sample for analysis the mixture was forced through the corona tube by displacing with water and without any further drying. A sample of the effluent gas from the discharge tube was taken just as the last of the mixture was leaving the carboy. About 58,000 volts a. c. were applied to this tube, producing a beautiful corona discharge.

The oxygen used was obtained from commercial cylinders. The carbon monoxide was prepared by treating oxalic acid with sulfuric acid and removing the carbon dioxide from the evolved gas by passing through 4 wash bottles containing caustic potash. The pure carbon monoxide was then stored in a small gasometer over water and used as needed for preparing mixtures.

The determinations of ozone were made by passing the gas into neutral potassium iodide solution and, after making the solution acid, titrating the liberated iodine with sodium thiosulfate.

The determinations of carbon monoxide in gas mixtures were all made by passing the gas slowly through a U-tube containing iodine pentoxide on glass wool heated by means of a glycerine bath to 150°, absorbing the iodine set free in a potassium iodide solution and titrating with sodium thiosulfate. Great care was always taken to insure the driving over of the last traces of iodine which had a tendency to condense upon the cooler portions of the U-tube and in the tube leading into the potassium iodide solution. With proper care the determinations of small amounts of carbon monoxide by this method are very accurate.

For the determinations of carbon dioxide a standard barium hydroxide solution was used. For the absorption of the last traces of carbon dioxide it was necessary to bubble the gas mixture by means of very efficient bell gas bubblers through standard barium hydroxide solution held in 4 small Erlenmeyer flasks (50 cc. in each). The determinations of carbon dioxide were then made by titrating the solution with standard hydrochloric acid run directly into the flasks. All the usual precautions were observed

in working with the barium hydroxide solutions. It is believed that the determinations are quite accurate.

**Ozone Formation.**—In order to obtain some idea of the amount of oxygen which could be activated in the silent discharge, the yield of ozone was studied. There are at least a dozen factors which affect the yield of ozone in the silent discharge. Among these are the strength, polarity, wave form and frequency of the current; the pressure, temperature and composition of the gas being ozonized, as well as the material and dimensions of the electrodes and dielectrics. In addition the concentration of ozone is often decreased catalytically by the presence of moisture, by the electrodes, if in contact with the ozone, and by the dielectrics. Dust or any substance capable of being oxidized will also tend to remove some of the ozone. Occasionally other factors may alter the amount of ozone formed.

When dry air was passed through Apparatus A, a maximum of 3.2 mg. of ozone per liter was obtained in the effluent gas, while with dry cylinder oxygen the greatest yield was 7.5 mg. of ozone per liter. The optimum flow rate was 2 liters per hour. Results obtained with Apparatus B are given in Fig. 2. The chief cause for the deviation of the results from the curve was the variation in the voltage supplied as read on a voltmeter in the primary circuit. Since the current strength is nearly proportional to the voltage above a point called the critical voltage where the corona starts, and since the yield, other things being equal, is proportional to the current strength, these deviations are readily explained. Air from outside the room was used in these experiments and was dried fairly well

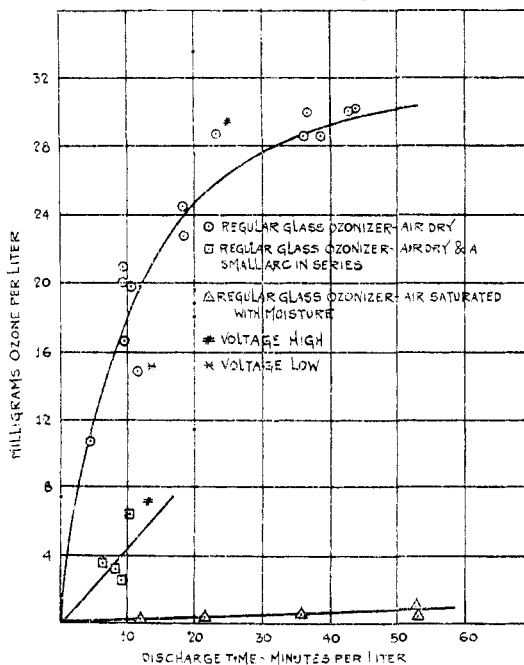


Fig. 2.

but not completely by passing through a U-tube containing conc. sulfuric acid. In order to show the detrimental effect of water vapor some runs were made with air saturated with water vapor at 20°. The results are also given in Fig. 2.

In the investigations of ozone production in direct current corona<sup>1</sup> it had been noted that the initial yield was greater with an arc in series. The effect was to increase the frequency of the discharge. The results obtained with a 1 mm. arc are shown in Fig. 2. The arc decreases the efficiency of the discharge, partly at least, because of the loss of energy in the arc.

With the silvered electrode of Apparatus C in contact with ozone the yield was reduced for the first three runs to only 0.1–0.4 mg. per liter. Later the yield of ozone was increased to as high as 4.9 mg. when one liter of air passed through the discharge in 25 minutes. The silver appeared to lose its first effectiveness and it would seem likely that it might have been poisoned by hydrogen sulfide, traces of which were present at all times in the room as well as just outside. However, during a large number of later runs the ozone concentration was never as great as shown in the upper curve given in Fig. 2 so that the silver never completely lost its decomposing action.

In a similar manner in Apparatus D the silver reduced the ozone concentration. Its yield was about the same with induction-coil current as with alternating current. With Apparatus E analyses were made for ozone at varying velocities. The air was dried fairly well by sulfuric acid in 2 bottles. The flow rate was read on a large gas meter and part of the effluent gases was drawn through neutral potassium iodide solution. The wattage was measured as described by Harding and McEachron<sup>2</sup> and was maintained nearly constant at 102 watts. The results given in Table I were obtained at a pressure of 743 mm. and at a temperature of 20°.

TABLE I.  
FORMATION OF OZONE IN SILENT DISCHARGE (APPARATUS E).

Rate of passage (Liters per min.)	Mg. ozone per liter.	G. ozone per k. w. hour.
0.43	0.72	3.33
1.26	0.90	4.16
2.28	1.36	6.28
5.97	2.42	11.2
7.72	3.68	17.2
12.07	2.34	10.8

A maximum yield was obtained at 7.72 liters per minute. At this velocity and pressure the optimum yield of nitric acid also was obtained. At this rate of flow the discharge had a flickering appearance. A manometer connected with the tube showed pressure vibrations of a period of 2 to 3 seconds and the electrical measuring instruments all showed similar vibrations. Above this velocity the discharge steadied down and there

<sup>1</sup> THIS JOURNAL, 39, 2592 (1917).

<sup>2</sup> Harding and McEachron, *loc. cit.*

was less chemical action as evidenced by both the ozone and nitric acid yields.

**Oxidation of Carbon Monoxide in the Silent Discharge.**—The data given in Table II regarding the oxidation of carbon monoxide when mixtures of this gas and cylinder oxygen or air are passed through the silent discharge show conclusively that while the oxidation takes place under these conditions it is in no case complete. This fact, also observed by Berthelot,<sup>1</sup> has been discussed above. Other conditions being constant, the rate of passage through the silent discharge determines the amount of oxidation. It is also shown that the nature of the gas, the electrical conditions, and the catalytic decomposing actions of substances in contact with the ozone formed affect the oxidation reaction.<sup>2</sup>

TABLE II.  
OXIDATION OF CARBON MONOXIDE IN THE SILENT DISCHARGE.

Apparatus.	Rate of flow through ozonizer. (Liters per hour.)	Original gas mixture.		Effluent gas mixture.		
		% CO.	Diluent.	% CO <sub>2</sub> .	% CO.	% O <sub>3</sub> .
A	6.0	2.38	Cyl. oxygen	0.50	1.86	Some
A	3.0	2.38	Cyl. oxygen	0.98	....	Some
A	4.3	4.0	Dry air	1.05	....	Some
A	1.5	4.0	Dry air	2.85	....	Some
A	0.75	4.0	Dry air	3.15	....	Some
A	0.375	4.0	Dry air	3.37	....	Some
B	9.7	1.0	Dry air	....	0.19	0.60
B	9.0	1.0	Dry air	....	0.19	0.54
C	20.0	1.0	Dry air	....	0.79	0.15
C	6.3	1.0	Dry air	....	0.29	0.23
C	2.4	1.0	Dry air	....	0.63	0.25
D	10.9	1.0	Dry air	....	0.51	Trace
D	6.0	1.0	Dry air	....	0.54	0.03
D <sup>a</sup>	3.75	1.0	Dry air	....	0.18	0.004
D <sup>a</sup>	2.73	1.0	Dry air	....	0.17	0.002
D <sup>a</sup>	4.0	1.0	Dry air	....	0.54	0.01
E	462.0	1.14	Moist air	....	1.01	Trace

<sup>a</sup> A freshly silvered outer electrode was used in these runs. The source of current was an induction coil. The presence of a spark in the discharge favored the oxidation of nitrogen.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> In this connection it is desired to correct certain statements regarding our work which are found in the article by Lamb, Bray and Frazer previously referred to. The paragraph in question is quoted as follows.

"...Ray found that in a 5 per cent. carbon monoxide-air mixture, passed at a rate of 500 cc. in 15 min. through an ozonizer capable of generating 3.5 per cent. of ozone in air under the same conditions a 50 per cent. conversion to carbon dioxide occurred at room temperature, while at one-fifth the rate an 85 per cent. conversion occurred. When oxygen was used in place of air no oxidation of the carbon monoxide could be detected."

In the experiments referred to a 4% carbon monoxide-air mixture was passed through an ozonizer capable of producing under optimum conditions a concentration

An examination of the data reveals the fact that the conditions for maximum yield of ozone in the effluent gas are not the optimum conditions for maximum oxidation of carbon monoxide. Decreasing the rate of passage tends to reduce the yield of ozone and increase the amount of oxidation. The obvious explanation of this fact is that during the slow passage more ozone is actually formed, but decomposed, and so causes the oxidation, or that the oxidation results from the formation of an active modification of carbon monoxide or of oxygen other than ozone. In other words, the formation of ozone may or may not be necessary for the oxidation. It is hoped that further work will throw more light upon the mechanism of the reaction.

**Oxidation of Carbon Monoxide by Ozone Undergoing Catalytic Decomposition.**—To take advantage of the oxidizing power of the ozone present in the effluent gases, as well as to eliminate the ozone which, at the concentration produced, has disagreeable physiological effects, several catalysts were tried to bring about the decomposition. Because of its well-known property of readily causing the complete decomposition of ozone, silver in a finely divided condition was first tried. Then with the idea of using cheaper catalyzing materials finely divided lead, lead dioxide, and manganese dioxide (the last two held on glass wool) were tried. In the tests the decomposing agents were placed in a U-tube through which the gas mixtures were led.

In the experiments made to determine the oxidizing action resulting when ozone was decomposed catalytically in the presence of carbon monoxide, mixtures of ozonized oxygen and carbon monoxide were passed over silver and analyses made of the effluent gases. Experiments were also made to determine whether ozone alone, in the concentrations employed in the tests, had any oxidizing action. In these experiments, with one exception, cylinder oxygen was passed through Ozonizer A and then carbon monoxide was introduced into the ozonized gas. The results obtained are tabulated in Table III.

These results show that under the conditions of the experiments ozone, unless decomposed by some suitable catalyst, does not exert any oxidizing action upon carbon monoxide but that ozone catalytically decomposed by silver does practically completely oxidize the carbon monoxide present.

of 1.5% ozone in the effluent gas. A maximum of 3.5% ozone in the effluent gas was obtained when oxygen was ozonized. The statement that no oxidation of the carbon monoxide could be detected when oxygen was used in place of air is obviously at variance with the facts recorded in this paper, and it is also obvious that this reputed fact does not confirm the results of Remsen and his co-workers referred to. The references cited have to do with experiments in which prepared ozone was mixed with carbon monoxide. Our results do confirm the results obtained by these workers in that no oxidation was detected when a mixture containing 4% carbon monoxide, about 3.5% ozone and the rest cylinder oxygen was held for a short time.



TABLE III.

OXIDIZING ACTION OF OZONIZED OXYGEN UPON CARBON MONOXIDE IN THE PRESENCE OF A CATALYST AND WITH NO CATALYST.

Rate of flow through ozonizer. (Liters per hour.)	Catalyst. (Not in ozonizer.)	Gas mixture.		Effluent gas.		
		% CO.	% Ozone.	% CO <sub>2</sub> .	% CO.	Ozone.
2	Nothing	4.00	3.5	None	.....	Some
3	Silver	0.38	3.0	0.364	0.006	None
3 <sup>a</sup>	Silver	0.40	1.5	0.324	0.016	None

<sup>a</sup> Air ozonized.

A number of experiments were next made, with the idea of utilizing the maximum oxidizing power of the ozone and the silent discharge effect, in which the mixtures of oxygen or air and carbon monoxide were passed through the silent discharge and then over the catalyst. In Table IV are tabulated the results obtained.

TABLE IV.

OXIDATION OF CARBON MONOXIDE WHEN PASSED WITH DRY OXYGEN OR AIR THROUGH SILENT DISCHARGE AND OVER CATALYSTS. (APPARATUS A USED.)

Rate of passage. (Liters per hour.)	Catalyst.	Gas mixture.		Effluent gas.			Remarks.
		% CO.	Diluent.	% CO <sub>2</sub> .	% CO.	Ozone.	
3	Silver	0.0	Cyl. oxygen	0.0	Trace	None	I <sub>2</sub> O <sub>5</sub> slowly decomposed
3	Nothing	2.38	Cyl. oxygen	0.98	....	Some	
3	Silver	2.38	Cyl. oxygen	....	0.12	None	
2	Silver	2.38	Cyl. oxygen	2.13	0.17	None	CO <sub>2</sub> not all absorbed
1	Silver	2.38	Cyl. oxygen	2.20	0.08	None	
1.5	Nothing	4.00	Air	2.85	....	Some	
0.67	Silver	4.00	Air	3.62	....	None	
1.5	Silver	4.00	Air	3.19	....	None	
3	Silver	4.00	Air	1.87	....	None	
4.7	Silver	4.00	Air	1.30	....	None	
4.7	Nothing	4.00	Air	1.05	....	Some	
6	Silver	4.00	Air	1.01	....	None	
5	Silver	1.85	Air	0.97	....	None	
3	Silver	1.85	Air	1.735	0.116	None	
2	Lead	4.00	Air	2.14	....	Some	
1.5	Lead	4.00	Air	2.53	....	Some	
0.75	Lead	4.00	Air	3.28	....	Trace	
0.6	Lead	4.00	Air	3.85	....	Trace	
0.5	Lead	4.00	Air	3.92	....	Trace	
3	PbO <sub>2</sub>	1.85	Air	1.01	....	Some	
1.5	PbO <sub>2</sub>	1.85	Air	1.25	....	Some	
3	MnO <sub>2</sub>	1.85	Air	0.67	....	None	
2	MnO <sub>2</sub>	1.85	Air	0.77	....	None	
1.5	MnO <sub>2</sub>	1.85	Air	0.87	....	None	

In additional experiments asbestos, which had been impregnated with metallic silver by saturating with a very concentrated silver nitrate

solution and igniting, was used as the catalytic material. In two runs made with Apparatus B using the freshly silvered asbestos catalyzer the carbon monoxide present was reduced from 1% to 0.035% and 0.069% respectively; but in subsequent runs using the same silvered asbestos the oxidation was not so complete.

In the experiments previously recorded the gases were dried more or less completely before entering the ozonizer. The results obtained with gases which were not dried are given in Table V.

TABLE V.

OXIDATION OF CARBON MONOXIDE BY PASSAGE WITH MOIST AIR THROUGH APPARATUS E AND OVER SILVERED ASBESTOS.

Rate of passage. (Liters per min.)	% Ozone in dry air.	% Carbon monoxide.		Fraction of CO oxidized.
		Initial.	Final.	
5	0.12	0.387	0.129	0.67
6.7	0.16	0.43	0.065	0.85
8	0.18	1.49	0.52	0.65
10	0.16	1.54	1.07	0.31

The flow rate of about 7 liters per minute seems to be the best with this apparatus for carbon monoxide oxidation as well as for ozone and nitric acid formation.

The experiments show that silver causes complete decomposition of ozone and the most efficient oxidation of the carbon monoxide present. Neither the lead nor the lead dioxide caused complete decomposition of the ozone but they did assist in causing oxidation of the carbon monoxide. The decomposition of ozone noted was more than that recorded by Perman and Greaves.<sup>1</sup> Since the degree of fineness and past history of the material affect the catalytic action so greatly it is not surprising that our results do not check the older ones. The manganese dioxide used (stock material) completely decomposed the ozone but did not assist appreciably in the oxidation of the carbon monoxide. Again we believe, however, that the history of this material may have considerable effect upon its catalytic action. As has been previously pointed out and is further evidenced by these results, ozone may be decomposed, as by heat and certain decomposing agents, without causing any oxidation of carbon monoxide present or it may be catalytically decomposed, as by silver, so as to cause oxidation.

It is obvious that part of the oxidation takes place in the ozonizer while the gases are under the influence of the silent discharge and that part takes place while the gases are under the influence of the catalyst. The total oxidation can be assumed to take place as a result of the decomposition of ozone either in the ozonizer or in contact with the catalyst, or it can be assumed that part of the oxidation is the result of the activation of carbon monoxide or oxygen under the influence of the silent dis-

<sup>1</sup> *Proc. Roy. Soc. (London)*, [A] **30**, 353-69 (1908).

charge or catalyst. Some little evidence as to the probability of this latter action is given by the data presented in Table V. It seems that the total oxidation obtained is much greater than can be accounted for on the assumption that it is all caused as the result of ozone decomposition—one molecule of carbon monoxide being oxidized by one molecule of ozone. The maximum concentration of ozone present in the effluent gas when dry air was ozonized was 0.18%, and under the condition of the experiments in which moist air was ozonized even a lower concentration would be expected (Fig. 2). It seems fairly evident therefore, that the concentration of ozone coming in contact with the silver catalyst was less than 0.18%, and that the carbon monoxide oxidized as a result of its decomposition must be less than 0.18%. It is not indicated from the results given in Table II that the great amount of oxidation occurs in the discharge since a run with the same apparatus caused a decrease in carbon monoxide content from 1.14% to 1.01%. It is suggested that the data possibly indicate the formation of some active modification of oxygen other than ozone under these conditions which in contact with the catalyst reacts with carbon monoxide. Or it may be that the carbon monoxide itself is activated in the presence of moisture so that it is oxidized by ordinary oxygen in contact with the silver.

The presence of hydrogen has apparently no effect upon the oxidation of carbon monoxide as the results given in Table VI show.

TABLE VI  
OXIDATION OF CARBON MONOXIDE IN PRESENCE OF HYDROGEN WHEN PASSED THROUGH APPARATUS A AND OVER SILVER CATALYST.

Rate of passage. (Liters per hour).	Original gas mixture.			% CO <sub>2</sub> formed.
	% CO.	% H <sub>2</sub> .	Diluent.	
2	5.0	None	Air	1.41
1.5	5.0	None	Air	1.45
2	5.0	5.0	Air	1.45
2	5.0	5.0	Air	1.45

This agrees with the observation of Berthelot<sup>1</sup> that a dry mixture of hydrogen and oxygen will not combine when subjected to long continued discharge in an ozonizer.

### Summary.

1. The yield of ozone obtained in the effluent gas by passing air or oxygen through the silent discharge is decreased by the presence of water vapor, by using a silvered electrode, and by having a small arc in series. There is an optimum rate of passage of the gas through the discharge.

2. No appreciable oxidation of carbon monoxide present in small amounts in air or oxygen is effected by a low concentration of ozone unless the ozone is decomposed by special catalysts.

3. Carbon monoxide may be almost completely oxidized by passage

<sup>1</sup> *Compt. rend.*, **8**, 50 (1879).

with pure oxygen or air through the silent discharge. The optimum conditions for obtaining maximum yields of ozone in effluent gas are not necessarily the conditions for obtaining maximum oxidation. Other conditions being constant the slower the rate of passage through the ozonizer the greater the amount of oxidation. The fact that under certain conditions more carbon monoxide is destroyed than can be oxidized by the maximum yield of ozone obtained in the effluent gas when oxygen or air is ozonized under similar conditions is accounted for by assuming the formation and decomposition of sufficient ozone *in the ozonizer tube* or by assuming the formation of an active modification of carbon monoxide or of oxygen other than ozone. The evidence is not sufficient to clear up this point.

4. By passing a mixture of air or oxygen containing relatively small amounts of carbon monoxide and ozone over a catalyst such as silver, the carbon monoxide is readily oxidized, presumably as a result of the catalytic decomposition of ozone. Lead and lead dioxide are less effective catalysts and manganese dioxide, unless specially prepared, is ineffective as a catalyst for the oxidation reaction although it completely decomposes ozone.

5. The carbon monoxide is most efficiently oxidized as regards time and energy when it is passed with air or oxygen through the silent discharge and over the silver catalyst. Best results have been obtained when the undried air mixture is passed through a very large discharge unit, and over silvered asbestos. The total oxidation obtained is apparently greater than can be accounted for by the assumption that it is all caused as a result of simple ozone decomposition—one molecule of ozone oxidizing one molecule of carbon monoxide. The formation under these conditions of an active modification of carbon monoxide or of oxygen other than ozone is possibly indicated.

6. The presence of hydrogen does not reduce the oxidation of carbon monoxide under the conditions previously described.

7. Until a much more efficient form of ozonizer is developed the oxidation of carbon monoxide by electrical means will not be commercially practical.

8. With the hope of devising a more efficient apparatus the study of the laws of ozone formation in the silent discharge is being continued by one of us at Purdue University.

CLEVELAND, OHIO, AND  
LAFAYETTE, INDIANA.