number." In any use of the catalysis by platinum of the decomposition of hydrogen peroxide for the measurement of protective action, there should be a careful standardization of the method.

Summary

1. A study has been made of the influence of different concentrations of acid and alkalies on the inhibitory effect of gelatin upon the catalytic decomposition of hydrogen peroxide by colloidal platinum.
2. In the acid range the variation of the inhibition is evidently a function of the specific effect of the acid anion as well as of the hydrogen-ion concentration.
3. In the alkaline range the variation of the inhibition depends chiefly upon the hydroxyl ion concentration.
4. At any *P*H the inhibition depends upon the concentration of the hydrogen peroxide and platinum used.
5. The results indicate that not only the gelatin but also the catalysis itself is influenced by the acids and alkalies; therefore the variation of the inhibitive effect is not similar to the protective effect as shown by the "gold number."

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE COLLEGE]

THE EQUILIBRIUM BETWEEN HYDROGEN-CARBON MONOXIDE AND METHANE-CARBON DIOXIDE IN THE CORONA DISCHARGE

BY GERALD L. WENDT AND GREGG M. EVANS

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Introduction

The subject of chemical reaction in the electrical discharge has long been of interest. Andrews and Tait,[1] Brodie,[2] Thenard,[3] and Berthelot[4] seem to have been the earliest workers. Since then a large number of investigators[5] have studied various reactions, and many others have worked on

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[1] Andrews and Tait, *J. Chem. Soc.*, **13,** 344 (1861).

[2] Brodie, *Phil. Mag.*, [4] **44,** 470 (1872).

[3] Thenard, *Compt. rend.*, **75,** 118 (1872).

[4] Berthelot, *ibid.*, **82,** 1357 (1876); *Bull. soc. chim.*, [2] **26,** 101 (1876).

[5] Anderegg, THIS JOURNAL, **39,** 2581 (1917); **47,** 2429 (1925); *Trans. Am. Electrochem. Soc.*, **44,** 203 (1923); *Proc. Indiana Acad. Sci.*, **1921,** p. 157; (b) Briner, Meiner and Rothen, *Helv. Chim. Acta.*, **9,** 409 (1926); (c) Collie, *J. Chem. Soc.*, **79,** 1149 (1901); (d) Comanducci, *Rend. accad. sci. Napoli*, **15,** 15 (1909); (e) Crespi and Lunt, *J. Chem. Soc.*, **127,** 2051 (1925); (f) Crocker, *Phys. Rev.*, **8,** 344 (1916); (g) Dem'yanov and Pryanishnikov, *J. Russ. Phys.-Chem. Soc.*, **58,** 462 (1926); (h) Elliott, Joshi and Lunt, *Trans. Faraday Soc.*, **23,** 57 (1927); (i) Elliott, *ibid.*, **23,** 60 (1927); (j) Grubb, *Thesis.*

the electrical considerations. In general two types of apparatus have been used: the ozonizer, with the discharge taking place between two concentric cylinders, and the type here used, with the discharge between a central wire and a concentric cylinder. Although both of these have been called by the name of corona, the name having been applied as early as 1872 by Reynolds[6] to the phenomenon on the balls of a static machine, the wire-in-cylinder type corresponds more closely to the corona of the electrical engineer,[7] and will be so called in this paper.

Since the gases are important commercially, and since from at least one side the reaction has been studied catalytically, it seemed worth while to study the effect of the corona discharge upon the reaction, $2H_2 + 2CO = CO_2 + CH_4$. This reaction has accordingly been investigated with emphasis upon the gaseous phase, and this has been found to reach a constant composition from both sides of the reaction. The method of constant pressure has been used to avoid any influence of pressure changes upon the course of the reaction. Since the gas volume continues to contract even after this constant composition is reached, it is evident that some other reaction accompanies or follows the one given, and probably goes to completion.

The Experiments

Gases Used.—Carbon monoxide was generated from sodium formate and concentrated sulfuric acid, stored over saturated brine containing sodium hydroxide, analyzed and transferred as soon as possible to the gas holder. Hydrogen and carbon dioxide were taken from tanks, the former being led over hot copper for removal of oxygen. Natural gas[8] was used for methane. This contained about 0.4% of carbon dioxide and 3.4% of ethane.

Hydrogen and carbon monoxide, or methane and carbon dioxide, whichever pair was being used, were mixed in as nearly equal proportions as possible by means of approximate calibrations on a gas holder of the type suggested by Burrell, Seibert and Jones,[9] but constructed entirely of glass, mercury being used as the confining liquid.

Univ. of Chicago, **1921**; (k) Jackson and Northal-Laurie, *J. Chem. Soc.*, **89**, 1190 (1906); (l) Joshi, *Trans. Faraday Soc.*, **23**, 227 (1927); (m) Rideal and Kunz, *J. Phys. Chem.*, **24**, 379 (1920); (n) Lob, *Z. Electrochem.*, **12**, 282 (1906); (o) Losanitsch and Jovitschitsch, *Ber.*, **30**, 135 (1897); (p) Lunt, *Proc. Roy. Soc. London*, **108A**, 172 (1925); (q) Lunt and Ramavenkatasubbier Venkateswaran, *J. Chem. Soc.*, **1927**, 857; (r) Montemartini, *Gazz. chim. ital.*, II, **52**, 96 (1922); (s) Newsome, THIS JOURNAL, **48**, 2035 (1926); (t) Ott, *Ber.*, **58**, 772 (1925); (u) Sacks, *Ann. Phys.*, **47**, 886 (1915); (v) Wendt and Farnsworth, THIS JOURNAL, **47**, 2494 (1925); (w) Wendt and Snyder, *ibid.*, **50**, 1288 (1928).

[6] Osborne Reynolds, *Chem. News*, **25**, 113 (1872).

[7] Peek, "Dielectric Phenomena in High Voltage Engineering," McGraw-Hill Book Co., New York, **1920**; Whitehead, "Dielectric Phenomena," D. Van Nostrand Co., New York, **1927**.

[8] We are indebted to Mr. Walter F. Booth, of the Little Rock Gas and Fuel Co., Little Rock, Arkansas, for the gift of several cylinders of natural gas unusually high in methane content and practically free from non-hydrocarbons.

[9] Burrell, Seibert and Jones, *U. S. Bur. Mines Bull.*, No. 197, p. 61.

The mixture was analyzed after standing for several hours and the calculated amount of gas added to correct the composition of the mixture to equality in the two constituents. After standing overnight a check analysis was made to determine the final composition of the mixture. Preparing gas mixtures of equal parts was difficult and it was impractical to make corrections to within 1% of the exact amounts. Special efforts were made to exclude oxygen from the mixture because of pronounced effects on the reaction caused by even small quantities of this gas. The mixture was drawn off from this holder with a gas buret, dried over concentrated sulfuric acid in a Hempel gas buret and loaded into the corona tube.

The Corona Tube.—The corona tube is shown in Fig. 1. It was constructed of Pyrex glass, the foundation being a twenty-inch, sealed-in Liebig condenser. To the ends of the inner tube were sealed as shown the 3-way stopcocks for manometer, vacuum and loading connections, and to the lower end the large cylinder D. In this latter was inserted a piston made from a rubber stopper and a jointed rifle cleaning rod, by means of which the volume of the apparatus could be varied. The total length of the main tube was 103.5 cm. The length of the short top segment was 6.5 cm., and its volume 16.7 cc. The length of the tube within the condenser jacket, to which the discharge was confined, was 51 cm. and its diameter 1.15 cm. Its actual volume was 53.8 cc. The distance from the lower end of the jacket to the center of the stopcock B was 8.5 cm. The length of the large cylinder was 37.5 cm. and its internal diameter 2 cm. The 85cc. calibration mark was slightly below the lower stopcock, and with the piston inserted at its lowest possible point the total volume was 175 cc. The reaction space was then approximately one-third of the total volume. This is small, but experiments showed that diffusion of bromine from the lower end of the tube was practically complete in five minutes; nor could any difference greater than the experimental error be found in the analysis of samples taken from the top of the tube immediately after cessation of the discharge, and the next sample from lower down in the tube. The volume of the tube could be varied from about 83 cc. to the maximum by movement of the piston. The 2mm. capillary connecting the stopcock A with the main tube was 4 cm. long and that for C, 8 cm. The manometers were both of 2mm. capillary. The amount of dead space was therefore negligible. The high potential electrode consisted of a platinum wire 0.51 mm. in diameter (B. and S. gage 24), centered in the inner tube and

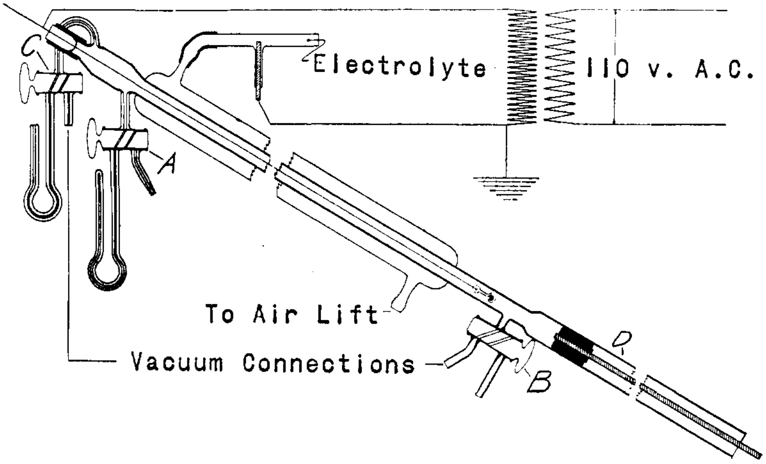


Fig. 1.

fastened at its lower end to a heavy platinum wire hook, which in turn engaged a glass cross bar in the tube about two centimeters above the lower stopcock. At the upper end it was sealed through the lower end of a short cylinder of glass tubing of the same size as the corona tube, a flexible connection for the purpose of centering and putting tension upon the wire being obtained by means of a piece of heavy rubber tubing, wired and shellacked. A cord from the top of the wire was led over a pulley to a weight. A dilute solution of acid was circulated by means of an air lift through the outer jacket and a reservoir set above the tube and served both as the grounded electrode and a cooling medium. A thermometer for measuring the temperature of the electrolyte was inserted at the lower opening of the condenser jacket.

Electrical Equipment.—The power was taken from the 110-volt, 60-cycle lighting circuit, through a Thordarsen transformer with a secondary rating of 20,000 volts. The line voltage was subject to fluctuations of at times as much as 10%, so that it was impossible, even with careful watching of the meters, to keep the input absolutely constant. The primary amperage, the voltage drop across the transformer and the secondary milliamperage were measured by means of appropriate Weston instruments. The secondary voltage was obtained by means of a 10,000 volt Braun electrostatic voltmeter with a series condenser, the effect of the condenser being obtained by means of low voltage measurements with and without the condenser inserted. These measurements are believed to be accurate to within 5%.

Manipulation.—Each time before using the reaction tube was cleaned with boiling dichromate-sulfuric acid cleaning solution, washed with distilled water until the washings no longer tested acid to methyl orange, and dried by means of air which had been run through two wash bottles of concentrated sulfuric acid and a tube filled with glass wool to remove acid spray. To make a run the piston was lubricated with a small amount of paraffin stopcock grease (which did not measurably absorb the gases used) and inserted in the cylinder D to its upper end. The mercury in the open manometer was drawn to the stopcock at C and the stopcock was turned to connect with the vacuum. The open end of B was connected by means of a rubber tube with a leveling bottle of mercury, the mercury raised just to the stopcock and held by turning the cock. The stopcock at A was connected with the vacuum manometer and evacuation begun. A pressure as low as twenty millimeters was ordinarily easily obtainable with the water pump used. The tube was then shut off from the vacuum line and held under vacuum to test for leaks. The gas buret containing the dried mixture was next connected with the opening at A and the gas allowed to enter the tube. The buret was then disconnected and the end of the capillary capped. This evacuation and filling were twice repeated, evacuating once from C and once from B, so as to sweep out as completely as possible all air in the side tubes. After the last filling a second buret-full was drawn in by pulling the piston carefully down to the calibration mark for the desired initial volume. This was ordinarily 160 cc. The stopcock C was then connected with the open manometer, the gases were brought down to atmospheric pressure by momentarily opening A, and the power was turned on. During the run the pressure was kept constant by changing the volume as required by means of the piston. At the end of the run the analytical buret was connected with A and the sample forced out by means of the piston, or by running in the mercury at B, first sweeping out the capillary at A. To get samples of the tube washings a few cubic centimeters of the solvent were drawn in at A and run up and down in the tube by means of the mercury, finally being ejected into a container.

As a milliameter was available only toward the latter part of the work, the runs were made unless otherwise stated with a constant primary current of two amperes. This gave a primary voltage drop of 87 to 88 volts, corresponding to fifteen kilovolts in the secondary circuit, as calibrated. The secondary current increased during an experiment from 6.4 to somewhat over 7.0 milliamperes, depending upon the length of the run.

Analytical Methods.—The Hempel type of gas analysis apparatus was used, as any of the Orsat types suitable for complete analysis were found insufficiently portable for use in this connection. A calibrated 50cc. buret was employed, made from an Exax titration buret, with mercury as the confining liquid. Carbon dioxide was absorbed in potassium hydroxide, oxygen in alkaline pyrogallol, carbon monoxide in ammoniacal cuprous chloride, and hydrogen and methane were determined by combustion over mercury. In the preliminary analyses of the carbon dioxide and methane mixtures the ethane could be determined separately, but in the final analyses both ethane and methane show under methane. In the preliminary analyses of the hydrogen and carbon monoxide mixtures carbon monoxide was more conveniently determined by combustion. No unsaturated compounds beyond the error of the analytical methods could be found, so that after the first ten or fifteen experiments this determination was omitted. The formaldehyde titrations were made with potassium iodide, 0.01 *N* dichromate and 0.01 *N* thiosulfate solutions.

The Results

The Equilibrium.—The initial expansion due to the "corona pressure," as recorded by former investigators in this field, was evident on closing the switch. This was followed by a slower expansion caused in part by temperature increase. An expansion would be expected when carbon dioxide and methane were used for the starting gases. Actually this lasted for only about twenty-five minutes and a correction for the temperature increase taking place during that time showed that the actual corrected maximum came after fifteen minutes. From then on the gas contracted. When starting with hydrogen and carbon monoxide, and correcting for temperature, an almost linear contraction began at once.

The analyses of a series of runs are shown in Table I and plotted in Fig. 2. No exact analysis of the starting mixture is shown because the runs were made from several mixtures differing slightly in composition. All contained, however, from 48 to 49% of each of the gases used. It will be seen that the same percentage composition of the resulting gas mixture is obtained from both sides of the reaction. Averaging the results from runs of 180 minutes and longer gives this composition as 13.3% carbon dioxide, 37.1% carbon monoxide 8.7% methane, and 37.6% hydrogen.

Since contraction continued even after attainment of this constant composition, the record of the actual volumes throughout the reaction is also important. In Table II are shown the volumes as actually recorded in the longest run in each part of Table I, and for each gas the number of

Table I

Percentage Composition of the Gases during the Reaction

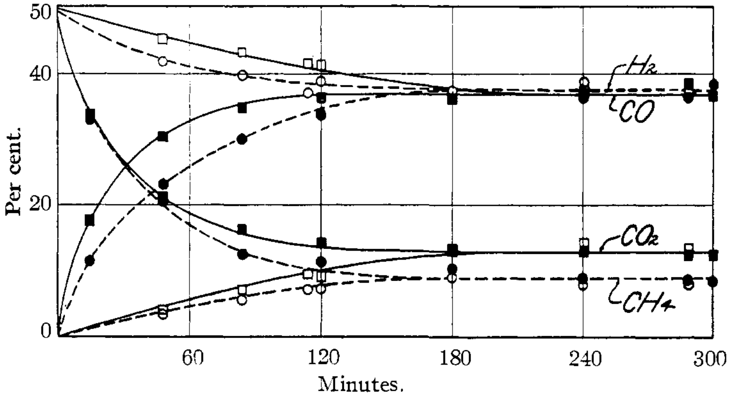
Starting with equal amounts of carbon dioxide and methane

	Minutes							
	15	48	84	120	180	240	289	300
CO_2	33.6	21.2	16.4	14.3	13.1	13.0	12.4	12.4
O_2	0.2	0.4	0.2	0.3	0.3	0.2	0.3	0.2
CO	17.6	30.4	34.8	36.2	36.1	37.0	38.6	36.7
CH_4	32.9	20.5	12.6	11.6	10.3	9.0	8.7	8.4
H_2	11.6	23.0	30.0	33.7	36.7	36.4	36.5	38.5
N_2 (diff.)	4.1	4.5	5.0	3.9	3.5	4.4	3.5	3.8

Starting with equal amounts of hydrogen and carbon monoxide

	Minutes						
	48	84	112	120	180	240	289
CO_2	4.1	7.4	9.5	8.9	13.4	14.5	13.7
O_2	0.0	0.2	0.2	0.2	0.2	0.0	0.0
CO	45.3	43.4	41.5	41.3	36.6	36.7	37.1
CH_4	3.7	5.8	7.3	7.6	9.0	7.9	8.0
H_2	41.8	39.9	37.2	38.8	37.1	38.8	38.8
N_2 (diff.)	5.1	3.3	4.3	3.2	3.7	2.1	2.4

cubic centimeters which may be assumed to have been present at the times stated, judged by the analyses of the individual runs stopped at those points. These amounts are plotted in Fig. 3. It will be seen that the amounts of the gases being formed in the reaction reach a maximum and then decrease, the slope of the line finally being the same as that of the same constituent when starting from the opposite side of the reaction. Due to difference in starting volume and to the initial increase in volume from the carbon dioxide and methane side, they would not be expected to reach the same actual amount. It is evident then, that some other reaction takes place simultaneously with the one we are discussing and causes



□, ○—from CO and H_2; ■, ●—from CO_2 and CH_4.

Fig. 2.—Percentage composition of gases during reaction.

TABLE II

GAS VOLUMES DURING THE REACTION—CUBIC CENTIMETERS AT STANDARD CONDITIONS

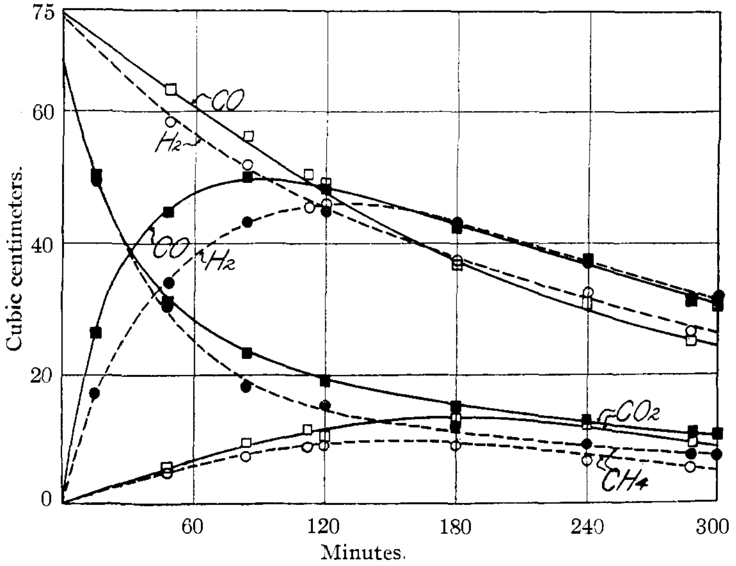
Starting with carbon dioxide and methane

	Minutes								
	0	15	48	84	120	180	240	289	300
Total vol.	140	149	148	143	133	118	101	86.4	83
CO_2	68.3	50.0	31.4	23.5	19.0	15.4	13.1	10.7	10.3
CO	...	26.2	45.0	48.8	48.1	42.4	37.4	31.7	30.4
CH_4	68.0	49.0	30.3	18.0	15.4	12.1	9.1	7.5	7.0
H_2	...	17.3	34.1	43.0	44.8	43.3	36.8	31.6	32.0

Starting with hydrogen and carbon monoxide

	Minutes							
	0	48	84	112	120	180	240	289
Total vol.	152	140	130	122	119	101	84	69
CO_2	...	5.7	9.6	11.6	10.6	13.5	12.2	9.5
CO	75.7	63.5	56.4	50.6	49.2	37.0	30.8	25.6
CH_4	...	5.2	7.5	8.9	9.1	9.1	6.6	5.5
H_2	73.6	58.5	51.9	45.4	46.1	37.5	32.6	26.8

the contraction in volume. This was confirmed by the formation of a solid deposit. It is important that there is no further change in gas composition during this change in volume.



□, ○—from H_2 and CO; ■, ●—from CO_2 and CH_4.

Fig. 3.—Gas volumes during reaction.

The equation for the equilibrium constant for the reaction $2CO + 2H_2 = CO_2 + CH_4$ would be written $K_p = [CO_2]\ [CH_4]/[H_2]^2\ [CO]^2$. Inserting the average percentages given above, the actual value would be $K = (0.133 \times 0.087)/(0.1413 \times 0.1377)$. This gives for the experimental value of the equilibrium constant $K = 0.5946$. Using the equation for the free energy change in this reaction as given by D. F. Smith,[10] $\Delta F = -56{,}950 + 15.075\, T \ln T - 0.01078\, T^2 + 0.00000031\, T^3 - 30.34\, T$, and substituting the free energy values calculated therefrom for the temperatures 900 and 950° absolute in the Equation, $\Delta F = -RT \ln K$, we have, $K_{900} = 0.7686$ and $K_{950} = 0.2084$. The equilibrium point for this reaction reached under the conditions of this investigation would therefore seem to correspond to an absolute temperature of between 900 and 950°. Lunt[5p] and Wendt and Farnsworth[5v] have previously found evidence of a high temperature effect in the corona discharge.

Other reactions are possible from the mixture of gases employed in these experiments, for instance, $3H_2 + CO = CH_4 + H_2O$. All such reactions, however, involve the formation of water. A number of experiments were made in which a vessel containing phosphorus pentoxide was inserted in the reaction tube, being attached to the piston. In no case did this result in a change in the composition of the equilibrium gas mixture. If water had been a component of the equilibrium its removal in this manner should have had a marked effect on the equilibrium concentrations. The presence of even a small quantity of free oxygen, for instance, entirely altered all the concentrations. The fact that phosphorus pentoxide had no effect indicates that these reactions involving water need not be considered in this equilibrium.

The intensity of the electric discharge influences the rate at which equilibrium is obtained. In order to measure the effect of changes in the corona, runs were made with carbon dioxide and methane with the secondary milliamperage at 6.4, and at 4.0. The first was a two-hour run and the second was run until the volume contracted to that reached by the first. The volume loss in the first run for the last linear part of the time–volume curve was at the rate of 8 cc. per hour, and for the second run, 4.9 cc. per hour. The secondary voltage in the first run was 14,000 and in the second 9700. The reaction velocity seems more nearly proportional to the secondary current than to voltage or volt-amperes. There is, of course, an unknown amount of surface leakage involved but as the milliameter was in the grounded line this was reduced to a minimum. Neither of the analyses differed by more than the experimental error from that for the corresponding two-hour run shown in Table I.

To study the effect of the proportion of the total gas mixture which was actually in the discharge region upon the velocity of the reaction, a run was made with a starting volume of only 82 cc. of carbon dioxide and methane, and run to the maximum volume at fifteen minutes. The final volume was 92 cc., and the composition of the resulting gas mixture was as follows: CO_2, 25.3%; O_2, 0.1%; CO, 24.3%; CH_4, 26.3%; H_2, 19.8%;

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[10] D. F. Smith, *Ind. Eng. Chem.*, **19**, 801 (1927).

N_2, 5.2%. This, when compared with the fifteen-minute run in Table I in which 160 cc. was used, shows that the rate of reaction is roughly proportional to the fraction of the total volume exposed to the discharge.

Non-Gaseous Products.—The continued reduction in volume indicated that other products besides the above gases were formed. In fact some of them were visible. In from five to ten minutes from the closing of the electrical circuit brown spots appeared on the central wire, which soon blackened, and by the end of three hours the wire was entirely covered. Location of the original spots seemed to coincide with the position of the negative beads of the discharge. In runs of more than two hours' duration a brown deposit appeared on the inside of the glass tube itself. In preliminary work when aluminum carbide was used as the source of methane, so that hydrogen as well as methane and carbon dioxide were present in the starting mixture, there was evidence of drops of clear liquid on the walls of the glass tube; this was no longer obtained after the use of the natural gas began. Investigation of the brown deposit showed that the greater part of it was carbon suboxide, as it had the properties attributed to that substance by Brodie[2] and Crespi and Lunt[5e] as prepared under slightly different circumstances. In addition, however, the water solution from washing the tube gave a decisive though weak test for aldehyde with Schiff's solution, although the water which had stood in contact with the gaseous phase alone showed only a very faint trace. A slight roughening of the wire due to sputtering was visible after the removal of the deposit.

The Decrease in Volume after Equilibrium.—In order to study the continuous decrease in volume after the composition of the gases had reached equilibrium a number of possibilities were investigated. To determine whether the contraction continues indefinitely or comes to an end while reactive gases are still present, a mixture of methane and carbon dioxide was exposed to the action of the corona for a total of forty-five hours. The discharge was confined to a length of about two and a half centimeters of the upper end of the wire by emptying the jacket of electrolyte and using for a grounded electrode a strip of aluminum foil of the above width wrapped around the tube where the two upper stopcocks are attached. An air blast was used to cool the tube and sweep away ozone. During a run totaling forty-five hours with this small discharge, 170 cc. of gas contracted to less than 17 cc. The last part of the contraction was followed by allowing mercury to flow up into the region inside the condenser, as was done in taking samples for analysis. The stoppage of the reaction was necessitated only by the approach of this mercury, which was, of course, at high potential, to the outer aluminum electrode. The contraction had not up to that time shown any signs of stopping, and probably would have gone to completion had it been possible to continue the experiment. As deposition of solids took place only in the discharge region, such products were in this case thus left within the influence of the corona throughout the run. The deposit on the walls as well as on the wire was black, indicating considerable carbonization of the primary deposit. It was not possible to obtain a sufficiently large sample of gas for an accurate analysis, but it was possible to determine that all four gases of the equilibrium mixture were still present.

The effect of the corona on pure carbon monoxide and on pure methane was tested in order to determine whether either gas alone was responsible. Hydrogen alone could not be responsible, and Wendt and Farnsworth[5v] have investigated carbon dioxide alone and found no such effect. The contraction might have been due to the formation of carbon suboxide according to the equation $4CO = C_3O_2 + CO_2$. Crespi and Lunt[5e] studied this reaction in an ozonizer under constant volume conditions and found that contraction stopped after 225 minutes. Carbon suboxide was the principal solid product. We made a run with pure carbon monoxide and contraction in our case stopped after eight hours, when an original volume of 173 cc. had contracted to 133 cc. The analysis of the gas was as follows: CO_2, 10.7%; O_2, 0.1%; CO, 86.3%; CH_4, 0.0%; total absorbed, 97.1%. The deposit on the walls of the tube was similar in appearance and properties to the deposit formed on the glass during the regular reaction, but was lighter in color, indicating that while the deposit in the regular reaction was principally carbon suboxide, some carbonization had taken place. This reaction of carbon monoxide alone, therefore, could not account for the continued contraction, both because the deposit appeared to be different and because contraction did not continue indefinitely.

A run was made with methane alone in the tube, but in this case, also, equilibrium was reached, indicated by a stoppage of expansion when an original volume of 80 cc. had expanded to 88 cc. The composition of the final gas was as follows: CO_2, 0.0%; unsaturated compounds, 0.5%; O_2, 0.5%; CO, 0.8%; CH_4, 38.4%; H_2, 57.2%; total absorbed, 97.4%. The deposit on the tube in this case took the form of droplets of viscous liquid, probably polymerization products similar to those found by Lind and Glockler[11] in their experiments with ethane in electrical discharges. The action of methane alone thus fails to explain the large contraction taking place in the experiments with gas mixtures.

Since no single constituent accounts for the contraction, those reactions which give condensed products deserved further study. Two possible reactions which might cause a complete contraction without affecting the proportions of the four gases present at equilibrium are, $H_2 + CO = HCHO$, and $H_2 + CO = C + H_2O$. Schiff's solution, as mentioned above, showed the presence of aldehyde, but a titration with thiosulfate, potassium iodide and potassium dichromate of a solution of the deposit from a five-hour run

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[11] Lind and Glockler, Preprint No. 6, *Trans. Am. Electrochem. Soc.*, Sept. 22, 1927.

reduced only half a cubic centimeter of the 0.01 *N* dichromate, an amount hardly above the error of the method. Contardi[12] has shown that polymers of formaldehyde which would be insoluble in water are not stable in the electrical discharge. It is evident, then, that the influence of the formaldehyde reaction is small.

To study the possibility that the formation of carbon and water is involved, an attempt was made to produce the reaction $2C + 2H_2O = 2H_2 + 2CO = CO_2 + CH_4$, by depositing carbon on the wire from methane and running the discharge with the tube filled with steam. We were unable to keep the discharge region sufficiently hot to prevent condensation of the steam, even though boiling salt solution was used in the jacket; the vacuum so created caused air leakage through the melted stopcock grease and only a trace of methane was found.

The calculation of the carbon, hydrogen and oxygen balances in the remaining gaseous constituents during the course of the contraction gives an indication of the nature of the volume loss and the fate of the gaseous materials apparently lost. Table III shows a balance of the gaseous constituents at the beginning and end of the long runs in Table I. Inasmuch as these losses appear to be very close to the proportions in CH_2O, or C and H_2O, and the amount of formaldehyde formed has been found to be very small, carbon and water seem the most probable end products of the reaction under these conditions. Losanitsch and Jovitschitsch[50] state that their final product from hydrogen and carbon monoxide in the ozonizer at seventy volts was glycolaldehyde. Due to the higher voltage used in this investigation and the greater current density at the small diameter

TABLE III

CARBON, HYDROGEN AND OXYGEN BALANCE FROM CARBON DIOXIDE AND METHANE

	C, g.	H, g.	O, g.
Start of reaction			
68.3 cc. CO_2 = 0.1340 g.	0.0367	.....	0.0978
68.0 cc. CH_4 = .0486 g.	.0364	0.0121	.....
Total	0.0731	0.0121	0.0978
End of reaction			
10.3 cc. CO_2 = 0.0202 g.	0.0055	.....	0.0147
30.4 cc. CO = .0380 g.	.0163	.....	.0217
7.0 cc. CH_4 = .0050 g.	.0038	0.0013	.....
32.0 cc. H_2 = .0029 g.	.....	.0029	.....
Total	0.0256	0.0042	0.0364
Losses	.0475	.0079	.0614
Atoms	.00396	.0079	.00384
Ratio	*n*	2.0 *n*	0.97 *n*

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[12] Contardi, *Gazz. chim. ital.*, **51**, I, 109 (1921).

Table III (*Concluded*)

From Hydrogen and Carbon Monoxide

		C, g.	H, g.	O, g.
	Start of reaction			
75.7 cc. CO	= 0.0947 g.	0.0406	.....	0.0541
73.6 cc. H_2	= .00657 g.	.....	0.00657	.....
Total		0.0406	0.00657	0.0541
	End of reaction			
9.5 cc. CO_2	= 0.0186 g.	0.0051	.....	0.0136
25.6 cc. CO	= .0320 g.	.0137	.....	.0183
5.5 cc. CH_4	= .00393 g.	.00295	.00098	.....
26.7 cc. H_2	= .00238 g.	.....	.00238	.....
Total		0.02175	0.00336	0.0319
Losses		.01885	.00321	.0222
Atoms		.00157	.00321	.00139
Ratio		n	2.2 n	0.9 n

wire electrode, different results might well be expected from those obtained in the ozonizer type apparatus at the low voltage. It is interesting to note, however, that in glycolaldehyde, as well as in formaldehyde and with carbon plus water, the ratio of carbon, hydrogen and oxygen is the same, namely, $C_nH_{2n}O_n$, and that this is the same as the ratio in either pair of starting gases, hydrogen and carbon monoxide, or methane and carbon dioxide. Hence the contraction and condensation do not change this ratio. The fact that the removal of water during the reaction by means of phosphorus pentoxide does not change the equilibrium concentrations indicates that water can take part only in this final reaction, whereby all gaseous constituents are removed in the form of carbon and water, a reaction which is under the experimental conditions apparently irreversible.

Summary

The reaction $2CO + 2H_2 = CO_2 + CH_4$ has been studied under the conditions existing in a corona discharge. The reaction reaches an equilibrium when approached from either side in which the composition is 13.3% carbon dioxide, 37.1% carbon monoxide, 8.7% methane, and 37.6% hydrogen. This equilibrium would under purely thermal conditions correspond to an absolute temperature of 900 to 950°. The gas volume continues to contract after the equilibrium is reached and the most probable end products are carbon and water according to the equation $CO + H_2 = C + H_2O$.

State College, Pennsylvania