[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE EQUILIBRIUM OF CARBON DIOXIDE WITH CARBON MONOXIDE AND OXYGEN IN THE CORONA DISCHARGE

BY GERALD L. WENDT AND MARIE FARNSWORTH[1,2]

RECEIVED MAY 25, 1925 PUBLISHED OCTOBER 6, 1925

The mechanism of the chemical reactions which take place under the influence of a rapid but diffuse electron stream such as is present in the "corona" discharge is not yet understood. A large number of reactions can be produced by the aid of the corona, many of which are listed by Berthelot[3] and by Löb and Lorentz.[4] These are of various types but their general relation to thermodynamic considerations has not been established.

One frequent interpretation of these reactions is that they are purely thermal. The dispute concerning the mechanism of the reaction between nitrogen and oxygen to give nitric oxide in the electric arc is classical.[5] In the Schönherr process conditions are such that the thermal explanation by purely thermodynamic principles is practically excluded but here, as in the corona reactions where high temperature as such is excluded, this thermal point of view implies regarding the average temperature as admittedly low but considering the velocities given to individual molecules as extremely high, a sort of selective high temperature at which reaction takes place. It need not be urged that such a view is not in accord with the thermodynamic conception of temperature or of energy distribution in a kinetic gaseous system. That such a view is inadequate is best indicated by the great discrepancy between the sensible average temperature and the temperature required on a thermodynamic basis for the equilibrium which is reached in such reactions. Thus, Haber[6] has shown that in order to give the concentrations of nitric oxide which the arc process actually gives, the temperature must be some 4000° K., while actually the maximum average temperature reached by the gases was not above 3000° K.

The discrepancy between the thermally required temperatures and those actually prevailing is even more striking in the case of corona reactions, for here the temperature actually reached is elevated by scarcely a few degrees, while the reaction equilibrium thermodynamically requires very high temperatures. The simple reaction $2CO + O_2 = 2CO_2$ has already

---

[1] Presented to the Faculty of the University of Chicago in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Presented orally at a regional meeting of the mid-western sections of the American Chemical Society, University of Illinois, Urbana, Illinois, May, 1923.

[3] Berthelot, "Chemical Mechanics," Dunod, Paris, **1879**.

[4] Löb and Lorentz, "Electrochemistry of Organic Compounds," J. Wiley and Sons, New York, **1906**.

[5] Knox, "Fixation of Atmospheric Nitrogen," D. Van Nostrand Co., New York, **1914**.

[6] Haber and Koenig, *Z. Elektrochem.*, **13**, 725 (1907); **14**, 689 (1908).

been studied in the silent discharge by Thenard,[7] Brodie,[8] Noda,[9] Holt[10] and Moser and Isgarischew.[11] The study by Moser and Isgarischew is the most complete but the experimental data are not conclusive in that the chemical compositions at equilibrium were merely deduced from the pressure changes and were not obtained from analyses of the gases; furthermore, the reactions were carried on at constant volume and varying pressure, which ignores the effect of pressure on the reaction. They found that about 10% of the carbon dioxide was decomposed, judging by an increase in pressure from atmospheric to about 800 mm. They calculated the heat of decomposition from this fact, using the thermal equation of Nernst for the heat of decomposition of carbon dioxide and using room-temperature values for T. This is not justified, however, since Nernst actually found that only 1.58×10^{-5} of the carbon dioxide is decomposed even at 1000° K. In other words, an equilibrium at 10% cannot result at room temperature when only thermal factors are considered. The "effective temperature," including electrical factors, is much higher.

This reaction has also been fully studied from a purely thermal standpoint and the percentage decomposition at various temperatures is known. The aim of the present work was to study the equilibrium between carbon dioxide and its decomposition products, carbon monoxide and oxygen, in the corona discharge and to calculate the corresponding temperature thermodynamically. The work shows a percentage decomposition of the dioxide which corresponds thermodynamically to a temperature above 2500° K., a temperature which was certainly not present even fleetingly or in a minute quantity of the gas. It is important that equilibrium was reached from both sides and that a long extension of the corona treatment after equilibrium had been reached did not change the concentration of the three gases present. We are thus dealing with a true equilibrium which behaves exactly as if the entire volume of gas were above 2500° K., while actually the temperature was not above 35° C. or 300° K.

Experimental Methods

Carbon dioxide was prepared by dropping concd. sulfuric acid on pure sodium bicarbonate. The carbon dioxide was collected over water in a 15-liter bottle, another large bottle filled with water being used for pressure. Yellow phosphorus was used in the bottle of carbon dioxide to remove traces of oxygen. This was held in place by a cylinder of copper gauze which extended the length of the tube. As the water came up over the phosphorus it removed the layer of oxide and a fresh layer of phosphorus was exposed when new carbon dioxide was made. The gas was dried by bubbling through a small absorption tube containing concd. sulfuric acid and through a 40cm. Emmerling

---

[7] Thenard, *Compt. rend.*, **74**, 1280 (1872).

[8] Brodie, *Phil. Trans.*, **164**, 83 (1874).

[9] Noda, *Ann. Physik*, **19**, 1 (1906).

[10] Holt, *J. Chem. Soc.*, **95**, 30 (1909).

[11] Moser and Isgarischew, *Z. Elektrochem.*, **16**, 613 (1910).

tower which contained phosphorus pentoxide packed in glass wool. The carbon monoxide was made by dropping concd. sulfuric acid on sodium formate; traces of carbon dioxide and sulfur dioxide were removed by 30% potassium hydroxide, oxygen by phosphorus as with carbon dioxide, and the gas was stored and dried in the same way as the carbon dioxide. The oxygen was taken from a cylinder of commercial Linde oxygen made from liquid air and was dried in the same manner as the carbon dioxide and the carbon monoxide.

The corona tube (A, Fig. 1) was made of ordinary, thick-walled, soft glass tubing. The tube was 80 cm. long and 1.1 cm. in internal diameter. Platinum wire 0.2 mm. in diameter (B. and S. No. 24) running the entire length of the tube served as the high-tension electrode. A condenser jacket B, through which dil. sulfuric acid H was circulated, surrounded the tube. This acid served for cooling and for a ground electrode. The platinum wire was held in place by sealing it into capillary tubing which was inserted in rubber stoppers. The wire had to be well centered, as otherwise the discharge took place only along part of the tube, and taut, since if it was loose the wire vibrated. The rubber stoppers were protected from the ozone formed in the corona by about 0.5 cm. of paraffin. The paraffin was melted in place and allowed to solidify while the tube was in an upright position. In all there were four side arms to the tube. The first was a T-tube, one arm of which was connected to the corona tube, another arm through a stopcock to a mercury manometer C and the other side arm through a stopcock D to the water pump. Another side arm was connected to a two-way stopcock E which served as an inlet and outlet for the reacting gases. The gases were admitted and removed over mercury by means of a gas buret connected with a leveling tube. In order to protect the necessary rubber connections from the action of the ozone, the gases after having been subjected to the corona were led off through an absorption bulb F containing neutral potassium iodide. The other two side arms were used for admitting and removing the dielectric and will be discussed below.

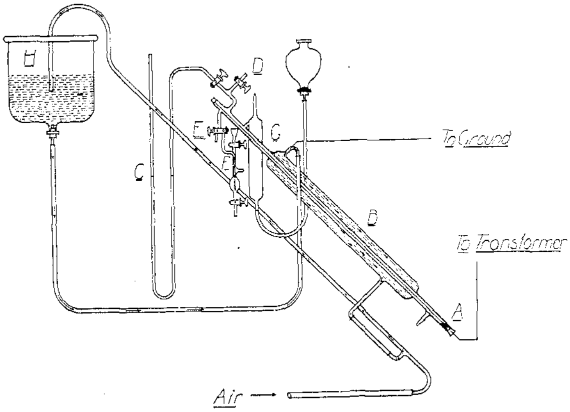

Fig. 1.

The power for the corona was taken from the ordinary 110-volt, 60-cycle, alternating current lighting circuit. The potential of the circuit was increased about 100 times by a T-2 Thordarsen transformer. The flow of current through the primary was regulated by a reactance so that about 1 milliampere flowed through the secondary.

In the reaction $2CO + O_2 = 2CO_2$, three volumes of gas change into two volumes. Now pressure is very important in determining the degree of dissociation where the numbers of molecules change during the course of the reaction. Therefore it was necessary to keep the pressure constant. Serious difficulties were encountered here as the volume of the corona tube had to be varied during the course of the reaction. A substance that could be used for this purpose must be mobile, a good dielectric and must not be affected by the corona, carbon dioxide, carbon monoxide, oxygen or ozone. Such a substance is hard to find. Dielectric liquids were all easily oxidized. Ordinary transformer oil was first tried but under the influence of the corona this oil absorbed the oxygen. So also did a highly purified paraffin oil, sold commercially under the trade name of Nujol. Non-reactive, conducting liquids such as sulfuric acid and mercury were next tried. The condenser jacket was removed from the corona tube and the tube was tightly wrapped with tin foil which served as the ground connection. As the volume decreased (starting with carbon monoxide and oxygen) the tin foil was removed in sections and the liquid was introduced into the tube to reduce the gas volume; but the liquid wet the tube, the current jumped across from it to the tin foil and no discharge took place along the length of the wire. Glass seemed to be the only substance inert enough to serve. To secure mobility, small glass pearls of about 1–2 mm. diameter were used. A layer about 3 cm. deep of these beads could be floated on mercury in a tube of fairly wide bore. Width was needed, as otherwise the friction along the walls of the tube became so great that the mercury came up through the crevices of the beads and the beads would not float. Therefore a container G about 3 cm. in diameter and 9 cm. long was built. There was an inlet for the beads at the top, and at the bottom a leveling tube filled with mercury was attached. When the volume of the corona tube was to be reduced the mercury was raised and the floating beads fell into the top of the corona tube through a side arm attached to the top of the corona tube. The latter was slanted at an angle of about 45° so that when the beads came over they fell to the lower end. While the pressure was decreasing, as many beads as were necessary to maintain a constant pressure were introduced. When starting with carbon dioxide the pressure increased rather than decreased. The mercury was then set near the top of the tube containing glass beads so as to fill up the interstices between them, and as the pressure increased the stopcock E was momentarily opened to let out the excess pressure. When the corona was first turned on there was always an increase of pressure, due partly to the heating effect of the corona and partly to pressure which is characteristic of the corona.

Equilibrium was obtained starting both from the carbon monoxide and oxygen side and from the carbon dioxide side. The following procedure was adopted. The tube was evacuated and 100 cc. of gas, $66^2/_3$ cc. of carbon monoxide and $33^1/_3$ of oxygen in one case, of 100 cc. of carbon dioxide in the other, which had been collected in gas burets over mercury, was drawn up into the tube. Then the tube was again evacuated and refilled in the same manner. If any water was present the mixture of carbon monoxide and oxygen exploded and a flame ran quickly down the tube; but when the gases were fairly dry they did not explode and the reaction proceeded quietly and fairly rapidly.

Runs of 5, 10, 15, 30, 45, 60 and 120 minutes were made. Equilibrium was reached from both sides in from 30 minutes to 45 minutes. As each determination was completed the gases were drawn off through an absorption tube containing neutral potassium iodide solution. This potassium iodide was then acidified with dil. sulfuric acid and the iodine was estimated by means of 0.01 *N* sodium thiosulfate solution. The amount of oxygen thus found was added to the oxygen found later on analysis of the gas for oxygen. The mixture of gases drawn from the corona tube was then analyzed over water in a water-jacketed gas buret. The carbon dioxide was absorbed in potassium hydroxide solution, the oxygen in alkaline pyrogallol and the carbon monoxide in ammoniacal cuprous chloride solution.

Results

The equilibrium data are given in Table I and are shown graphically in Fig. 2. The data are average values for at least two separate determinations.

TABLE I

PERCENTAGE COMPOSITIONS OF RESIDUAL GAS

INITIAL GAS, $2CO + O_2$

Time corona was applied Min.	% of CO_2	% of O_2	% of CO
5	29.25	24.45	46.30
10	41.35	20.73	37.92
15	58.25	15.20	26.55
30	68.70	9.70	21.60
45	71.86	8.98	19.16
60	71.25	9.54	19.21
120	70.63	9.67	19.70
	INITIAL GAS, CO_2		
5	81.07	6.77	12.16
10	77.90	7.46	14.64
15	75.99	8.54	15.47
30	74.70	8.63	16.67
45	71.60	9.58	18.84
60	72.83	9.25	17.92
120	70.57	9.90	19.53

The general average of the runs in which equilibrium was reached, that is, $^3/_4$, 1 and 2 hours is 71.46% of carbon dioxide, 9.48% of oxygen and 19.06% of carbon monoxide. The average decomposition of the carbon dioxide is, therefore, 28.54%.

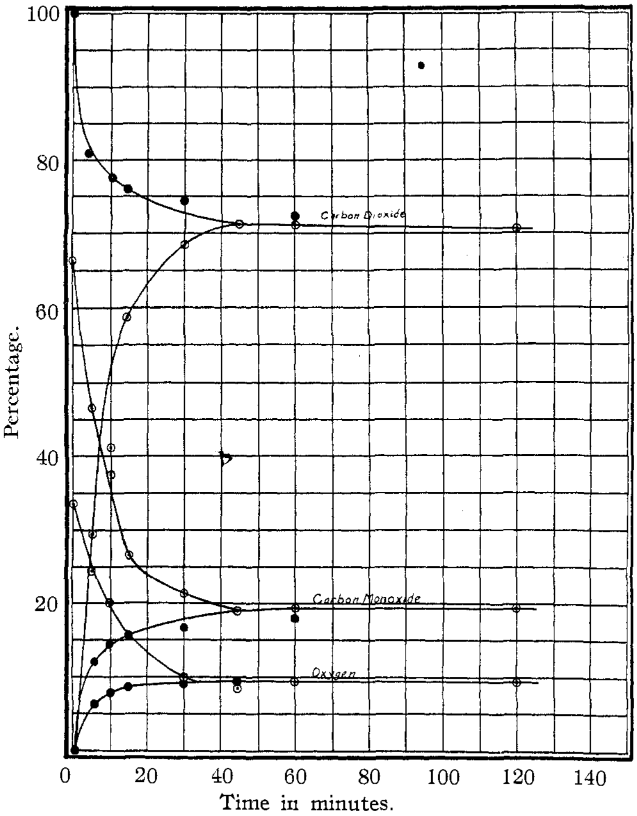

Fig. 2.

Calculation of Effective Temperature

The free energy for the reaction $CO + {}^1/_2O_2 = CO_2$ is given by the equation[12]

$$\Delta F = -RT \ln K \qquad (1)$$

where ΔF is the free energy, R the gas constant, T the temperature and K the equilibrium constant. The numerical value of ΔF is given by the equation[13]

$$\Delta F = -67{,}510 + 2.75\, T \ln T - 0.0028\, T^2 + 0.00000031\, T^3 + 4.46\, T \qquad (2)$$

Substituting the value 2600° for T in Equation 2 gives $\Delta F = -13{,}160$. Substituting this value of ΔF in Equation 1 gives $13{,}160 = RT \ln K$, $\ln K = 13{,}160/RT$ and $K = 12.6$.

---

[12] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 294.

[13] Ref. 12, p. 575.

From the equilibrium data obtained by experiment, $K = C_{CO_2}/(\sqrt{C_{O_2}} \times C_{CO}) = 0.7146/(\sqrt{0.0948} \times 0.1906) = 12.2$. This correspondence is ample. An assumption of 2500° K. gives a value of 21 for K. Hence the effective temperature is close to 2600° K.

Conclusions

Under the conditions obtaining in this corona tube the electrical factors in the reaction correspond to a temperature of 2600° K., which is certainly far above the temperature actually prevailing. Indeed, the entire energy which passed through the corona amounted to less than 10 watt-hours, which is inadequate for the heating of the gas to such a temperature. The amount of heat necessary to raise 100 cc. of carbon dioxide from 300° K. to 2600° K. is about 9200 calories, while the heat corresponding to 10 watt-hours is 8500 calories. Thus it is seen that even if all the heat present had been used in heating the reacting gases, which under the conditions of the experiment was absolutely impossible, the temperature of the gas would not have reached 2600° K. Hence, the effect of the electrical discharge is not merely to accelerate the molecular collisions but is, on the contrary, directly to increase the reactivity of all three types of molecules present, carbon dioxide, carbon monoxide and oxygen; in such a way as to increase the reaction velocities at ordinary temperatures and thus produce a shift of the equilibrium concentrations to those corresponding to high temperatures without in any way heating the gases. The detailed figures for equilibrium concentrations and temperature are valid only for this corona and no attempt has been made to study the effect of varying electrical conditions.

Summary

Carbon dioxide or a mixture of carbon monoxide and oxygen under the influence of the corona discharge reaches an equilibrium in about three-quarters of an hour. The equilibrium corresponds to a decomposition of 28.54% of the carbon dioxide.

This decomposition corresponds thermodynamically to a temperature of 2600° C., a temperature which was certainly never approached in the corona, for under the conditions of the experiment the temperature could actually have been elevated very little above room temperature.

The electrical discharge increases the reactivity of all three types of molecules present in such a way as to increase the reaction velocities at ordinary temperatures and thus produce a shift of the equilibrium concentrations to those corresponding to high temperatures without in any way heating the gases.

STATE COLLEGE, PENNSYLVANIA