Perhaps the most striking feature of the curves is the large difference between the apparent molal isochoric and isopiestic heat capacities, in the case of nearly all the solutes. It is often assumed that the thermal properties of solutions are not very different in the isochoric and isopiestic systems, but this proves to be far from true in the case of the solutes investigated.

The apparent molal isopiestic heat capacities are plotted against $c^{1/2}$ in Fig. 3, and the corresponding isochoric ones are similarly plotted in Fig. 4. We have drawn the latter by subtracting the calculated correction from the former, which were drawn straight through the experimental points. However, we do not wish to stress the slight curvature in the isochoric lines. If each experimental isopiestic point had been corrected separately, the resulting isochoric points doubtless would have lain along straight lines, within experimental error.

A comparison of the two plots shows that there is just as much individuality in the positions and slopes of the lines in the isochoric as in the isopiestic systems. We evidently must look elsewhere for the cause of the individuality of the lines, and cannot attribute it to the expansion term since, even in the isochoric system, which lends itself most easily to theoretical treatment, the differences between salts of the same valence type is so striking.

Summary

We have checked the applicability of Gibson's method and used it to reduce the compressibility data of Lanman and Mair to atmospheric pressure.

We have defined the apparent molal isochoric heat capacity $\Phi(C_{v_2})$ and developed equations to calculate it from the corresponding isopiestic quantity $\Phi(C_{p_2})$ and the coefficients of expansibility and compressibility. The limiting values of the difference and of its slope against $c^{1/2}$ are conveniently expressed in terms of the apparent molal compressibilities and expansibilities.

We have computed $\Phi(C_{v_2})$ for six 1–1 electrolytes up to two molal concentration and find it even *more negative* than $\Phi(C_{p_2})$. The difference (3 calorie units for hydrochloric acid and 11 for sodium hydroxide) changes but little with concentration. The values of $\Phi(C_{v_2})$ and the slopes of the $\Phi(C_{v_2})-c^{1/2}$ curves show as much individuality as those in the isopiestic system.

EVANSTON, ILLINOIS RECEIVED NOVEMBER 5, 1934

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Study of the Mechanism of Carbon Dioxide and Hydrogen Peroxide Formation[1]

BY W. F. JACKSON

The accelerating effect of water on the photochemical carbon monoxide–oxygen reaction at high temperatures[2] led to the assumption of a chain mechanism involving hydroxyl radicals and hydrogen atoms. The purpose of the experiments described in the following pages is to gain knowledge of the postulated chain steps

$$OH + CO \longrightarrow CO_2 + H \qquad (1)$$

$$H + O_2 + CO \longrightarrow CO_2 + OH \qquad (2)$$

An electric discharge through moist hydrogen or water vapor provides a reliable source of hydrogen atoms,[3] and there is some evidence that hydroxyl can be drawn from the water discharge.[4] With the hope that the presence or absence of hydroxyl in the products of this discharge could be established in the course of the research, I used it tentatively to examine reaction (1).

Many observations were focused on the formation of hydrogen peroxide, for synthesis of this substance accompanied the carbon monoxide oxidation. These permit a comparison between our work and the more recent study of Rodebush and Wahl.[5]

Experimental Part

Apparatus.—Since the experimental system underwent continual revision throughout the investigation it is impossible to include all the phases of its development. Figure 1 will serve as a reference diagram. Additions

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[1] See G. I. Lavin and W. F. Jackson, THIS JOURNAL, **53**, 383, 3189 (1931). This paper is an abstract of part of the thesis submitted to Princeton University by W. F. Jackson in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Jackson and Kistiakowsky, *ibid.*, **52**, 3471 (1930); Jackson, *ibid.*, **56**, 2631 (1934).

[3] Wood, *Phil. Mag.*, [6] **42**, 729 (1921); **44**, 538 (1922); *Proc. Roy. Soc.* (London), **A97**, 455 (1920); **102**, 1 (1923); Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924); Urey and Lavin, THIS JOURNAL, **51**, 3290 (1929).

[4] Lavin and Stewart, *Proc. Nat. Acad. Sci.*, **15**, 829 (1929); Taylor and Lavin, THIS JOURNAL, **52**, 1910 (1930).

[5] Rodebush and Wahl, *J. Chem. Physics*, **1**, 696 (1933).

will be mentioned in connection with experiments which demanded their use.

The essential parts of the apparatus are water-cooled Wood tubes T_1 and T_2 of the usual type, the exit tube E of Pyrex, 2.5 cm. in diameter, the trap D, a second trap in series with D and pumps (to which the arrow points). The pumping system consisted of an all-steel four-stage Gaede mercury pump of high capacity, backed by an oil pump. The discharge tubes were operated by current from a 110-volt a.c. line stepped up to *ca.* 1000 volts by 2 K.W. transformers. The current was altered in the discharge tubes by variable inductances in the primary circuits. Gases could be admitted at the points shown in the diagram. Hydrogen, oxygen, and carbon monoxide were admitted through calibrated metal stopcocks at known rates of flow. Pure water contained in a thermostated bath flowed into the apparatus through a capillary, the flow rate being regulated by varying the temperature of the thermostat. The quantity of water flowing into the apparatus at several temperatures from 0 to 50° was determined by freezing in trap D the water admitted for a definite period and weighing it. Hydrogen and oxygen were taken directly from cylinders and dried or left with their original moisture content depending on the experiment. Carbon monoxide was prepared by dropping C. P. formic acid on hot concentrated sulfuric acid, passed through concentrated potassium hydroxide, and collected over water. The pressure was measured by a modified McLeod gage;[6] pressures from 5 to 0.01 mm. could be determined with sufficient accuracy even in the presence of water vapor. The gage connections are indicated by A and B in Fig. 1.

The carbon dioxide formed in the apparatus was collected after it had passed through the pumps by allowing the gases to bubble through wash bottles containing a known volume of standardized barium hydroxide. The quantity of carbon dioxide was determined by titrating the excess barium hydroxide with 0.1 *N* hydrochloric acid.

For some experiments solid surfaces were introduced into the gas stream from the discharge tubes. One of the devices attached to the system to facilitate this introduction is illustrated by the tube at Q. Thermometers whose bulbs were incased in the desired solid were introduced into the tube through a ground glass joint and pushed into or withdrawn from the active gas stream by an electromagnet.

For spectroscopic experiments, quartz windows, F and G, were connected to the rest of the system by graded seals. A tungsten filament lamp W, provided with a quartz window H, was used as a light source in absorption experiments. The spectrograph, a small quartz Hilger, was supported at S. This arrangement gave an absorption tube one meter long. The bulb V and the tubes leading from the discharge tubes to E were painted black to prevent stray light from entering the spectrograph. An auxiliary high frequency discharge could be excited in the liter bulb L.

Experiments

1. Fraction of the Water Admitted Dissociated by the Discharge.—Water was admitted to the discharge at a known rate and the gases produced were collected after they had passed through the pumps. These were analyzed for oxygen by absorbing this gas in alkaline pyrogallol. Taking into account the quantity of hydrogen peroxide formed (see section 6), which under these conditions reverts to water and oxygen, the ratio of the amount of oxygen recovered to the amount calculated for complete dissociation gives a minimum value for the fraction of the water dissociated. For various water concentrations and currents from 0.15 to 0.7 ampere the water was found to be approximately 50% dissociated.

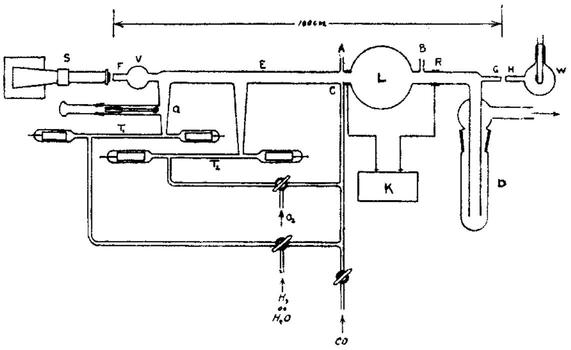

Fig. 1.

2. Interaction of Carbon Monoxide with the Products of the Water Vapor Discharge.—Water vapor was passed through T_1 at 20×10^{-4} mole per minute while the current in the discharge was maintained at 0.5 ampere. Carbon monoxide was admitted at C at 1.78×10^{-4} mole per minute. Carbon dioxide was collected at a rate of 8.5×10^{-5} mole per minute. Blanks were made to study the effect of the hot mercury of the pump on carbon monoxide–oxygen–water mixtures. No carbon dioxide was formed in this way. That the observed oxidation of carbon monoxide cannot be attributed to back diffusion is shown by the following arguments. (a) The spectrum of the discharge was identical whether carbon monoxide was being admitted at C or not. When a small quantity of carbon monoxide was purposely run through the discharge, strong blue bands were visible in the spectrum. (b) When an auxiliary discharge was passed through the exit tube, the blue glow due to carbon monoxide was visible for only two or three cm. on the discharge side of the inlet C. (c) When nitrogen, which also gives a characteristic color to the discharge, was run in at C at 20×10^{-4} mole per minute, no change could be seen in the spectrum of the discharge. (d) When a platinum wire was introduced at Q, it was heated red hot by the active gases. Even with atomic oxygen issuing from the discharge, the carbon dioxide yield was not increased.

In order to show that a large fraction of the observed carbon dioxide yield was not due to atomic oxygen, experiments were made with both oxygen and water vapor passing through T_1. Oxygen flowed through the discharge at 10×10^{-4} mole per minute, while the flow of water was varied from run to run. Carbon monoxide was admitted at C at 1.78×10^{-4} mole per minute. During the thirty-minute runs a current of 0.2 ampere was maintained in the discharge. Figure 2 contains the results of these experiments. Each point on the graph is the average of at least two runs made after the carbon dioxide had become constant.

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[6] Foote and Dixon, THIS JOURNAL, **52**, 2170 (1930).

These experiments show that the yield of carbon dioxide depends chiefly on the amount of water passed through the discharge. Comparison of the yields at a given water concentration obtained with and without oxygen indicated, however, that oxygen increased the yield *ca.* 15%. To find whether this increase should be attributed to atomic or molecular oxygen, the latter gas was admitted at 10 × 10^{-4} mole per minute either through the discharge or into the exit tube at one of three points: 11 cm., 31 cm. and 49 cm. from the discharge. The last inlet was 9 cm. farther from the discharge than the carbon monoxide inlet. The flow of water through the discharge was maintained at 20 × 10^{-4} mole per minute. Carbon monoxide was admitted at C at 1.66 × 10^{-4} mole per minute. A series of more than fifty experiments gave the following results: the admission of oxygen 49 cm. from the discharge did not affect the yield of carbon dioxide; oxygen admitted 11 and 31 cm. from the discharge increased the yield 20% in the first case and 30% in the second.

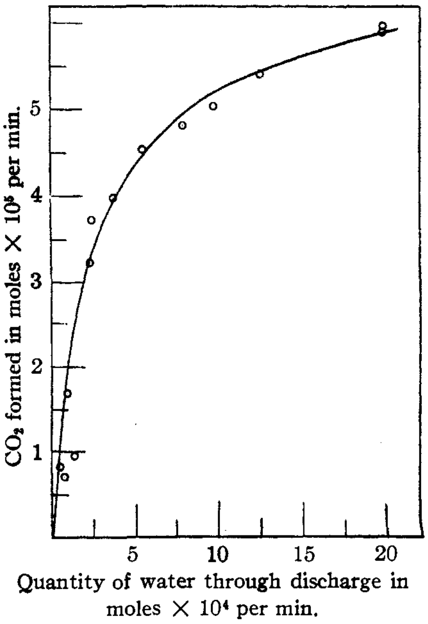

Fig. 2.

A series of experiments was made to discover the effect on the rate of carbon dioxide formation of various solid surfaces introduced into the gas flowing from the water discharge. Taylor and Lavin[4] concluded that the heat effect produced on a solid dehydrogenating catalyst placed in such a gas stream was caused principally by the recombination of hydrogen atoms, while the heat evolved at a dehydrating catalyst surface was liberated during the removal of hydroxyl from the gas. In an apparatus similar to that described by Taylor and Lavin the following runs were made. Water vapor dissociated in the discharge T_1 flowed through the tube E into which thermometers could be introduced at two positions, No. 1 at 11 cm. and No. 2 at 35 cm. from the discharge, by means of an electromagnet. Forty cm. from the discharge the gases encountered carbon monoxide flowing in at C. Though many experiments were performed, the description of one will suffice to typify the results. Water was admitted at 20 × 10^{-4} mole per minute to the discharge carrying a current of 0.05 ampere, and carbon monoxide was admitted at 1.66 × 10^{-4} mole per minute. A thermometer, its bulb wrapped with platinum wire, was thrust in at position No. 2 and a maximum temperature rise of 45° observed. This thermometer was then withdrawn from the gas stream and the carbon dioxide collected for thirty minutes. Titration showed that carbon dioxide was formed at a rate of 0.94 × 10^{-5} mole per minute. A platinum wrapped thermometer was next introduced at position No. 1 and a maximum temperature rise of 117° recorded. The thermometer at position No. 2, pushed in long enough to allow the maximum temperature rise to be observed, rose 10°. With position No. 1 occupied and No. 2 vacant, the carbon dioxide yield was 0.80 × 10^{-5} mole per minute. Since the temperature rise at position No. 2 decreased from 45 to 10° when the platinum was thrust in at No. 1, it appears that the concentration of atomic hydrogen at No. 2 and hence at C was reduced 77% by the metal surface at No. 1. The corresponding decrease in the carbon dioxide yield, however, was only 15%. Similar experiments at various currents and water concentrations with both platinum and tungsten surfaces confirmed that the removal of 80 to 90% of the atomic hydrogen reduced the rate of carbon dioxide formation from 10 to 15%.

The experiments with the dehydrating catalyst, alumina, required a slightly different apparatus. The thermometer at No. 2 was removed and a Pyrex U-tube, 2.5 cm. in diameter, was sealed into the exit tube. The active gases from the discharge entered one end of the U-tube, passed over the solid material spread on the bottom, and left the other end to mix with carbon monoxide streaming into the apparatus 40 cm. farther on. The U-tube was provided with two ground glass joints, so that it could be removed from the apparatus. When in place, the bottom of the U-tube was 35 cm. from the discharge. The ground glass joints of the U-tube were greased only on the upper half so that the active gases would not strike the Lubriseal directly. Alumina was prepared by precipitating aluminum hydroxide from a solution of C. P. aluminum nitrate with ammonium hydroxide, and dehydrating the hydroxide overnight at 130°, then at 300° for four hours. Beads were made from Pyrex rod and carefully cleaned before they were placed in the U-tube. The alumina was introduced in granules the size of peas. Care was taken to have the glass beads of similar size and arranged similarly to the alumina in the U-tube. Carbon dioxide was determined as usual. Water was allowed to flow through the discharge at 20 × 10^{-4} mole per minute and carbon dioxide was introduced at C at 1.66 × 10^{-4} mole per minute. In the first series the current through the discharge was 0.2 ampere and the pressure in the U-tube was 0.33 mm. In the second, the amperage was 0.4 and the pressure, 0.40 mm. The results are graphed in Fig. 3.

3. Carbon Dioxide from a Mixture of Oxygen, Carbon Monoxide and Atomic and Molecular Hydrogen.

—The water discharge produces, among other things, atomic hydrogen. From a discharge through hydrogen alone atomic hydrogen can be drawn admixed with nothing but the undissociated molecules. Consequently it seemed of interest to determine the yield of carbon dioxide produced when atomic hydrogen is pumped into a mixture of carbon monoxide and oxygen. Table I summarizes the results of experiments in which hydrogen was passed through discharge T_1. Carbon monoxide was introduced at C in all experiments. Oxygen was admitted either at C or through T_2 without apparent effect on the yield. No current was passed through the oxygen. For Series I and III dry hydrogen was used. In Series II 1.5×10^{-4} mole of water was admitted per minute along with the hydrogen. From Series I it appears that varying both the amount of hydrogen passed through the discharge and the current does not greatly affect the carbon dioxide yield. From Series II and III one sees that the concentration of molecular oxygen affects the yield. As the rate of admission of oxygen is decreased the carbon dioxide yield increases to a maximum and then decreases.

TABLE I

Current in discharge in amp.	Rate of admission of gases in moles $\times 10^4$/min.			Press., in mm. at C	CO_2 yield moles $\times 10^5$/min.
	H_2	O_2	CO		
		Series I			
0.2	14.3	13.4	2.68	...	3.81
.28	14.3	13.4	2.68	0.56	4.48
.4	68.7	29.0	1.34	1.16	3.48
.4	68.7	13.4	1.34	0.85	3.28
.1	27.0	12.5	1.34	...	4.53
.2	27.0	12.5	1.34	...	4.14
		Series II			
0.2	29.0	17.0	2.68	0.86	3.24
.2	29.0	17.0	2.68	.86	3.51
.2	29.0	11.0	2.68	...	4.82
.2	29.0	11.0	2.68	...	4.79
.2	29.0	4.5	2.68	.61	3.42
.2	29.0	4.5	2.68	.60	3.43
.2	29.0	2.2	2.68	.50	1.65
.2	29.0	2.2	2.68	.49	1.76
		Series III			
0.3	8.75	8.5	2.07	0.48	3.6
.3	8.75	8.5	2.07	.45	3.8
.3	8.75	8.4	2.07	.45	4.3
.3	8.75	4.0	2.07	.36	3.5
.3	8.75	4.0	2.07	.39	4.7
.3	8.75	4.0	2.07	.40	5.3
.3	8.75	2.04	2.07	.33	2.7
.3	8.75	2.04	2.07	.37	3.0
.3	8.75	2.04	2.07	.33	3.2
.3	8.75	8.5	2.07	.46	3.7
.3	8.75	2.04	2.07	.30	2.9

An electrically calibrated calorimeter similar to that described by Bichowsky and Copeland[7] was constructed and used in conjunction with the experiments of Series II. The calorimeter was so fashioned that it could be lowered into or raised from the gas stream at a point in the exit tube opposite the carbon monoxide inlet. From the rate of temperature rise of the calorimeter and its heat capacity the atomic hydrogen concentration could be calculated. Determinations made before and after each experiment indicated that atomic hydrogen reached C at a rate of $(1.5 \pm 0.1) \times 10^{-4}$ mole per minute throughout Series II. In the third experiment of this series, where the carbon dioxide yield reached its maximum, only one molecule of carbon dioxide was formed for three atoms of hydrogen reaching the carbon monoxide–oxygen mixture.

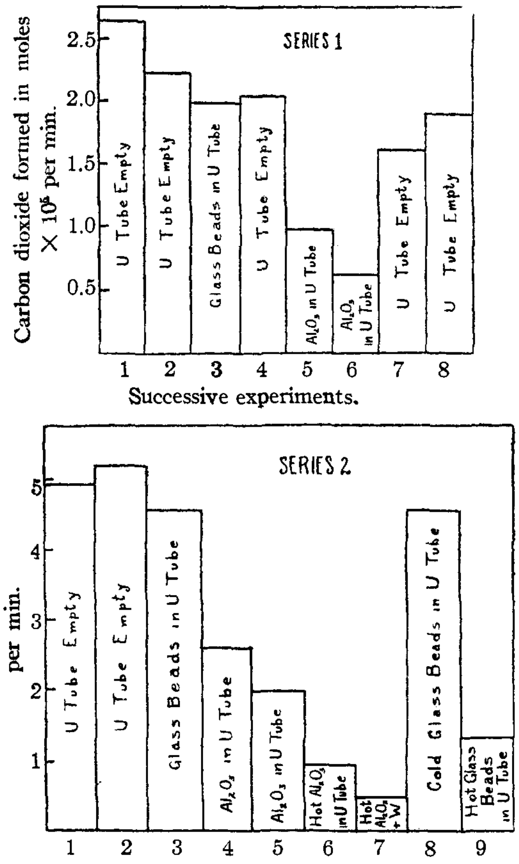

Fig. 3.

4. **The Effect of an Oxygen Discharge on the Carbon Dioxide Yield.**—Several experiments were made in which a discharge was passed through oxygen in tube T_2. Under conditions identical with those of the first four experiments of Series I above, except for a current of 0.2 ampere passing through T_2, the carbon dioxide yield was the same, within the limits of experimental error, as when no current was passed through the oxygen. With the oxygen discharge on and the hydrogen discharge off the yield was only a small fraction of that obtained when the current was passed through the hydrogen instead of the oxygen.

5. **Spectra of Gases in the Exit Tube.**—Attempts were made to obtain the hydroxyl bands in absorption under conditions similar to those operative in the experiments described in the preceding sections. These were unsuccessful. The auxiliary discharge between C and R produced the hydroxyl bands in emission when water was passed through the discharge. These bands were often obtained in emission when the auxiliary discharge was off. The conditions under which the emission spectra appeared are listed in Table II in the order of decreasing intensity of the hydroxyl bands, the auxiliary discharge not being operated.

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[7] Bichowsky and Copeland, THIS JOURNAL, **50**, 1315 (1928).

Table II

Relative intensity of OH emission	Experimental conditions
30	H_2 and O_2 both through their respective tubes (on)
20	O_2 and H_2O both through one tube (on)
10	O_2 through T_1 (on); H_2 through T_1 (off)
10	O_2 through T_2 (on); H_2 admitted at C
2	H_2O alone through T_1 (on)
2	H_2O and H_2 both through T_1 (on)
1	H_2 through T_1 (on); O_2 through T_2 (off)
1	H_2 through T_1 (on); O_2 admitted at C
0	H_2O through T_1 (on); tungsten in at Q

Incidentally, it should be noted that when the water discharge and the auxiliary were operating, the bulb and exit tube from C to R were filled with a red glow in which the Balmer lines of atomic hydrogen were clearly distinguishable in a hand spectroscope. When the tungsten grid was thrust into the active gas stream at Q, the red color of the auxiliary discharge faded and the Balmer lines became practically invisible. While the tungsten grid was in the flow of active gas, however, a substantial yield of carbon dioxide was obtained.

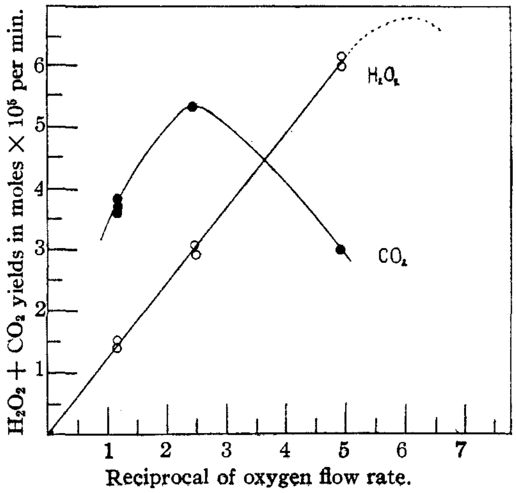

Fig. 4.—Flow rate expressed in moles × 10^4 per min.

6. **Hydrogen Peroxide.**—Several series of experiments were performed to determine the hydrogen peroxide yield from the water and hydrogen discharge tubes, and to contrast the mechanism of hydrogen peroxide and carbon dioxide formation. The hydrogen peroxide formed was frozen out along with other condensable matter in trap D (Fig. 1) by liquid air. The solid so collected was dissolved in water, acidified, and titrated for hydrogen peroxide with 0.1 *N* potassium permanganate. A second trap in series with D, also immersed in liquid air, never collected an appreciable quantity of hydrogen peroxide. With the apparatus used, however, carbon dioxide and hydrogen peroxide could not be collected simultaneously since the liquid air did not freeze out all the carbon dioxide, yet it collected so large a fraction that the customary method of carbon dioxide analysis failed. When comparisons were desired, carbon dioxide and hydrogen peroxide yields were determined in alternate runs. The results of experiments in which hydrogen peroxide was formed by reactions in the effluent gas from the water vapor discharge alone can be summarized as follows.

I. Under optimum conditions (*i. e.*, low current, absence of carbon monoxide and added oxygen, cleanest possible surface in exit tube) 25% of the water admitted to the discharge was recovered as hydrogen peroxide.

II. The peroxide yield was reduced by admitting carbon monoxide to the exit tube, but the number of moles of carbon dioxide formed was from 3 to 20 times as great as the loss in the hydrogen peroxide yield, in moles, due to the presence of carbon monoxide.

III. The peroxide yield increased with decreasing current and reached a maximum at 0.15 ampere.

IV. At constant current the peroxide yield increased with increasing water concentration.

V. Oxygen admitted either through the discharge or into the exit tube decreased the peroxide yield tremendously. Nitrogen also reduced the yield, but not as markedly. Table III illustrates this effect.

Table III

Gas admitted	Rate of inflow in moles × 10^5/min.	H_2O_2 yield
..	...	7.40
O_2	33	1.05
O_2	94	0.00
N_2	33	2.21
N_2	132	0.16

Hydrogen peroxide was found among the products of reaction when the gas flowing from a discharge through dry hydrogen was passed into molecular oxygen. A summary of the results follows.

I. With hydrogen passing at a rate of 8.75×10^{-4} moles per minute through a discharge operating at 0.3 ampere into oxygen admitted at C, the peroxide yield was inversely proportional to the rate of admission of oxygen throughout the range studied. Figure 4 is a graphical representation of the results. The black circles represent the carbon dioxide yield obtained under similar conditions.

II. When a mixture of atomic and molecular hydrogen was passed into a one-to-one mixture of carbon monoxide and oxygen, 1.6 moles of hydrogen peroxide were formed per mole of carbon dioxide produced. Between 1.3 and 2.3 moles of carbon dioxide were formed per mole of hydrogen peroxide lost by the addition of carbon monoxide.

III. The fraction of oxygen reacting which combined with hydrogen to form hydrogen peroxide was determined. Table IV contains the results of the two experiments made.

Table IV

Vol. O_2, cc./min.	discharge off	4.57	4.75
	discharge on	3.10	3.00
Vol. O_2 reacting, cc./min.		1.47	1.75
Moles O_2 reacting × 10^5/min.		6.57	7.82
Moles H_2O_2 formed × 10^5/min.		4.85	5.55
% O_2 reacting which formed H_2O_2		74	71

The error in the determination of the volume of oxygen flowing from the apparatus did not exceed 0.5%. Consequently the error in the value for the oxygen reacting was not greater than 2%. The rate of peroxide formation was not more than 0.3% lower than the value given. The actual yield, however, may have been somewhat higher than the recorded value, since some of the peroxide may have decomposed between the time the discharge was stopped and the titration made. The results, then, give a lower limit for the percentage of oxygen reacting which formed hydrogen peroxide.

Discussion

The data show that carbon monoxide is oxidized by the products of an electrical discharge through water vapor. Numerous substances stream from such a discharge: atomic and molecular hydrogen, atomic and molecular oxygen, hydrogen peroxide, ozone, perhaps hydroxyl and other hydrogen–oxygen complexes. Evidently hydrogen, molecular or atomic, cannot oxidize carbon monoxide in a simple bimolecular process. Molecular oxygen likewise cannot convert carbon monoxide to the dioxide at room temperature. The work of many experimenters indicates that neither ozone nor hydrogen peroxide oxidize carbon monoxide at room temperature.[8]

The carbon dioxide yield cannot be attributed to a reaction involving oxygen atoms. That the reaction $O + CO + X \longrightarrow CO_2 + X$ is very inefficient at room temperature has been proved by one of us[2] and corroborated by Harteck and Kopsch.[9] They found that carbon monoxide admitted to an excess of oxygen atoms was oxidized to the extent of only 3%. The results recorded in Fig. 2 substantiate the view that atomic oxygen alone is not accountable for the carbon dioxide yield. For, with a constant quantity of oxygen passed through the discharge, the carbon dioxide yield rises rapidly from scarcely detectable to large values as the quantity of water accompanying the oxygen is increased. Harteck and Kopsch stated that the quantity of atomic oxygen which can be drawn from a discharge tube is not appreciably increased by the presence of water vapor. The increase in carbon dioxide yield with increasing water vapor must be attributed not to an increase in oxygen atom concentration but to some product of the discharge through water vapor itself.

Other mechanisms involving oxygen atoms can be postulated. The atomic oxygen could react with water or atomic hydrogen to form hydroxyl

$$O + H_2O \longrightarrow 2OH \qquad (3)$$

$$O + H + X \longrightarrow OH + X \qquad (4)$$

or with hydrogen molecules to form hydroxyl and hydrogen atoms

$$O + H_2 \longrightarrow OH + H \qquad (5)$$

The hydroxyl could then react with carbon monoxide

$$OH + CO \longrightarrow CO_2 + H \qquad (1)$$

According to Bonhoeffer and Reichardt[10] reaction (3) is strongly endothermic (14 kcal.). The quantity of hydroxyl formed in this way would be far too small to account for the observed carbon monoxide oxidation. If reaction (4) is a three-body process, its rate at pressures below 1 mm. must be small. For reaction (5) Kistiakowsky[11] found a low collision efficiency, and Harteck and Kopsch calculated an activation energy of 6 kcal. from its temperature coefficient. The experiments of Section 4 agree with these observations of reactions (4) and (5). It appears, therefore, that atomic oxygen cannot be held accountable for any large fraction of the carbon dioxide produced by the action of the products of the water discharge on carbon monoxide.

One substance which can be drawn from the water discharge in large quantities is atomic hydrogen. The results recorded in Table I show that hydrogen atoms propelled into a mixture of oxygen and carbon monoxide cause the oxidation of the latter. A simple calculation from the data of Section 3 shows that there are just enough triple collisions of the type

$$H + O_2 + CO \longrightarrow CO_2 + OH \qquad (6)$$

to account for the observed oxidation, if one assumes the most favorable conditions: maximum reaction zone, minimum loss of atomic hydrogen by other processes, 100% collision efficiency. These are drastic assumptions. It is more probable that the reaction takes place in two steps with the formation of an intermediate, HCO or HO_2.

The question arises as to whether or not all the carbon dioxide obtained when carbon monoxide reacts with the products of the water discharge, is formed by a process involving hydrogen atoms. The experiments with catalytic surfaces point to a negative answer. The data presented in Section 2 indicate that 80% of the atomic hydrogen can be removed by recombination on tungsten or platinum before the discharge gases encounter

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[8] Remsen and Southworth, *Ber.*, **8**, 1414 (1875); *Am. J. Sci.*, [3] **11**, 136 (1876); Remsen, *Am. Chemist*, **4**, 50 (1882); M. Traube, *Ber.*, **15**, 2326 (1882); F. Phillips, *Am. Chem. J.*, **16**, 255 (1894); W. Jones, *ibid.*, **30**, 40 (1903).

[9] Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327 (1931).

[10] Bonhoeffer and Reichardt, *ibid.*, **139A**, 75 (1928).

[11] Kistiakowsky, THIS JOURNAL, **52**, 1868 (1930).

carbon monoxide without decreasing the carbon dioxide yield more than 10%. From Section 3 it appears that three atoms of hydrogen lead to the formation of only one molecule of carbon dioxide under optimum conditions. If the oxidation process were to be attributed entirely to hydrogen atoms, a much greater decrease in the carbon dioxide yield would be expected on the removal of 80% of the hydrogen atoms. The data plotted in Fig. 3 also favor the view that some agent other than atomic hydrogen is operative in the oxidation. The introduction of alumina into the active gas stream causes a marked reduction in the carbon dioxide yield. The experiments of Taylor and Lavin[4] led them to conclude that alumina was a poor catalyst for the recombination of hydrogen atoms.

The identity of the substance other than atomic hydrogen which can be drawn from the water discharge, and which is capable of causing the observed oxidation of carbon monoxide, is difficult to determine. It must be some hydrogen–oxygen complex. There are apparently only two possibilities, free hydroxyl radicals, and hydrogen dioxide (HO_2). HO_2 has been assumed as an intermediate compound in the formation of hydrogen peroxide in mercury photosensitized hydrogen–oxygen mixtures.[12] OH can be detected in the products of the water discharge after they have been drawn from the tube. Lavin and Stewart[4] obtained the hydroxyl bands in emission under these circumstances. Their observation is confirmed by the experiments recorded in Section 5. Bonhoeffer and Pearson,[13] failing to obtain hydroxyl bands in absorption from the products of the water discharge, concluded that the radicals have too short a life to permit their withdrawal. Yet it seems possible that they may be withdrawn in sufficient concentration to account for the fraction of the carbon dioxide yield which cannot be attributed to hydrogen atoms. In order to account by means of reaction (1) for a yield of 1.6×10^{-5} mole per minute of carbon dioxide, the maximum found in the experiments in Section 2 when atomic hydrogen was being removed, an equal quantity of hydroxyl must reach the carbon monoxide inlet per minute. The partial pressure of hydroxyl need be only 0.0025 mm. This is less than 0.1 the limiting pressure at which the hydroxyl absorption spectrum can be observed. Recent experiments of Rodebush and Wahl[5] lead them to conclude that hydroxyl produced in the water discharge disappears so rapidly by

$$OH + OH \longrightarrow H_2O_2 \qquad (7)$$

in the gas phase that no detectable quantity of hydroxyl can be withdrawn. The assumption that this reaction takes place slowly in the gas phase but completely on the walls of a liquid air trap seems consistent with their data and ours.

Some conclusions regarding the mechanism of hydrogen peroxide formation initiated by hydrogen atoms in hydrogen–oxygen mixtures can be drawn from the experimental data. Frankenburger and Klinkhardt[14] from the results of their investigation of the mercury photo-sensitized reaction concluded that the mechanism of hydrogen peroxide formation could best be explained by the steps

$$H + O_2 + H_2 \longrightarrow H_2O + OH \qquad (8)$$
$$OH + OH \longrightarrow H_2O_2 \qquad (9)$$

Our results are not in accord with such a mechanism. In the first place, (8) requires trimolecular collisions. Unless they are 100% efficient, our experimental conditions do not furnish enough of them to account for the yield. In the second place, the mechanism requires that not more than 50% of the oxygen reacting appears in the products as hydrogen peroxide. It is seen from Table IV that at least 74% of the oxygen taking part in the reaction forms hydrogen peroxide.[15]

The chain postulated by Taylor and Marshall[16]

$$H + O_2 \longrightarrow HO_2 \qquad (10)$$
$$HO_2 + H_2 \longrightarrow H_2O_2 + H \qquad (11)$$

affords a more satisfactory explanation. Frankenburger and Klinkhardt objected to this mechanism on the grounds that reaction (10) is a pure association reaction requiring the presence of a third body, and that reaction (11) is 36 kcal. endothermic. A recent study by Bates and Lavin[17] indicates that this reaction occurs more frequently than can be accounted for by a triple collision mechanism and that the HO_2 molecule is capable of existing considerably longer than the time required for one vibration of its atoms. If one assumes that the HO_2 molecule, formed in reaction (10) by a bimolecular collision, retains the energy of reaction until deactivated by collision with an-

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[12] Bates, *J. Chem. Physics*, **1**, 457 (1933).

[13] Bonhoeffer and Pearson, *Z. physik. Chem.*, **14B**, 1 (1931).

[14] Frankenburger and Klinkhardt, *Trans. Faraday Soc.*, **27**, 431 (1931).

[15] See Bates and Salley, THIS JOURNAL, **55**, 110 (1933).

[16] Taylor and Marshall, *Trans. Faraday Soc.*, **21**, 560 (1925).

[17] Bates and Lavin, THIS JOURNAL, **55**, 81 (1933).

other molecule, and that only this energy rich HO_2 can react with hydrogen to form hydrogen peroxide, one can explain the experimental results. Experiments in which the effect of varying oxygen concentration on the hydrogen peroxide yield was studied show that the yield is inversely proportional to the oxygen concentration when atomic hydrogen is run into a mixture of hydrogen and oxygen (See Fig. 4). Energy rich HO_2 may be deactivated by collision with oxygen molecules.

The author wishes to take this opportunity to thank Dr. G. I. Lavin for assisting with this work and Professor H. S. Taylor for his advice and criticism.

Summary

1. The products of an electrical discharge through water vapor at pressures below 1 mm. cause the oxidation of carbon monoxide even when they have been drawn several decimeters from the discharge.

2. One of the products of such a discharge recoverable in large quantities is hydrogen peroxide.

3. The effects of added gases and of varying the discharge current on the yields of carbon dioxide and hydrogen peroxide have been determined.

4. The effect of interposing dehydrogenation and dehydration catalyst surfaces in the active gas stream from the water vapor discharge on the carbon dioxide yield has been studied.

5. The yields of hydrogen peroxide and carbon dioxide from mixtures of oxygen, carbon monoxide, and atomic and molecular hydrogen have been determined under various conditions.

6. Mechanisms have been postulated to explain the observed carbon dioxide and hydrogen peroxide yields.

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The Mercury-Sensitized Decomposition of Hydrogen Azide

BY ALBERT E. MYERS AND ARNOLD O. BECKMAN

Introduction

The thermal decomposition of aqueous solutions of hydrogen azide with platinum as a catalyst has been studied by E. Oliveri-Mandalà,[1] who found that it decomposes slowly according to the equation

$$3HN_3 \longrightarrow 4N_2 + NH_3$$

Upon heating hydrogen azide with concentrated sulfuric acid, Schmidt[2] obtained a considerable amount of hydroxylamine together with nitrogen. His investigation of the decomposition products led him to conclude that only the oxidative action of the sulfuric acid, as indicated by the formation of sulfur dioxide, prevents the reaction from being quantitatively representable by the equation

$$HN_3 + H_2O \longrightarrow N_2 + NH_2OH$$

He also found traces of ammonia, but nothing else.

Gleu[3] illuminated aqueous solutions of hydrogen azide with ultraviolet light from a quartz mercury lamp and found that the products were mainly hydroxylamine and nitrogen with small amounts of ammonia and traces of hydrazine.

Beckman and Dickinson[4] studied the photochemical decomposition of gaseous hydrogen azide, using monochromatic radiation of wave length 1990 Å. They concluded that the decomposition proceeded by two concurrent reactions, one resulting in the formation of hydrogen and nitrogen, and the other in ammonia and nitrogen. They found[5] that over a pressure range of from 2 to 130 mm. the quantum yield was substantially constant at 3.0 ± 0.5 molecules of hydrogen azide decomposed per quantum absorbed.

The present paper is concerned with the quantum yield and products of the mercury-photosensitized decomposition of gaseous hydrogen azide.

Part I. The Products of Decomposition

Preparation of Hydrogen Azide.—Gaseous hydrogen azide was obtained by dropping sulfuric acid (two volumes of concentrated sulfuric acid to one volume of water) on solid sodium azide which had been purified by repeated recrystallization from aqueous solutions. The hydrogen

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[1] E. Oliveri-Mandalà, *Gazz. chim. ital.*, **46**, II, 137–159 (1916).

[2] K. F. Schmidt, *Ber.*, **57**, 704–706 (1924).

[3] Karl Gleu, *ibid.*, **61**, 702–707 (1928).

[4] Beckman and Dickinson, THIS JOURNAL, **50**, 1870–1875 (1928).

[5] Beckman and Dickinson, *ibid.*, **52**, 124–132 (1930).