the following salts: sodium sulfate, calcium chloride, sodium chloride, ammonium chloride, magnesium chloride, sodium dichromate, sodium chromate, sodium silicate and sodium hydroxide.

2. Data are given whereby the solubility of ferrous hydroxide may be calculated in non-oxidizing salt solutions in which the ionic strength does not exceed unity.

3. From the data on the solubility of ferrous hydroxide and the hydrogen-ion concentration of its saturated solution the dissociation constant is calculated as 6×10^{-10}, and the ionization in saturated water solution as 30% at 25°.

4. The free energy of formation of ferrous hydroxide has been calculated from the specific electrode potentials and the solubility to be —57,200 calories.

5. It has been shown that the precipitation of colloidal ferric hydroxide in salt solution has apparently no direct connection with the rate of corrosion.

6. The rate of corrosion in salt solutions parallels the solubility of ferrous hydroxide in these solutions. It is suggested that this is due to changes in film protectivity with the solubility of the ferrous rust.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ACTION OF ULTRAVIOLET LIGHT UPON CARBON DIOXIDE AND WATER

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As early as 1870 Baeyer[1] suggested that the first step in the photosynthesis of sugars and starches in plants might be the formation of formaldehyde from carbon dioxide and water. At an earlier date Butlerow[2] had observed that reducing sugars are formed by the action of dilute aqueous alkali upon formaldehyde. Emil Fischer[3] isolated from the mixture of sugars thus produced some of the well-known hexoses that occur in nature.

To confirm the Baeyer theory many investigators have tried to reduce carbon dioxide to formaldehyde by water under the influence of visible and ultraviolet light. Among those who have reported successful attempts are Usher and Priestley,[4] Moore and Webster,[5] Baly, Heilbron and Barker.[6]

[1] Baeyer, *Ber.*, **3**, 63 (1870).

[2] Butlerow, *Ann.*, **120**, 295 (1861).

[3] Fischer, *Ber.*, **21**, 989 (1888).

[4] Usher and Priestley, *Proc. Roy. Soc.*, **84B**, 101 (1911).

[5] Moore and Webster, *ibid.*, **90B**, 168 (1918).

[6] Baly, Heilbron and Barker, *J. Chem. Soc.*, **119**, 1025 (1921).

In 1916 Spoehr[7] called attention to the fact that the Baeyer theory represents a mechanism that is far more definite than experimental results justify, and in a later paper[8] he reported his failure to obtain formaldehyde by the action of ultraviolet light upon a solution of carbon dioxide in water.

In our preliminary experiments a mixture of water vapor and carbon dioxide was passed through a quartz tube 15 cm. from a 220-volt mercury arc. Connections in the apparatus were made by means of rubber tubing, and the flow of gases through the apparatus was controlled by means of stopcocks. In many of these early experiments we obtained measurable quantities of formaldehyde after an exposure to the light during an interval of six or eight hours. In every run where the illuminated gases came in contact with rubber tubing, sealing wax, de Khotinsky cement, or stopcock grease, small quantities of formaldehyde were obtained, but the results were never quantitatively reproducible. We finally constructed the apparatus in such a way as to avoid contamination with any source of organic matter. The quartz tube in which the exposure was made was sealed to Pyrex glass by means of graded quartz-to-glass seals and the rate of flow was controlled by water pressure upon the gas and by the size of the capillary tube through which it was forced. The water vapor was derived from conductivity water and the carbon dioxide was made from pure sodium bicarbonate. The mixed gases were passed through the apparatus under atmospheric pressure at the rate of 5 cc. per minute for 60 hours. The distance from the arc was 15 cm. The temperature of the gas passing through the tube varied between 28° and 35°. After passing through the illuminated cell the mixture was bubbled through water which was kept at 30° and at the end of the experiment this water was tested, by means of Schryver's reaction, for the presence of formaldehyde. Not a trace of formaldehyde was found, although the test is sensitive to one part by weight of formaldehyde in a million parts of water.

Believing that we might secure an accumulation of formaldehyde by using the same carbon dioxide and water repeatedly, we constructed another apparatus in which the same gas was run back and forth through the tube and kept in contact with the same small volume of water throughout the experiment.

The apparatus consisted of two bulbs having a capacity of about 300 cc. each, connected at the lower ends by a capillary tube which regulated the rate of flow from one bulb to the other and connected at the upper ends through a quartz tube. Graded quartz-to-glass seals were made. The apparatus was filled with conductivity water; then half of the water was displaced with pure carbon dioxide. By tilting the apparatus, water could be made to flow from one bulb to the other through the capillary tube,

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[7] Spoehr, *Plant World*, **19,** 1 (1916).

[8] Spoehr, This Journal, **45,** 1184 (1923); *Biochem. Z.*, **57,** 110 (1913).

thereby crowding 300 cc. of the mixture of carbon dioxide and water vapor through the quartz tube under the light. When all of the water had flowed from the upper bulb into the lower one the apparatus was reversed so that the same water would flow back through the capillary. This experiment was conducted for 45 hours, the average rate of flow being 10 cc. per minute. The apparatus was turned 90 times in the 45-hour interval. The water was then removed and analyzed for formaldehyde. The Schryver test was negative, as was also Benedict's test for reducing sugars.

A third attempt to produce formaldehyde was made by allowing ultraviolet light to fall upon a saturated aqueous solution of carbon dioxide. The solution was exposed in a sealed quartz tube. The sealed tube was placed in a slightly larger quartz tube through which water at 25° was flowing. The surface of the inner tube was 15 cm. from the lamp. In this case the intensity of radiation was reduced, for the rays had to penetrate an additional quartz tube and a thin layer of water. After 36 hours' exposure the solution gave no test for formaldehyde or for reducing sugars.

Professor Baly has observed that the transparency of quartz for high frequency radiation is impaired by prolonged exposure to ultraviolet radiation, but our failure to secure formaldehyde cannot be attributed to this cause. The results have been checked with new quartz and photographs of the spectrum of the mercury vapor arc taken through the old tubes indicate transmission between 4000 Å. and 2100 Å., the wave length limits in the range of our spectrograph.

These experiments compel us to believe that if formaldehyde is formed from carbon dioxide and water alone, under the influence of ultraviolet radiation, the reaction is reversible and the ordinary mercury vapor arc provides the energy required to decompose formaldehyde as fast as it is formed. The question must be settled by determining whether or not there is a definite region in the ultraviolet spectrum that will invariably supply the energy required for the reduction of carbon dioxide and which lacks the power to bring about the polymerization or decomposition of formaldehyde. The next experiment in this field must be made with monochromatic ultraviolet light.

Summary

In one experiment 18 liters of carbon dioxide saturated with water vapor was forced through a quartz tube 15 cm. from a 220-volt mercury vapor lamp during an interval of 60 hours. The gas, after passing the lamp, was bubbled through 15 cc. of distilled water.

In the second experiment 300 cc. of carbon dioxide, saturated with water vapor and in contact with 300 cc. of water in a sealed container, was passed back and forth under the mercury vapor lamp at the rate of 10 cc. per minute for 45 hours.

In the third experiment an aqueous solution of carbon dioxide in a sealed quartz tube was exposed for 36 hours.

No formaldehyde nor reducing sugar was produced in any of these experiments.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

THE ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN SOLUTIONS OF ETHYL ALCOHOL

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In the present investigation, an extended series of measurements has been made of the cells

$$H_2 \mid HCl(M) \mid AgCl \mid Ag \qquad (I)$$

in which the solvent was either alcohol or an alcohol water mixture. Cells of the types, containing hydrochloric acid in ethyl alcohol,

$$H_2 \mid HCl(c_1) \mid HCl(c_2) \mid H_2 \qquad (II)$$

and

$$Ag \mid AgCl \mid HCl(c_1) \mid HCl(c_2) \mid AgCl \mid Ag \qquad (III)$$

as well as the cells

$$Hg \mid HgCl \mid HCl(c_1) \mid HCl(c_2) \mid AgCl \mid Ag \qquad (IV)$$

have been measured by Lapworth and Partington[1] and by Hardman and Lapworth.[2] Cells II and III combined correspond to Cell I. Direct measurements of Cell I should afford a more accurate measurement of the activity coefficients than measurements of Cells II and III owing to the difficulties inherent in reproducing the liquid-junction potentials. More recently, Danner[3] has measured the electromotive forces of the cells, $H_2 \mid HCl(c) \mid HgCl \mid Hg$, throughout the concentration range from 0.00886 to 0.302 N acid. In this investigation, measurements of the cells, $H_2 \mid HCl(m) \mid AgCl \mid Ag$, throughout a greater concentration range have been made both in alcohol and in alcoholic solutions containing 50 mole per cent. of water. Measurements of the same cell at 0.01 and 0.1 M acid concentrations in a solvent of variable composition have also been made.

Materials

Alcohol.—The method employed for purifying the alcohol was chosen after consulting the large number of methods described in the literature.[4]

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[1] Lapworth and Partington, *J. Chem. Soc.*, **99**, 1417 (1911).

[2] Hardman and Lapworth, *ibid.*, **99**, 2248 (1911); **101**, 2250 (1912).

[3] Danner, THIS JOURNAL, **44**, 2832 (1922).

[4] Some of the more important references are as follows. (1) *Sulfuric acid distillation:* (a) Bishop, Kittredge and Hildebrand, THIS JOURNAL, **44**, 135 (1922). (b)