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Solutions studies on carbon dioxide: I. The variation of hydrogen-ion concentration with carbon dioxide pressures above one atmosphere

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SOLUTIONS STUDIES ON CARBON DIOXIDE
I. THE VARIATION OF HYDROGEN-ION CONCENTRATION
WITH CARBON DIOXIDE PRESSURES ABOVE THE ATMOSPHERE

By

Marjorie E. Moore

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Food Chemistry

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1928

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TABLE OF CONTENTS

| | <u>Page</u> |
|---|-------------|
| I. INTRODUCTION | 3 |
| II. HISTORICAL AND THEORETICAL | 5 |
| 1. Calculation of H-ion concentrations and ioniza- tion constants from conductivity measurements of other authors | 5 |
| III. EXPERIMENTAL | 15 |
| 1. Colorimetric measurement of pH. | 15 |
| a. Apparatus | 15 |
| b. Method and results | 18 |
| 2. Potentiometric measurement of pH | 25 |
| a. Apparatus | 26 |
| b. Method and results | 29 |
| c. Theoretical discussion of errors | 35 |
| IV. SUMMARY AND CONCLUSIONS | 40 |
| V. ACKNOWLEDGMENT | 42 |
| VI. LITERATURE CITED | 43 |

I. INTRODUCTION

It is known that the hydrogen-ion concentration of neutral water changes very rapidly with small carbon dioxide pressures, and that this concentration continues to increase up to a pressure of one atmosphere, where the solution becomes 0.0338 molar in CO_2 at 25° (11). Kendall (6) found the first ionization constant at 25° to be 3.50×10^{-7} for the concentration range corresponding to less than one atmosphere pressure. This constant is based upon the total CO_2 in the solution, not upon the hydrated form only.

With the aid of the above data, one may readily calculate the hydrogen-ion concentration to be expected for a CO_2 pressure of 1 atm. at 25° to be 1.088×10^{-4} or $10^{-3.96}$.

It should be of interest to determine whether this increase of acidity continues as the pressure becomes much greater. In view of the known value of carbon dioxide as a germicidal agent, especially in the case of beverages, it should be a matter of both theoretical and practical importance to determine whether the germicidal action of carbon dioxide under moderate pressure may be due to the development of sufficiently high acidity to inhibit the growth of organisms.

The values so obtained should also afford a means of

calculation of the ionization constant for CO_2 solutions at greater concentrations than have heretofore been studied, and thus show whether or not this value is a constant over a wide range of pressures.

II. HISTORICAL AND THEORETICAL

Calculation of H-ion Concentrations and
Ionization Constants from Conductivity
Measurements of Other Authors

Pfeiffer (13) and Haehnel (4) have measured the conductivities of CO₂ solutions at pressures up to 25 atm. and 52 atm., respectively. Pfeiffer's experiments were carried out at 0° and 12.5°, while the results of Haehnel are for 0° and 15°.

The ionization constants and hydrogen-ion concentrations corresponding to the conductivity values found by these two authors have been calculated, and these calculated values, together with the original data, are tabulated below (Table I). Pfeiffer's original paper gives conductivities in Siemens' units, but these have been converted into reciprocal ohms in the table.

Table I

| (1) Haehnel | | (a) Temperature 0° | | | | Li = 264 | | | |
|------------------------|---|--|--------------------------------------|------------|-------------------------|---|------|--------------------------------------|--|
| Pres- sure (atm) | vol. CO ₂ :0°, 760mm per one | m= mols CO ₂ per 1 L. | Spe- cific K X 10 ⁴ | Molar L | a :X 10 ⁴ | (H ⁺) :X 10 ⁴ | pH | k ₁ :X 10 ⁷ | |
| : | vol. H ₂ O | H ₂ O | : | : | : | : | : | : | |
| 1 | 1.80 | 0.0804 | 0.140 | 0.174 | 6.59 | 0.53 | 4.28 | 3.49 | |
| 5 | 8.71 | 0.389 | 0.667 | 0.171 | 6.48 | 2.52 | 3.60 | 1.63 | |
| 10 | 15.89 | 0.709 | 0.919 | 0.130 | 4.92 | 3.49 | 3.46 | 1.72 | |
| 15 | 21.82 | 0.974 | 1.063 | 0.109 | 4.13 | 4.02 | 3.40 | 1.66 | |
| 20 | 26.53 | 1.184 | 1.186 | 0.100 | 3.70 | 4.48 | 3.35 | 1.62 | |
| 25 | 30.46 | 1.360 | 1.250 | 0.0919 | 3.48 | 4.73 | 3.32 | 1.65 | |
| 30 | 33.65 | 1.502 | 1.282 | 0.085 | 3.23 | 4.86 | 3.31 | 1.57 | |
| 35 | 36.73 | 1.640 | 1.318 | 0.0804 | 3.05 | 4.99 | 3.30 | 1.53 | |
| 38 | 37.87 | 1.691 | 1.326 | 0.0784 | 2.97 | 5.02 | 3.30 | 1.49 | |

Table I (continued)

| (1 Haehnel) | | (b) Temperature 15° | | | | Li = 340 | | | |
|--------------|-----------------------|---------------------|----------------------|-------------------|-------------------|-------------------|-------------------|-------|-------------------|
| Pressure | vol. CO ₂ | m= | Conductivity | Specific | Molar | a | (H ⁺) | pH | k ₁ |
| (atm) | per one | per l | L. X 10 ⁴ | X 10 ⁴ | X 10 ⁴ | X 10 ⁴ | X 10 ⁴ | | X 10 ⁷ |
| | vol. H ₂ O | H ₂ O | | | | | | | |
| 1 | 1.00 | 0.0446 | 0.4055 | 0.909 | 26.7 | 1.19 | 3.92 | 3.18 | |
| 5 | 4.59 | 0.205 | 0.789 | 0.385 | 11.3 | 2.32 | 3.63 | 2.62 | |
| 10 | 8.39 | 0.375 | 1.088 | 0.290 | 8.53 | 3.20 | 3.49 | 2.73 | |
| 15 | 11.85 | 0.529 | 1.339 | 0.253 | 7.44 | 3.94 | 3.40 | 2.93 | |
| 20 | 15.21 | 0.679 | 1.515 | 0.223 | 6.56 | 4.45 | 3.35 | 2.92 | |
| 25 | 17.64 | 0.7875 | 1.678 | 0.213 | 6.26 | 4.93 | 3.31 | 3.09 | |
| 30 | 20.31 | 0.907 | 1.764 | 0.194 | 5.71 | 5.18 | 3.29 | 2.96 | |
| 35 | 22.52 | 1.005 | 1.831 | 0.182 | 5.35 | 5.38 | 3.27 | 2.94 | |
| 40 | 24.44 | 1.091 | 1.911 | 0.175 | 5.15 | 5.62 | 3.25 | 2.89 | |
| 45 | 25.59 | 1.142 | 1.940 | 0.170 | 5.00 | 5.71 | 3.24 | 2.855 | |
| 50 | 27.06 | 1.208 | 1.971 | 0.163 | 4.80 | 5.80 | 3.24 | 2.78 | |
| 52 | 27.67 | 1.235 | 1.983 | 0.161 | 4.73 | 5.85 | 3.23 | 2.77 | |
| (2 Pfeiffer) | | (a) Temperature 0° | | | | Li = 264 | | | |
| | 0.92 | 0.0411 | 0.277 | 0.673 | 25.5 | 1.05 | 3.98 | 2.67 | |
| | 0.95 | 0.0424 | 0.273 | 0.644 | 24.4 | 1.03 | 3.98 | 2.52 | |
| | 1.00 | 0.0446 | 0.296 | 0.664 | 25.15 | 1.12 | 3.95 | 2.82 | |
| | 1.67 | 0.07455 | 0.345 | 0.463 | 17.5 | 1.30 | 3.88 | 2.28 | |
| | 1.67 | 0.07455 | 0.341 | 0.458 | 17.3 | 1.29 | 3.89 | 2.23 | |
| | 1.68 | 0.0750 | 0.344 | 0.459 | 17.4 | 1.305 | 3.88 | 2.27 | |
| | 5.10 | 0.228 | 0.537 | 0.236 | 8.94 | 2.04 | 3.69 | 1.82 | |
| | 5.82 | 0.260 | 0.556 | 0.214 | 8.106 | 2.11 | 3.68 | 1.71 | |
| | 7.30 | 0.326 | 0.614 | 0.188 | 7.12 | 2.32 | 3.63 | 1.65 | |
| | 8.17 | 0.365 | 0.635 | 0.174 | 6.59 | 2.41 | 3.62 | 1.59 | |
| | 9.46 | 0.422 | 0.705 | 0.167 | 6.33 | 2.67 | 3.57 | 1.69 | |
| | 10.55 | 0.471 | 0.738 | 0.156 | 5.93 | 2.79 | 3.55 | 1.66 | |
| | 12.55 | 0.560 | 0.789 | 0.141 | 5.34 | 2.99 | 3.52 | 1.60 | |
| | 12.85 | 0.574 | 0.798 | 0.139 | 5.26 | 3.02 | 3.52 | 1.59 | |
| | 13.44 | 0.600 | 0.799 | 0.133 | 5.04 | 3.02 | 3.52 | 1.52 | |
| | 14.09 | 0.629 | 0.853 | 0.135 | 5.13 | 3.23 | 3.49 | 1.66 | |
| | 14.76 | 0.659 | 0.856 | 0.130 | 4.92 | 3.24 | 3.49 | 1.59 | |
| | 15.93 | 0.711 | 0.942 | 0.132 | 5.00 | 3.55 | 3.45 | 1.78 | |
| | 15.98 | 0.713 | 0.918 | 0.128 | 4.87 | 3.45 | 3.46 | 1.69 | |
| | 16.53 | 0.738 | 0.970 | 0.131 | 4.98 | 3.67 | 3.43 | 1.83 | |
| | 17.95 | 0.801 | 0.986 | 0.123 | 4.66 | 3.73 | 3.43 | 1.74 | |
| | 18.29 | 0.816 | 0.986 | 0.121 | 4.58 | 3.74 | 3.43 | 1.71 | |
| | 19.87 | 0.887 | 1.073 | 0.121 | 4.58 | 4.06 | 3.39 | 1.86 | |
| | 19.95 | 0.891 | 1.018 | 0.114 | 4.32 | 3.85 | 3.41 | 1.66 | |
| | 23.34 | 1.042 | 1.138 | 0.109 | 4.13 | 4.30 | 3.37 | 1.78 | |

Table I (continued)

| Pfeiffer | | (b) Temperature 12.5° | | | Li = 323 | | | |
|---|---|----------------------------------|-------|------------------------|---|------|-------------------------------------|--|
| | | Conductivity | | | | | | |
| vol. CO ₂ : 0°, 760mm: per one | m= mols CO ₂ : per one | Specific: K X 10 ⁴ | Molar | a X 10 ⁴ | (H ⁺): X 10 ⁴ | pH | k ₁ X 10 ⁷ | |
| vol. H ₂ O: | L. H ₂ O | | | | | | | |
| 0.92 | 0.0411 | 0.390 | 0.949 | 29.4 | 1.21 | 3.92 | 3.55 | |
| 0.95 | 0.0424 | 0.400 | 0.943 | 29.2 | 1.24 | 3.91 | 3.62 | |
| 1.00 | 0.0446 | 0.421 | 0.944 | 29.2 | 1.30 | 3.89 | 3.80 | |
| 1.67 | 0.0745 | 0.500 | 0.671 | 20.77 | 1.55 | 3.81 | 3.22 | |
| 1.67 | 0.0745 | 0.491 | 0.658 | 20.4 | 1.52 | 3.82 | 3.10 | |
| 1.68 | 0.0750 | 0.495 | 0.660 | 20.4 | 1.53 | 3.82 | 3.12 | |
| 3.40 | 0.152 | 0.684 | 0.450 | 13.9 | 2.11 | 3.68 | 2.94 | |
| 4.15 | 0.185 | 0.778 | 0.421 | 13.0 | 2.40 | 3.62 | 3.13 | |
| 4.34 | 0.194 | 0.821 | 0.423 | 13.1 | 2.54 | 3.60 | 3.33 | |
| 6.35 | 0.283 | 0.989 | 0.350 | 10.8 | 3.06 | 3.51 | 3.32 | |
| 6.73 | 0.300 | 1.024 | 0.341 | 10.5 | 3.17 | 3.50 | 3.17 | |
| 7.33 | 0.327 | 1.041 | 0.318 | 9.84 | 3.22 | 3.49 | 3.17 | |
| 7.64 | 0.341 | 1.101 | 0.323 | 10.0 | 3.41 | 3.47 | 3.41 | |
| 8.44 | 0.377 | 1.090 | 0.289 | 8.95 | 3.37 | 3.47 | 3.02 | |
| 9.09 | 0.406 | 1.166 | 0.287 | 8.88 | 3.61 | 3.44 | 3.20 | |
| 9.79 | 0.437 | 1.229 | 0.281 | 8.70 | 3.80 | 3.42 | 3.31 | |
| 10.38 | 0.463 | 1.226 | 0.265 | 8.20 | 3.80 | 3.42 | 3.11 | |
| 10.46 | 0.467 | 1.293 | 0.277 | 8.58 | 4.01 | 3.40 | 3.44 | |
| 13.36 | 0.596 | 1.379 | 0.231 | 7.15 | 4.26 | 3.37 | 3.05 | |
| 13.89 | 0.620 | 1.430 | 0.231 | 7.15 | 4.43 | 3.35 | 3.16 | |
| 14.25 | 0.636 | 1.453 | 0.228 | 7.06 | 4.49 | 3.35 | 3.17 | |
| 15.06 | 0.672 | 1.473 | 0.219 | 6.78 | 4.56 | 3.34 | 3.09 | |
| 15.17 | 0.677 | 1.456 | 0.215 | 6.65 | 4.51 | 3.35 | 3.00 | |
| 15.70 | 0.701 | 1.467 | 0.209 | 6.47 | 4.53 | 3.34 | 2.93 | |
| 15.72 | 0.702 | 1.483 | 0.211 | 6.53 | 4.58 | 3.34 | 2.99 | |
| 17.75 | 0.792 | 1.542 | 0.194 | 6.02 | 4.77 | 3.32 | 2.87 | |
| 19.45 | 0.868 | 1.644 | 0.189 | 5.85 | 5.08 | 3.29 | 2.97 | |
| 20.03 | 0.894 | 1.665 | 0.186 | 5.74 | 5.13 | 3.29 | 2.35 | |

To show the method of calculation, one may consider the second row of values in Table I-1a. The solubilities of CO₂ in water are given by Haehnel as volumes of CO₂ (reduced to 0° and 760 mm.) per unit volume of water. Then the number of mols of CO₂ per liter of H₂O in the solution at 5 atm. pressure is given by:

$$m = \frac{v}{22.4}, \text{ where } m = \text{mols CO}_2/\text{liter H}_2\text{O} \\ v = \text{vol. CO}_2/\text{vol. H}_2\text{O}$$

For the set of values just mentioned above (row 2, Table I-1a), we should find

$$m = \frac{8.71}{22.4} = 0.389 \text{ mols/L. H}_2\text{O.}$$

Use of the exact value of 22.26 for the molecular volume of CO₂ gives slightly different values here, but this difference is too small to appreciably affect the pH finally calculated. Also, m is somewhat greater than the true molarity (mols CO₂/liter solution), and hence this error would act in the opposite direction to that caused by using the ideal molecular volume. Thus it seems advisable to make the calculation as illustrated above.

The specific conductivity (K) is given in the table as 0.667 X 10⁻⁴ reciprocal ohms, whence the molar conductivity (L) based on 1 mol. of CO₂ would be:

$$L = KV = 0.667 \times 10^{-4} \frac{1000}{0.389} \\ = 0.171$$

The fraction ionized (a) into H⁺ and HCO₃ is:

$$a = \frac{L}{L_1}, \text{ where } L_1 = L_{H^+} + L_{HCO_3^-}.$$

The value for L_1 at 15° may be calculated from that at 18° , according to the data and empirical equation given by Kolthoff (8).

$$L_t = L_{18} (1 + c (t - t_{18}))$$

where $L_{18H^+} = 316$, and $c = 0.015$

$$L_{18 HCO_3^-} = 40.5, \text{ and } c = 0.023$$

The values for L_1 at 0° , 12.5° , and 25° are taken from the paper by Kendall (6). Thus the following values for L_1 are obtained:

| | | | |
|-----------|--------------|------------|------------|
| 0° | 12.5° | 15° | 25° |
| 264. | 323. | 340. | 393.4 |

For the case considered, where $L = 0.171$ at 0° ,

$$a = \frac{L}{L_1} = \frac{0.171}{264} = 6.48 \times 10^{-4}$$

whence $(H^+) = am = 6.48 \times 10^{-4} \times 0.389 = 2.52 \times 10^{-4}$

and $pH = -\log (2.52 \times 10^{-4}) = 3.60$

By substituting the values found above, the first ionization constant may be readily calculated, for

$$\begin{aligned} k_1 &= \frac{(H^+)(HCO_3^-)}{(H_2CO_3 + CO_2)} = \frac{(am)^2}{m(1-a)} = \frac{a^2 m}{1-a} \\ &= \frac{(6.48 \times 10^{-4})^2 (0.389)}{1 - 6.48 \times 10^{-4}} \end{aligned}$$

But a is sufficiently small compared to 1, so that it may be neglected, and

$$\begin{aligned} k_1 &= (6.48 \times 10^{-4})^2 (0.389) \\ &= 1.63 \times 10^{-7}. \end{aligned}$$

Pressures used by Pfeiffer are not given in the table, as his work was carried out at temperatures only approximately constant, and corrections introduced to bring the conductivity values to those for the exact temperature sought.

Kendall (6) made a series of accurate conductivity measurements on CO₂ solutions in which the CO₂ pressure was below 1 atm. He has calculated the ionization constants at various temperatures from his data and compared them with those calculated from selected data of Pfeiffer (13), Knox (7), and Walker and Cormack (21). The results of his calculations may be summarized as follows:

Table II

| Temperature : k ₁ X 10 ⁷ | :Kendall | : Knox | :Walker & Cormack | :Pfeiffer |
|---|----------|--------|-------------------|-----------|
| 0° | 2.24 | -- | -- | 1.7 |
| 12.5° | -- | 3.34 | -- | 3.2 |
| 18° | 3.12 | 3.75 | 3.04 | -- |
| 25° | 3.50 | -- | -- | -- |

With the exception of those of Pfeiffer, the above conductivity measurements were all made at carbon dioxide pressures near to or below one atmosphere. If one considers only those results of Pfeiffer which were obtained at pressures below one atmosphere (up to 1.68 volumes CO₂ in the table) the average value of k₁ at 0° is found to be 2.5 X 10⁻⁷. This value agrees much better with that obtained by Kendall than

is the case if experimental results for higher pressures are included.

Kendall's data are probably most accurate for the pressure range used, being confirmed by comparison of measured heats of ionization and those calculated by the van't Hoff equation from his values of k_1 at different temperatures.

$$\log k_1 - \log k_1' = \frac{Q}{2.303R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

The same calculation using only those data of Pfeiffer taken at pressures below one atmosphere at both 0° and 12.5° gives $Q = -5840$ calories, which is not in as good agreement with the measured value of -2800 calories as are those calculated from Kendall's data; but agrees much better than the value of -7850 calories obtained by Kendall from Pfeiffer's data including the latter's values for k_1 at higher pressures.

Haehnel's results for 1 atm. give a higher value for the ionization constant at 0° than at 15°, which seems unreasonable and does not agree with other authors.

The values for k_1 calculated from the measurements of Haehnel and Pfeiffer at pressures above one atmosphere do not show any regular variation as the pressure is increased; and hence, on the basis of these data, it appears justifiable to assume that the ionization constant changes very

little, if at all, for pressures from 5 to 50 atm. The values calculated from the measurements of each author for each different temperature have been averaged, with the following results:

Table III

| Temperature | Haehnel | Pfeiffer |
|-------------|---------|----------|
| 0° | 1.61 | 1.69 |
| 12.5° | -- | 3.13 |
| 15.0° | 2.86 | -- |

It will be seen that the agreement is good for 0°, but the values for 12.5° and 15° appear to be in the wrong order.

Moreover, it appears inconsistent that there should be such a decided drop of the ionization constant between 1 and 5 atm., with no appreciable further change as the pressure is increased.

Since the above values are based solely on conductivity measurements, it appears to be desirable to determine the hydrogen-ion concentration, or activity, by a colorimetric or potentiometric method, which should give considerable information as to the correctness of the conductivity measurements and furnish additional information regarding the course of the ionization at high pressures.

A calculation of the ionization constant, based on the

hydrated portion of the total CO_2 was attempted. For this purpose the straight-line function given by Shipley and McHaffie (16) for log of fraction hydrated (n) against log of total concentration of CO_2 (m) was extrapolated, thus obtaining values for n at higher total concentrations of CO_2 . Using these in conjunction with the conductivity data of Haehnel (4), one may calculate the ionization constant,

$$k_1 = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)}$$

For a pressure of 5 atm., when $m=0.205$ at 15° , we find $n = 8.14 \times 10^{-4}$; and the calculation for k_1 gives it a negative value. This calculation is only rough, as n was obtained for 18° , but it is exact enough to show that it is not legitimate to extrapolate such a function of the log of total CO_2 content in order to obtain log n, or fraction hydrated, to a molar concentration as high as 0.205. In fact, it seems to cast doubt upon the reliability of this function for even a limited concentration range, which is not dispelled by a careful consideration of the method used in obtaining it. Shipley and McHaffie's data are calculated from theoretical consideration of the results obtained in titration of solutions of carbonates, and rest on the assumed constancy of the product $(\text{H}^+)(\text{CO}_3=)$. They found this product to remain practically constant in alkaline solutions and assume the constancy to hold also in acid solutions. In deriving values for

n, they use Walker and Cormack's value (21) of 3.04×10^{-7} for k_1 based on total dissolved CO_2 , and assume that their theoretical values of k_1' , based on only that portion in the form of H_2CO_3 , bear the relation to the value of k_1 :

$$k_1' = \frac{k_1}{n} \text{ , or } k_1' = \frac{3.04 \times 10^{-7}}{n}$$

However, n, according to their calculations, appears to be of nearly the same order of magnitude as "a", the fraction ionized, and hence "a" cannot be legitimately neglected in the denominator of the exact expression for the relation between these two ionization constants:

$$k_1' = k_1 \frac{1-a}{n-a}$$

The relation used by Shipley and McHaffie must inevitably give a straight line, if (H_2CO_3) remains practically constant, as given in their table of calculations.

The fraction of dissolved CO_2 existing in the form of H_2CO_3 has been determined by other investigators (1)(3)(14)(17)(18)(19)(20)(22) for certain concentrations, but none of these have attempted to express it as a function of concentration, and hence it is impossible to make a calculation of the true ionization constant of H_2CO_3 under higher CO_2 pressures from their data.

III. EXPERIMENTAL

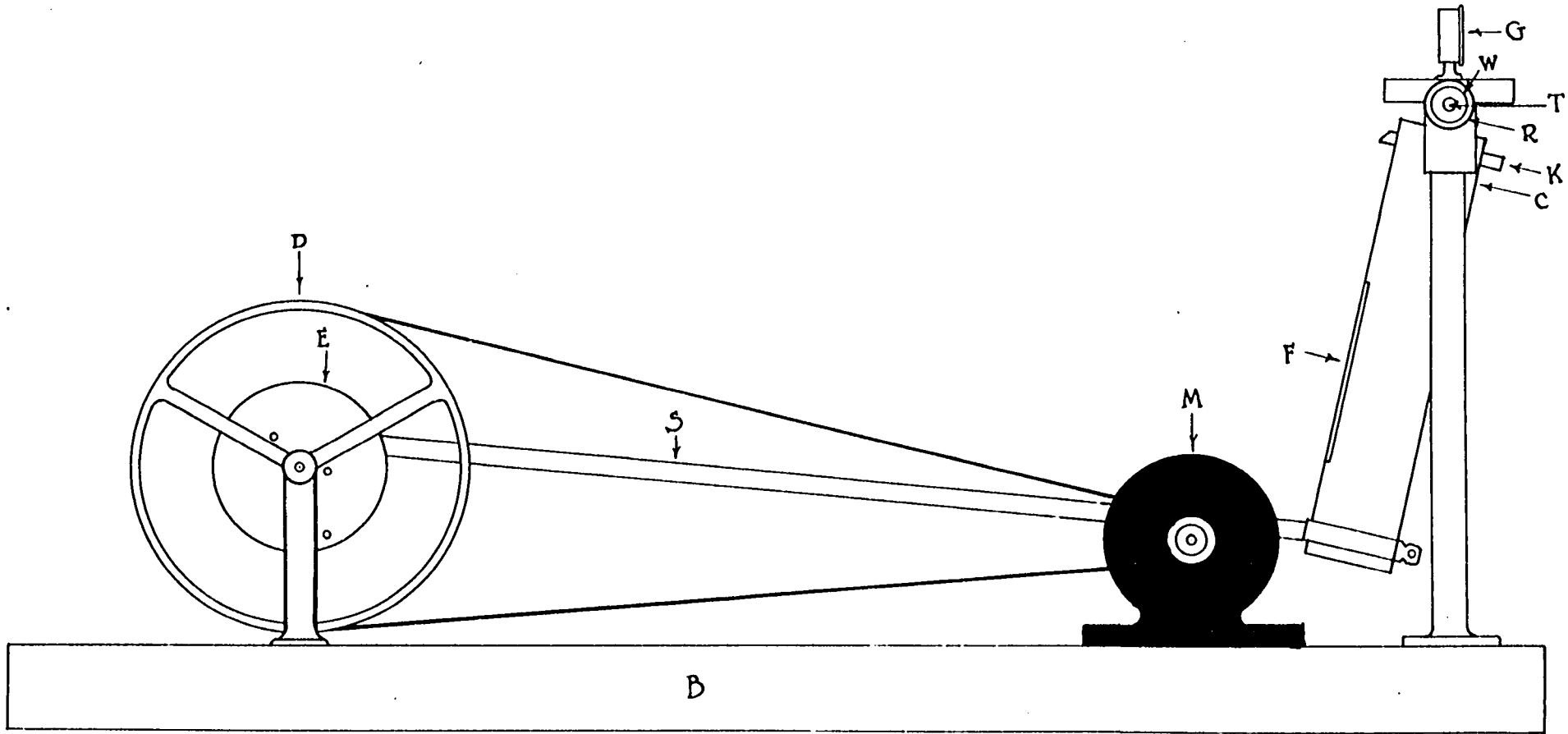
Colorimetric Measurement of pH

The first experiments were directed toward the determination of pH in solutions of carbon dioxide under various pressures by the colorimetric method.

It was first of all necessary to design an apparatus whereby the gas could be admitted under various pressures and allowed to reach equilibrium with its solution before readings were taken.

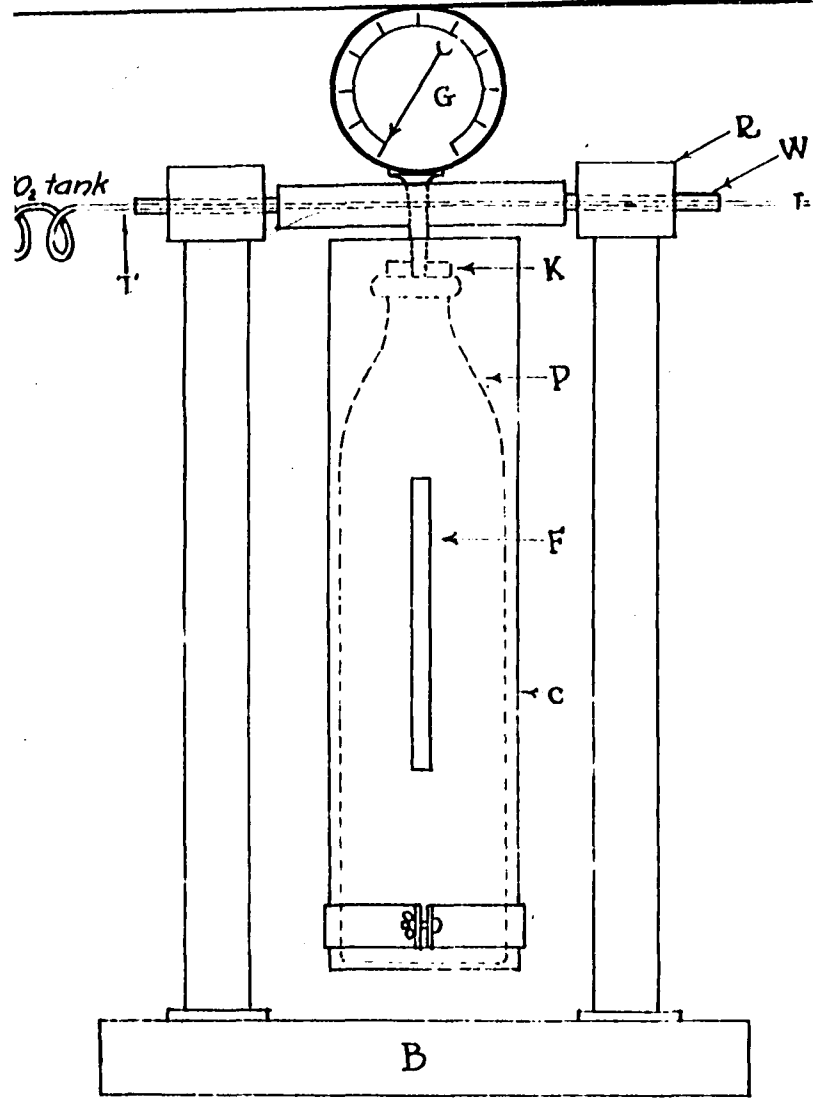
Apparatus.

The final form of apparatus used is sketched in the accompanying diagram (Fig. I). It consists of an electric motor (M), drivewheel (D) and eccentric (E) with shaft (S) all mounted firmly on a wooden base (B) together with a support for the brass case (C) which contains the bottle with its sample. The shaft from the eccentric may be clamped to the bottom of the brass case, as shown in the figure. The bottle is held firmly against the rubber gasket in the brass head by means of a key (K) of gradually increasing width which may be driven through slits in the case above the brass head-piece. In the center of the head is attached a pressure gauge (G), and the gas from the supply-tank is admitted at the side of this attachment by means of flexible copper tub-



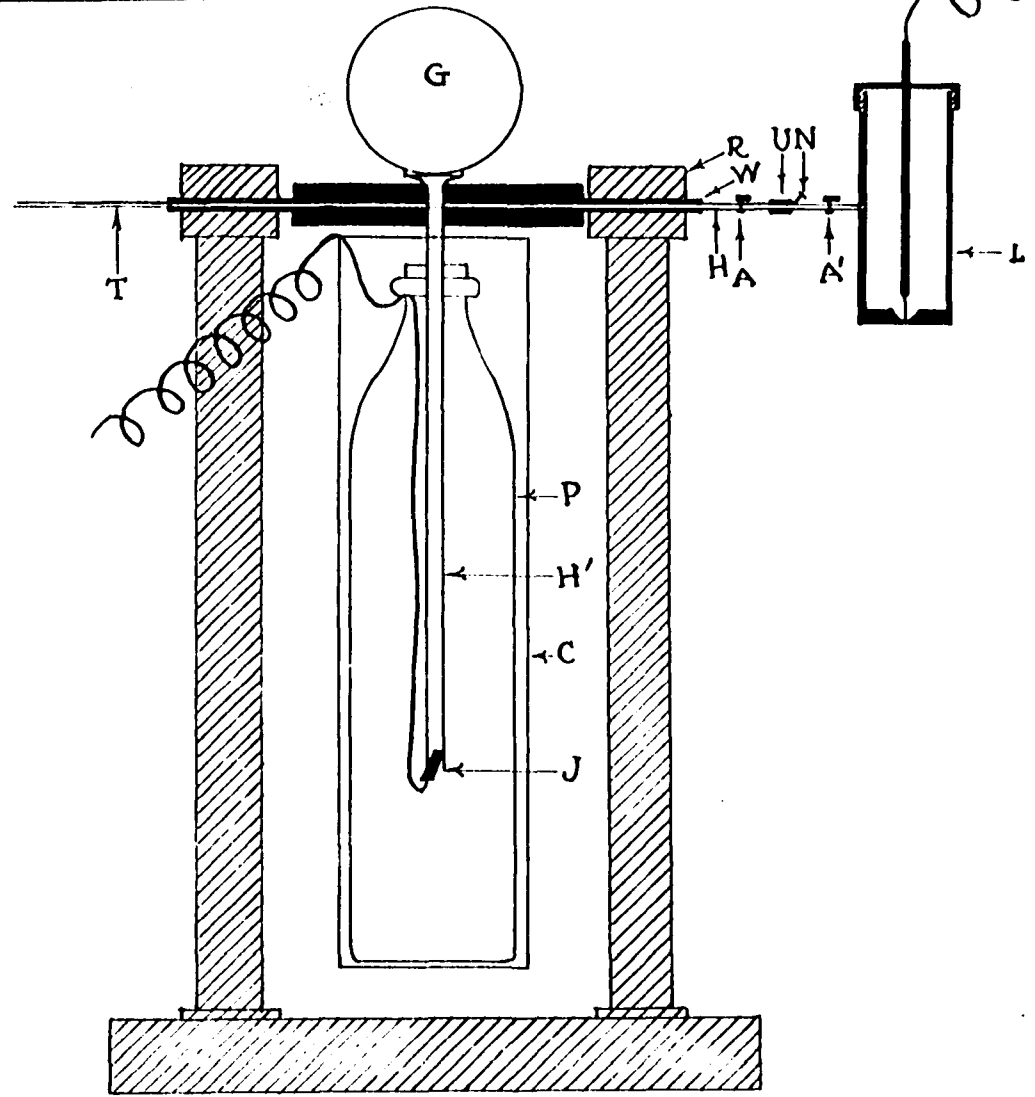
*Apparatus for
Carbonation and pH Measurement
Side View*

Figure I



Apparatus
for Carbonation and pH measurement
Front View

Fig. II



Apparatus
for Carbonation and pH measurement
Front View - Vertical Section

Fig. III

ing (T) which enters through the center of one of the wooden shoulders (W) which rotate in the supports (R) when the apparatus is shaken. The case contains vertical slits (F) on opposite sides through which the color can be viewed after equilibrium has been reached.

Figure II gives another view of the apparatus as arranged for colorimetric work. Figure III shows its adaptation to the potentiometric determination, and will be explained more fully later.

Method and results

In order to make a series of colorimetric determinations, 192 cc. of conductivity water and 8 cc. of 0.04 % solution of brom phenol blue are placed in a 6½ ounce bottle, and CO₂ gas is bubbled in for an hour under the atmospheric pressure in order to displace air dissolved in the water or present in the top of the bottle. The pH at 1 atm. pressure of CO₂ can now be read by comparison with the standards. This reading was found not to vary within the limit of accuracy of the experiment (0.1 pH unit) with any variation in barometric pressure in this vicinity. The barometer reading is normally near 740 mm., and this value was taken as the pH at 1 atm. for the colorimetric work.

After saturation of the water containing indicator with CO₂, the bubbling of gas is continued to prevent entrance of

air while the bottle is placed in the apparatus and the key driven in. If the bubbling was slow, there will be only a small pressure of carbon dioxide built up by this time. The needle-valve from the tank may now be closed and the apparatus shaken, the shaking being continued for some time after there appears to be no further change in the indicator or in the gauge reading.

A series of readings may be taken on the same sample by increasing the pressure. The sample is then again shaken until equilibrium is reached before the color is compared with the standards.

In order to maintain the temperature practically constant, the bottle of water was first immersed for a considerable time either in a 25° thermostat ($\pm 0.1^\circ$) or in a crock of melting ice which was frequently stirred. Water from the thermostat was used to maintain the temperature during the time CO₂ was bubbled in and after the sample was clamped in the apparatus. After shaking to insure equilibrium, sufficient time was allowed for this temperature to be regained. These precautions appeared to be unnecessary, as it was not possible to read any change in the indicator corresponding to a considerable change in temperature; and indeed there is little variation in the result for 0° and for 25°. It must be borne in mind, however, that the method is

sensitive to only 0.1 pH.

After a few preliminary trials, brom phenol blue was chosen as the indicator for all work in this range, both because its color change from blue to yellow seems easy to distinguish, and because the values obtained are all well within its range. The range of the indicator used here was checked by the electrometric method using a bubbling hydrogen electrode, and was found to extend from pH 3.0 to 4.6, which agrees with values previously reported for this indicator.

For use in these experiments an 0.04% solution of indicator was made up in water (alcohol was used in some preliminary experiments), using 3.0 cc. N/20 NaOH for each 0.1 gram of brom phenol blue powder, as directed by Reilly (15). The solution so obtained does not keep particularly well, but it is easy to prepare and by using water without any alcohol, we were not forced to consider the possibility of formation of alkyl carbonates in the solution.

The "double standard" method (12) was used for comparison. A total of 8 cc. of indicator solution was used in each pair, one bottle being sufficiently acid to insure all its indicator being in the acid form, and the other alkaline so that this fraction of the indicator was all in the alkaline form. The standards used were made up according to the

scheme given in Table IV, using a total volume of 200 cc. in each bottle.

Table IV

| Pair | Bottle 1 (alkaline) | Bottle 2 (acid) | pH |
|------|------------------------|--------------------|-----|
| 1 | 0.5 | 7.5 | 3.1 |
| 2 | 1.0 | 7.0 | 3.2 |
| 3 | 1.5 | 6.5 | 3.3 |
| 4 | 2.0 | 6.0 | 3.4 |
| 5 | 2.5 | 5.5 | 3.5 |
| 6 | 3.0 | 5.0 | 3.6 |
| 7 | 3.5 | 4.5 | 3.7 |
| 8 | 4.0 | 4.0 | 3.8 |
| 9 | 4.5 | 3.5 | 3.9 |
| 10 | 5.0 | 3.0 | 4.0 |
| 11 | 5.5 | 2.5 | 4.1 |
| 12 | 6.0 | 2.0 | 4.2 |
| 13 | 6.5 | 1.5 | 4.3 |
| 14 | 7.0 | 1.0 | 4.4 |
| 15 | 7.5 | 0.5 | 4.5 |

For comparison, the sample to be measured is viewed through the vertical slit of the apparatus after inserting a bottle of distilled water in the line of vision to correct for any color present in the glass of the bottles. This color is then compared with a pair of standards, one of which is placed in a can containing a vertical slit similar to the one in the brass case of the apparatus. The pH of the solution is then taken as corresponding to the pair most closely matched. In this way it was found possible to distinguish between the different pairs of the series, and

hence to read the pH to 0.1 unit.

The bottles used were ordinary 6½ ounce bottles such as are used for soda-water, and were quite uniform in color and thickness. The ones used in this work were selected for uniformity, though simply on general appearance; and it was found that some of these bottles would withstand as much as 550 lbs. per sq. in. gauge pressure, or about 37 atmospheres. None of the bottles used burst with pressures under 27 atmospheres.

The CO₂ used was from a commercial tank. It had been analyzed by Mr. J. H. Toulouse and found to contain 99.703% CO₂, 0.0503% O₂, and 0.0027% CO. Hydrocarbons and SO₂ were found to be absent.

The results obtained by the colorimetric method are tabulated below (Table V). Solubilities of CO₂ at 0° are taken as the average of measurements by Wroblewski (2) and by Haehnel (4), using interpolated values for intermediate pressures. The ionization constant may then be calculated at each concentration from the relation,

$$K_1 = \frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3 + \text{CO}_2)} = \frac{(\text{H}^+)^2}{m - (\text{H}^+)}$$
 where $m =$ mols total CO₂ per liter.

In cases where a good matching of colors was not obtained the second decimal in the pH reading was roughly estimated, these figures being added in parentheses in the tables.

Table V

| (a) Temperature 25° | |
|---------------------|--------------------|
| P (atm.) | pH Colorimetric |
| 1.0 | 3.7 |
| 1.7 | 3.5(3) |
| 2.5 | 3.4(3) |
| 2.9 | 3.4(2) |
| 3.7 | 3.4 |
| 3.8 | 3.4 |
| 5.4 | 3.3(3) |
| 5.8 | 3.3 |
| 7.2 | 3.3(2) |
| 7.8 | 3.3 |
| 9.5 | 3.3 |
| 10.5 | 3.3 |
| 12.7 | 3.3 |
| 18.7 | 3.3 |
| 33.3 | 3.3 |

| (b) Temperature 0° | | | | | | |
|--------------------|---|---|--------------------|--|---------------------|--|
| P (atm.) | vol. CO ₂ per 1 vol. H ₂ O | m-mols CO ₂ per 1 L. H ₂ O | pH colorimetric | (H ⁺) X 10 ⁴ | k ₁ X 10 | |
| 0.97 | 1.75 | 0.0781 | 3.5 | 3.16 | 12.8 | |
| 1.4 | 2.48 | 0.1107 | 3.4 | 3.98 | 14.3 | |
| 2.6 | 4.50 | 0.2009 | 3.3(2) | 4.79 | 11.5 | |
| 3.6 | 6.37 | 0.2844 | 3.3 | 5.01 | 8.85 | |
| 8.3 | 13.86 | 0.6187(5) | 3.3 | 5.01 | 4.07 | |
| 15.3 | 22.25 | 0.9933 | 3.2(7) | 5.37 | 2.91 | |
| 23.4 | 29.78 | 1.3294 | 3.2(5) | 5.62 | 2.38 | |

Above 9.5 atmospheres at 25° there appeared to be very little change in the color of the solution as the CO₂ pressure was increased. At the highest pressures used, it appeared still to match the pair corresponding to pH 3.3 better than that corresponding to pH 3.2, although the best match for the former pair was obtained at about 9.5 atm.

In order to test whether this apparent tendency to approach a limiting pH value between 3.2 and 3.3 may not be due to an indicator error at these high pressures, another indicator, Orange IV, whose range is from pH 1.0 to 3.0, was used. At 38.4 atm. pressure and room temperature, this indicator solution maintained its pure alkaline color.

A citric acid solution whose initial pH was 3.5 was treated at room temperature in the same way as the water samples. The pH of this solution was found to reach 3.3 at a CO₂ pressure of 5 atm., and thence to behave like the pure water solutions, not reaching pH 3.2 at a pressure of 24.4 atm. This result again is probably not due to an indicator error, as, when thymol blue (1.2 — 2.8) was used in place of brom phenol blue it did not change from the alkaline color at CO₂ pressures up to 24.8 atm.

A citric acid solution whose initial pH to thymol blue was 2.2 showed no change in the indicator at CO₂ pressures up to 26.5 atm.

The colorimetric results obtained therefore are probably accurate to 0.1 pH unit at the pressures considerably above 1 atm. At low pressures the error may be slightly greater, due to the fact that (H⁺) is so small that the ionization of the indicator itself may be not inappreciable in comparison.

However, the ionization constants calculated, from the colorimetric pH determinations must be quite inaccurate in comparison with those obtained by the conductivity method. This may be readily seen from consideration of the fact that an error of 0.1 in the pH reading at a value of pH 3.3 would mean an error of 1×10^{-4} in the (H^+) , or about 20% error.

Potentiometric Measurement of pH

After a careful study of the possibilities of the colorimetric method, it was decided to attempt a potentiometric determination of the hydrogen-ion activity in the same type of solutions used above. It was hoped to be able to determine the pH of the solutions with an accuracy of 0.01 pH, and thus reduce our error in calculation of hydrogen-ion concentration (activity) to an almost negligible percentage.

The potentiometric measurement of hydrogen-ion activities in solutions under high pressures presents many mechanical difficulties, all of which have not yet been mastered, although certain measurements have been made which appear to be quite accurate.

The usual types of hydrogen gas electrodes do not appear practicable for use here. An analysis of each sample of mixed hydrogen and carbon dioxide admitted would seem to be necessary, which would introduce additional mechanical difficulties as well as the labor involved in making the analyses.

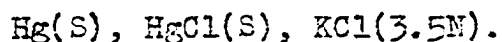
For these reasons it was decided to make use of the quinhydrone electrode in the solution to be measured.

Apparatus

The modification of the pressure apparatus for potentiometric work is shown in Figure III, which is a vertical section diagram of the apparatus as used for this purpose. The long hard-rubber tube (H') is screwed into the head which covers the bottle. This enables one to make a liquid junction by simply loosening the stopcock (A) and allowing the pressure in the bottle to force out some of the liquid. This operation makes very little change in the pressure within the apparatus, and gives a fairly representative portion of the solution for a liquid junction. The tube (H) which carries this liquid is again made of hard-rubber, as is the case for the calomel half-cell (L) which may be tightly connected to the tube H by means of a hard-rubber union (U). All the hard-rubber tubes are of small bore, and all hard-rubber parts are heavy-walled to enable them to withstand the pressures used. The two stopcocks (A,A') are made from hard rubber closely fitting into the openings in the tubes, and are threaded where they extend through on the lower side so that small nuts may be screwed on to hold them in place even under considerable pressure.

A gold electrode (J) is used, which is sealed on a long platinum wire reaching out of the top of the bottle between a pair of rubber gaskets and through a slit in the lower one to prevent contact with the brass head. The wire was lacquered as a means of insulation after it was found that shellac was softened by the action of the solution. The wire was also wrapped with tape from the point where it emerges from the gasket above the bottle. This tape also serves as an aid to insulation from the brass head.

The calomel half-cell used was of the type,



It was checked against a normal calomel half-cell made up in an ordinary glass vessel, and the potentiometer reading was 0.0325 volts at 27°C. The theoretical potential difference here may be calculated from the values given by Kolthoff and Furman (10) for calomel half-cells referred to the normal hydrogen electrode as zero.

$$0.1 \text{ N calomel} = -0.3580 + 0.00006 (t-18)$$

$$1.0 \text{ N calomel} = -0.2864 + 0.00024 (t-18)$$

$$3.5 \text{ N calomel} = -0.2549 + 0.00039 (t-18)$$

or, at 27°,

$$0.1 \text{ N calomel} = -0.33846 \text{ volts}$$

$$1.0 \text{ N calomel} = -0.28424 \text{ volts}$$

$$3.5 \text{ N calomel} = -0.25139 \text{ volts}$$

which gives,

$$-0.25139 + 0.28424 = 0.03285 \text{ volts as the theoretical}$$

value for the normal calomel against the 3.5 N calomel. Hence the measured value is in good agreement with the theoretical. This value was also checked each time it was necessary to prepare a new KCl solution for refilling the cell. The same bottle of KCl (C.P. Baker's analyzed) was used in making up these solutions, which were all found to be satisfactory. The mercury used had been purified by passage through HNO_3 and redistillation.

The 1.0 N calomel half-cell was checked against a 0.1 N calomel and found to give a potential difference of 0.0522 volts at 22.5° . The theoretical value, calculated as above, would be

$$0.33873 - 0.28532 = 0.05341.$$

The quinhydrone used was prepared from ferric alum and hydroquinone. It was recrystallized once from water. Contrary to the findings of Kolthoff and Bosch (9), the pH found in this unbuffered solution containing CO_2 at about 1 atm. pressure was not too acid, but appeared even slightly more alkaline than would be expected from Kendall's conductivity measurements (Figure IV). It was also possible to obtain a pH of 6.13 for conductivity water, by use of the quinhydrone electrode against the 3.5 N calomel. This may be due to the fact that the quinhydrone used was prepared a relatively short time before using, and the acid product which they mention did not have time to develop. It might also be

due to a difference in the chemicals used in preparation of the quinhydrone.

Method and results

In making a potentiometric determination of the pH of a CO_2 solution, an excess of quinhydrone is added to the sample of conductivity water, and CO_2 then bubbled in under 1 atm. pressure for about an hour, as in the colorimetric work. The bubbling is continued while the bottle is clamped in the apparatus, the stopcock A being open to prevent filling the tubes H and H' with solution. The calomel cell is now attached to H by means of the union, the stopcock A' being opened just before tightening the connection. Thus a CO_2 pressure is built up both in the bottle and in the calomel cell, without any of the liquid passing over. When the desired pressure is attained, A and A' are closed, and then the needle-valve from the supply tank. The calomel cell is now detached, and the sample shaken until equilibrium is reached. The gauge pressure is read and the calomel cell tightly connected by U. If A and N are now both opened, the solution will fill the tubes H and H', and the displaced air can escape through the needle-valve. (The apparatus was first constructed without N, but it was found very difficult to make the union without trapping an air bubble). A may now be closed, and A' opened, which serves to fill the side-

arm of the calomel cell with its solution and force the air out through the needle valve. N is closed, the two electrodes connected to the proper terminals of the potentiometer outfit, and the potential difference between the electrodes read by the ordinary null-point method, it being usually necessary to open A and A' for the final adjustment.

A great many difficulties were encountered in the attempt to obtain accurate and concordant results with the above apparatus, and the results obtained with the present apparatus were not entirely satisfactory.

Nevertheless it is believed that certain of the readings are sufficiently accurate to have a real significance in the study of the problem, and that modifications in the apparatus may be made which will allow the measurement of accurate voltages over the whole range of pressures up to the highest which the apparatus will stand without bursting the bottle.

The curves of Figure IV show graphically the results obtained both by colorimetric measurements, and by the potentiometric measurements which appeared to be of highest accuracy. The choice of data from the potentiometric readings is justified, both because the apparatus seemed to be most sensitive during these determinations, and because it was possible to obtain a balance within a very short time after opening the stop-cocks. It was found that a very sensitive reading could

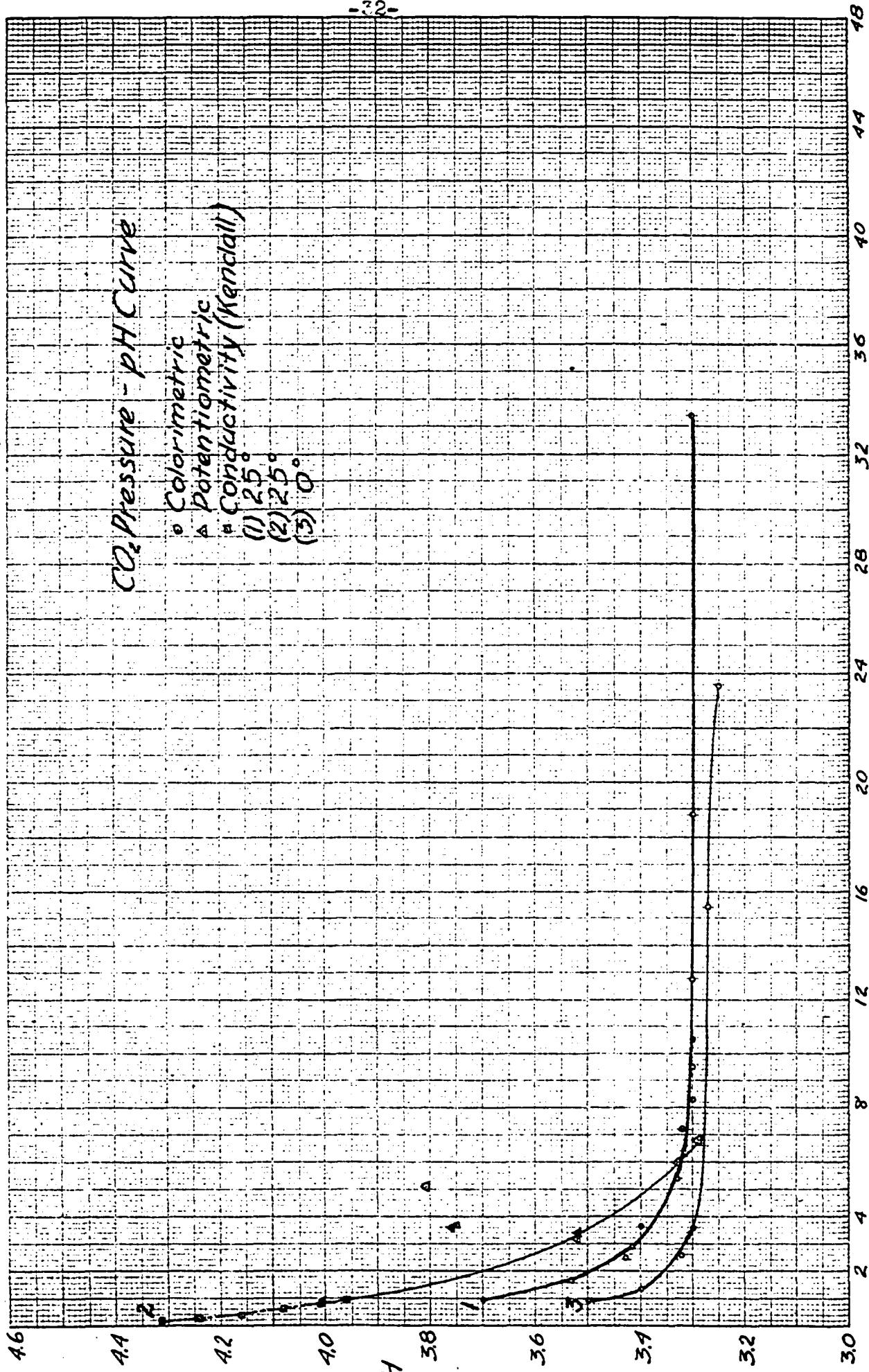
not be obtained with the stop-cocks closed, and the voltage was found to decrease rather quickly after they were once opened. Hence it is thought that the highest voltage readings must in all cases be most accurate, especially as the sources of error, which are later discussed, would all tend to give too low voltage readings. This view is also supported by the fact that these higher readings give pH values which check rather closely with the colorimetric results.

The potentiometric data which are considered sufficiently accurate for plotting on the curve (Figure IV) are tabulated below.

Table VI

| CO ₂ pressure (atm.) | Voltage (against 3.5 N calomel) | pH (calculated) |
|------------------------------------|------------------------------------|--------------------|
| 0.97 | 0.208 | 4.05 |
| 3.2 | 0.239 | 3.52 |
| 3.4 | 0.239 | 3.52 |
| 3.65 | 0.225 | 3.76 |
| 3.7 | 0.226 | 3.75 |
| 5.1 | 0.222 | 3.81 |
| 6.0 | 0.251 | 3.33 |
| 6.8 | 0.253 | 3.29 |

The voltage is reported to the nearest millivolt, although a Leeds and Northrup Students' Potentiometer was used, which may be read to another place. However, the accuracy of the readings with our present apparatus, does not appear to



Pressure (atm.)
Fig. IV

justify the use of another significant figure.

The pH is readily calculated, using the value for E^0 for the quinhydrone electrode given by Kolthoff and Furman (10) 0.7044 volt, and hence obtaining the formula:

$$\text{pH} = \frac{0.4496 - 0.00035 (t-18) - E_{3.5N}}{0.0577 + 0.0002 (t-18)}$$

where $E_{3.5N}$ = Potential measured against 3.5 N calomel.
Hence, at 25°:

$$\text{pH} = \frac{0.4496 - 0.00035 (7) - E_{3.5N}}{0.0577 + 0.0002 (7)}$$

$$\text{or, } \text{pH} = \frac{0.44715 - E_{3.5N}}{0.0591} = 7.57 - \frac{E_{3.5N}}{.0591}$$

If the assumption is made, according to Kendall (6), that in dilute solutions the concentration of ionized solute in a solution of carbonic acid is proportional to the square root of the partial pressure of CO_2 under which it exists, one may calculate the pressures corresponding to his different determinations, and so extend the pH - CO_2 pressure curve to cover the range of pressures below one atmosphere (Table VII). The points so calculated are plotted in Figure IV, using special symbols to distinguish them, and are found to fall very nearly on the same curve as that obtained from the potentiometric data secured in this work.

Table VII

| V | a | C _i X 10 ⁵ | P(atm.) | pH |
|-------|---------|----------------------------------|---------|-------|
| | | 11.0 | 1.00 | 3.96 |
| 36.4 | 0.00357 | 9.81 | 0.795 | 4.01 |
| 51.3 | 0.00422 | 8.23 | 0.559 | 4.085 |
| 72.8 | 0.00503 | 6.91 | 0.395 | 4.16 |
| 102.4 | 0.00595 | 5.81 | 0.279 | 4.24 |
| 145.5 | 0.00717 | 4.93 | 0.201 | 4.31 |

The values in the first two columns of the table are given by Kendall (6), as are those in the first row. C_i, the concentration of ionized solute, may be calculated from

$\frac{a}{V}$, where a = fraction of solute ionized, and V = dilution in liters which will contain one mol of total solute. Then

$$\text{pH} = -\log (H^+) = -\log C_i.$$

From the relation given by Kendall (6), C_i²/P = const., one may calculate the pressure corresponding to any given value of C_i. The constant is evaluated by means of the values in the first row of the table.

$$\frac{C_i^2}{P} = \frac{(1.1 \times 10^{-4})^2}{1} = 1.21 \times 10^{-8}.$$

Some potentiometric readings were taken which appear to be obviously in error, and so are not included in the table. These gave higher pH values for solutions under fairly high CO₂ pressure than that obtained at 0.97 atmosphere, the existing barometric pressure at the time of the experiment. As the measurement at atmospheric pressure was not attended by

any of the mechanical difficulties prevailing at higher pressures, it is probably very close to the correct value. This view is supported by the fact that it agrees closely with the pH value calculated from Kendall's conductivity data near this pressure.

Theoretical discussion of errors

It is quite difficult to formulate a theory which will account for all the probable sources of error in the determinations which if plotted would give points too far off the curve to be considered even approximately correct. To what cause or causes should one assign errors so great as to give a CO₂ solution in equilibrium under a fairly high CO₂ pressure an apparent pH greater than that of a solution under only 1 atm. pressure of the gas? And there are on record readings in which a cell was set up in the opposite direction from that expected, which phenomenon should be understood and explained before a thoroughly satisfactory and reliable apparatus can be designed.

The larger type of error is perhaps most easily explained. If contact is made between the brass head and the platinum wire from the electrode by means of a wetting of the whole with the solution studied, even through a minute crack in the insulating lacquer, a new cell would be set up in the circuit along with the one sought. The e.m.f. of the cell,

Brass, CO_2 solution, KCl (3.5N), $\text{HgCl}(\text{S})$, $\text{Hg}(\text{S})$ cannot be calculated, but certainly might be expected to have a very different value from that of the cell.

Pt , quinhydrone + CO_2 solution, KCl (3.5N), $\text{HgCl}(\text{S})$, $\text{Hg}(\text{S})$ on the assumption of which the calculations are made.

Although considerable precaution was taken in the insulation of the platinum wire as it passed through the gaskets under the brass head, it is easily possible that the solution might soak through the tape and enter any slight crack that might be present in the lacquer used to cover the wire. (The wire was frequently cleaned and re-lacquered in the attempt to overcome such a difficulty.) The solution can then come in contact with the brass by soaking in between the gaskets, and thus the above mentioned brass cell is introduced into the circuit. This can be expected to give highly erroneous results unless taken into consideration in the calculations. It is obvious that such a calculation is not possible unless the value of the half-cell,

Brass, CO_2 solution + quinhydrone is known for this particular sample of brass at each pressure studied.

It is known, moreover, that the solutions used react with brass. The needle-valve (N) in the side-arm of the calomel cell was at first constructed of brass. It began to leak,

and was broken in the attempt to stop this leak, when it was found that almost the entire piece below the valve had been converted into a blue-gray powdery substance. The next needle-valve used was constructed of hard rubber but it is now believed the entire apparatus should be re-designed so as not to necessitate the use of any brass whatever in its construction.

In the case of the readings whose values are not so obviously in error, it is more difficult to account for the trouble. Part of the error might be considered as due to diffusion, as it was necessary to open the stop-cocks at the moment of balancing in order to obtain a properly sensitive reading. It was in an effort to prevent diffusion of the CO_2 -quinhydrone solution into the calomel cell that the latter was placed under the same CO_2 pressure as the former solution before shaking. After this procedure was used, no color of quinhydrone was noticed in the solution left in the calomel cell after an experiment.

It is not believed that any additional error was introduced by the pressure on the calomel electrode, for when the 3.5 N calomel half-cell was placed under a CO_2 pressure of 85 pounds, its voltage against the 1 N calomel electrode was found to be 0.0330 volts. This is much closer to the value found for the same cell under atmospheric conditions than the

experimental error in measurements of the CO_2 solutions under pressure.

It seems unreasonable to suppose, however, that all the smaller errors can be due to diffusion. In order to overcome diffusion errors, a capacitance was introduced into the circuit in the manner described by Jones and Kaplan (5) for the measurement of cells of too high resistance to give sensitive readings by the ordinary method. The condensers used had a capacity of only about ten microfarads, whereas Jones and Kaplan used forty-four microfarads. In the use of this method, both stop-cocks (A, A') were kept closed during the entire measurement. The condensers were given about a minute to become charged and were then discharged through the galvanometer, as described by Jones and Kaplan. But this procedure is slow in obtaining a final balance, as one must wait each time for the condensers to become charged before testing the balance with the galvanometer. In the experiments with this method lower voltages were again obtained, the longer the time required to reach a balance. This effect can hardly be due to diffusion, as the stop-cocks were kept closed during the entire course of the reading. It is considered a reasonable conclusion, then, that the decrease in voltage readings may be due, at least in part, to small concentrations of metal ions gradually dissolved by those portions of the solution which come in contact with the brass.

Since many of the difficulties encountered may be theoretically explained as due to possible contact with the small portions of brass used in the apparatus, it is hoped that the accuracy of all the measurements may be improved by a new design of apparatus in which all parts which can possibly be touched by the solution may be composed of hard rubber. The method of Jones and Kaplan (5) can probably be used in measurement, to cut down diffusion errors. Such a method should then give data which will be accurate and reliable up to the limit of strength of the apparatus.

All the data in which most confidence is placed were taken in experiments for which the head had been carefully dried and a balance obtained within a very short time after shaking was completed. Such data are probably more accurate than those obtained by the colorimetric method.

The small changes of pH obtained at moderately high pressures of CO_2 , however, make it seem desirable to develop a more reliable method of measurement, which will enable us to accurately trace these small changes.

SUMMARY AND CONCLUSIONS

1. Values for the ionization constant of carbonic acid,

$$\frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{CO}_2 + \text{H}_2\text{CO}_3)} = k_1,$$

have been calculated from the conductivity measurements of Pfeiffer and of Haehtel at high pressures of carbon dioxide.

2. Calculation of the ionization constant

$$\frac{(\text{H}^+)(\text{HCO}_3^-)}{(\text{H}_2\text{CO}_3)} = k_1$$

has been attempted using extrapolated values taken from Shipley and McHaffie's curve for the fraction of the total CO_2 existing in the hydrated form at a given concentration. Such a calculation gives a negative value at 5 atm., and hence their curve must be inapplicable at high pressures.

3. By a colorimetric method, the hydrogen-ion concentration has been measured in CO_2 solutions at a series of pressures up to about 33 atm. and the pH was thus found to approach a limiting value between 3.2 and 3.3.
4. The potentiometric method, with special modifications in the electrode vessels has been used for the measurement of hydrogen-ion concentrations by means of the quinhydrone against the 3.5 N calomel electrode. By this means it was

possible to obtain a series of concordant results at CO₂ pressures up to about 6.8 atm.

When the values of pH calculated from these measurements are plotted against CO₂ pressures, the resulting points fall on the same smooth curve as that obtained by a plot of the pH-CO₂ pressure values calculated from Kendall's conductivity data.

Due to imperfections in the design of the apparatus used, no potentiometric measurements which are considered sufficiently accurate were obtained at CO₂ pressures above 6.8 atm.; but it is expected that modifications of the apparatus will allow reliable values to be obtained at much higher pressures.

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