num atom are occupied instead of three, one would expect a higher degree of ionization as indicated in Fig. 1.

The behavior of quinoline toward aluminum bromide apparently is similar to that of pyridine as shown by curves of similar shape and magnitude illustrated by the example in Fig. 2.

On the other hand, the behavior of quinoline and pyridine toward stannic chloride shows more difference than one might expect. Although Figs. 3 and 4 indicate that one mole of stannic chloride is neutralized by two moles of either base, two differences are evident: the higher conductance to the left, and the lower conductance to the right, of the break-point in Fig. 4.

To the left of the break-point in Figs. 3 and 4, the shapes of the curves, the formation of the precipitates, and the break at the 2–1 ratios indicate two equilibria, such as

$$C_5H_5N + SnCl_4 \rightleftharpoons C_5H_5N{:}SnCl_3^{+1} + Cl^{-1} \quad (1)$$

$$C_5H_5N + C_5H_5N{:}SnCl_3^{+1} + Cl^{-1} \rightleftharpoons \underset{\text{white precipitate}}{(C_5H_5N{:})_2SnCl_4} \quad (2)$$

The higher conductance of the quinoline compound is probably due to the larger size of the positive ion.

In Fig. 3 to the right of the break, the conductance increases at the same rate as it does when pyridine is added to thionyl chloride alone. Therefore, no further reaction is occurring. But in Fig. 4, the increase in conductance is much less than is caused by the addition of quinoline to thionyl chloride alone. In trying to account for this puzzling behavior several runs were made to higher molar ratios, one beyond 5–1. The same slight increase was observed in all the runs. Apparently the only explanation is that the quinoline must be combining with the precipitate.

BOSTON 15, MASS.

[CONTRIBUTION NO. 1164 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The High Field Conductance of Aqueous Solutions of Carbon Dioxide at 25°. The True Ionization Constant of Carbonic Acid[1]

BY DANIEL BERG AND ANDREW PATTERSON, JR.

RECEIVED JUNE 3, 1953

High field conductance measurements have been performed on solutions of carbon dioxide in water at 25.00°, approximately 0.15–0.16 M. At a field of 200 kv./cm. the high field conductance quotient is 4.6%. These data have been interpreted to obtain the true ionization constant, $K(0)_1$, of carbonic acid. This constant was found to have the value 1.32 ± 0.05 × 10^{-4} at 25°.

Of the several weak acids available to the chemist for study, one of the most interesting is carbonic acid. It is a common constituent of the atmosphere, a disturbing factor in many conductance measurements, and of vital importance in physiological processes. It is all the more interesting because only a small fraction of dissolved carbon dioxide is in the hydrated form and because the equilibrium between hydrated and unhydrated forms is attained only slowly. Because of this slow attainment of equilibrium, we have felt that it should be possible to use the high field conductance measurements, which of necessity must be performed in a short period of time (a few microseconds) to obtain the true constant of the first ionization

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad (1)$$

$$K(0)_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \quad (2)$$

We present herewith the results of high field conductance measurements on solutions of carbon dioxide and show how it is possible to use these results to obtain $K(0)_1$ for carbonic acid.[2]

Experimental

The experimental procedure was identical with that of Gledhill and Patterson,[3] employing a differential pulse transformer (DPT) bridge circuit and accessory equipment for the production and observation of brief high voltage pulses. For these measurements the pulse duration was four microseconds. Solutions of carbon dioxide were prepared by bubbling purified carbon dioxide into a volume of degassed conductivity water in the conductance cell until the resistance declined to a value of about 1400 ohms. The cell resistance then slowly fell to about 1000 ohms and remained at this equilibrium value. The concentration of carbon dioxide was determined by adding an excess of standard barium hydroxide to a measured sample of the cell solution and back-titrating carefully with standard hydrochloric acid using chlor phenol red as indicator. Three titrations were performed for each cell solution studied; the concentrations were determined with an average deviation of 3%. At low fields, conductance measurements were made with the DPT bridge by substitution of a suitable resistance and parallel capacitance for the second cell. For the high field measurements the reference cell contained a solution of hydrochloric acid of appropriate resistance, and concentration near 10^{-4} M; these measurements are thus relative to hydrochloric acid, and any high field conductance due to free ions is effectively compensated. The temperature was maintained at 25 ± 0.015°, referred to a recently calibrated platinum resistance thermometer.

Results

The results are shown in Fig. 1. The triangles pertain to 0.0165 M, the crosses to 0.0163 M, and the filled circles to 0.0152 M aqueous solutions of carbon dioxide. At 200 kv./cm. the fractional high field conductance quotient is 4.6%, compared

---

[1] This material is taken from a dissertation submitted by Daniel Berg to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1953.

[2] By the term $K(0)_1$ is meant the first ionization constant at zero field. All terms and symbols used in this paper and not defined herein are defined by F. E. Bailey and A. Patterson, THIS JOURNAL, **74**, 4428 (1952), or by H. S. Harned and B. B. Owen, ref. 4.

[3] J. A. Gledhill and A. Patterson, *J. Phys. Chem.*, **56**, 999 (1952).

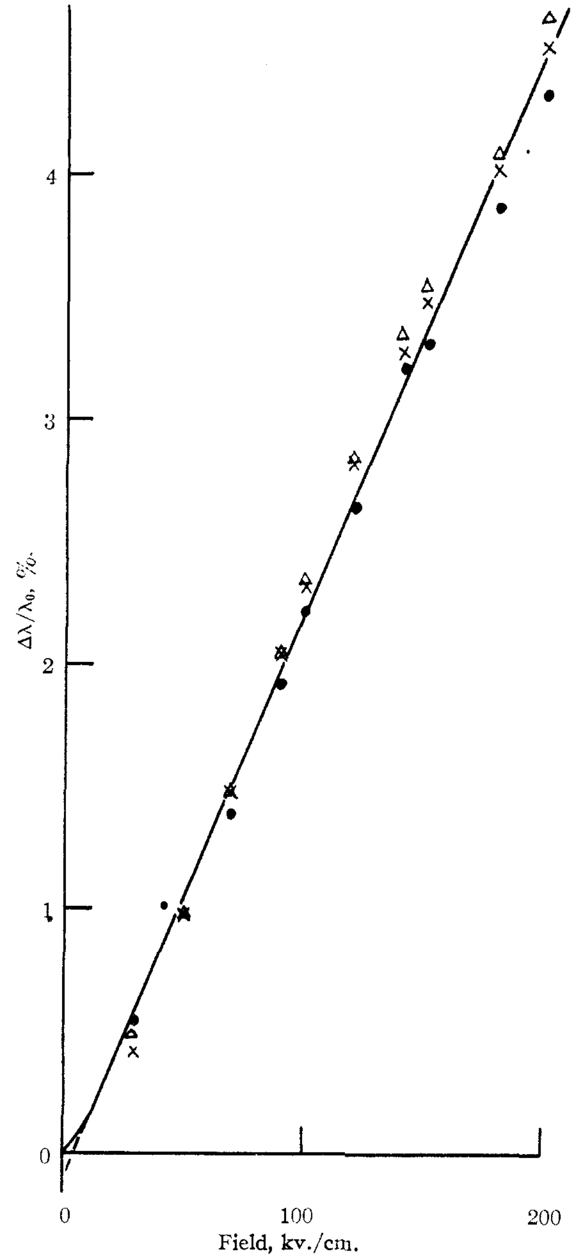

Fig. 1.—The high field conductance of carbonic acid relative to hydrochloric acid at 25.00 ± 0.015°. The triangles refer to a 0.0165 M CO_2 solution, the crosses to a 0.0163 M CO_2 solution, and the dots to a 0.0152 M CO_2 solution. The concentration of hydrochloric acid reference solution was 1×10^{-4} M.

to a computed value of 11.6% for acetic acid at the same field. The value of $K(0)$ for acetic acid is recorded as 1.754×10^{-5}, while $K(0)_1$ for carbonic acid is 4.45×10^{-7}.[4,5] It is evident from the high field conductance results that carbonic acid is the stronger of the two acids, although this is in contradiction to the values of the ionization constants.

Theoretical

The ionization constant measured by the usual methods, for example, with electromotive force cells or by conductance, is an apparent one, which may be written

$$K(0)_1(\text{apparent}) = \frac{[\text{H}^+][\text{HCO}_3^-]}{C_{\text{total}}} \qquad (3)$$

It is implied that the total carbon dioxide concentration is used without it being possible to separate analytically the hydrated and unhydrated forms of the carbon dioxide, which are in equilibrium according to the relation

$$\text{CO}_2(\text{dissolved}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \qquad (4)$$

The concentration determined by analytical methods is the total dissolved carbon dioxide in whatever form it may be present.

$$C_{\text{total}} = [\text{CO}_2] + [\text{H}_2\text{CO}_3] \qquad (5)$$

We shall show below that the high field conductance results may be interpreted to obtain the ratio $K(0)/C$, where $C = [\text{H}_2\text{CO}_3]$. It is possible to combine equations 2 and 3 with the ratio $K(0)/C$ to obtain the true value of $K(0)_1$ for carbonic acid.

The increase in dissociation constant due to the application of an electric field to a solution of a weak electrolyte has been given by Onsager[6] in terms of the parameter b, where

$$b = \frac{z_1{}^2 z_2{}^2(\lambda_1 + \lambda_2)}{z_2\lambda_1 + z_1\lambda_2}\, 9.636\, \frac{V}{DT^2} \qquad (6)$$

Onsager obtained the ratio of the dissociation constant in field X, $K(X)$, to that at zero field, $K(0)$, in the form

$$\frac{K(X)}{K(0)} = F(b) = 1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \ldots . \qquad (7)$$

The increase of the concentration C_i of free ions due to the altered dissociation constant is given by the mass-action law. For binary electrolytes

$$K(0) = \frac{C\alpha_0{}^2 y_\pm{}^2}{1 - \alpha_0} \qquad (8)$$

where C denotes the total concentration of electrolyte and where $\alpha_0 = C_{i_0}/C$ is the degree of dissociation. We shall assume that under a sufficiently high field gradient the term $y_\pm{}^2$ is equal to one, so that

$$K(X) = K(0)F(b) = \frac{C\alpha^2}{1 - \alpha} \qquad (9)$$

The increase of the conductance λ is nearly proportional to the displacement of the degree of dissociation; thus

$$\frac{\Delta\lambda}{\lambda_0} = \frac{\Delta C_i}{C_{i_0}} = \frac{\Delta\alpha}{\alpha_0} = \frac{\alpha}{\alpha_0} - 1 \qquad (10)$$

It is seen from equation 9 that the displacement due to a given change of K depends only on the initial degree of dissociation, α_0. Solving 8 for α_0 and 9 for α we find

$$\alpha_0 = \frac{-\rho_0 + (\rho_0{}^2 + 4y_\pm{}^2\rho_0)^{1/2}}{2y_\pm{}^2};\quad \alpha = \frac{-\rho + (\rho^2 + 4\rho)^{1/2}}{2} \qquad (11)$$

where

$$\rho_0 = \frac{K(0)}{C};\ \rho = \frac{K(X)}{C} = \rho_0 F(b) \qquad (12)$$

We shall now expand $\Delta\lambda/\lambda_0$ in a power series in b. The convergence of this series can readily be

---

(4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950.

(5) H. S. Harned and R. Davis, THIS JOURNAL, **65**, 2030 (1943).

(6) L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934), equation 36.

demonstrated for values of b less than 1.836. Since b contains valence factors, this expansion may not necessarily converge under all circumstances for higher valence-type electrolytes. The expansion has the form

$$\frac{\Delta\lambda}{\lambda_0} = \sum_{n=0}^{\infty} A_n b^n \tag{13}$$

and using equation 10 we find that

$$A_n = \frac{1}{n!}\frac{\mathrm{d}^n}{\mathrm{d}b^n}\left[\frac{\alpha}{\alpha_0} - 1\right]\Big|_{b=0} \tag{14}$$

We see also that

$$A_0 = \frac{y_{\pm}^2\{-\rho_0 + (\rho_0^2 + 4\rho_0)^{1/2}\}}{-\rho_0 + (\rho_0^2 + 4y_{\pm}^2\rho_0)^{1/2}} - 1 \tag{15}$$

and that

$$A_0 = \left(\frac{1-2Q}{1-Q} \times \frac{1}{\alpha_0}\right) - 1 \tag{16}$$

where Q is defined by

$$\rho_0 = \frac{(1-2Q)^2}{(Q-Q^2)} \tag{17}$$

For $n \neq 0$ equation 14 simplifies to the expression

$$A_n = \frac{1}{n!}\frac{1}{\alpha_0}\frac{\mathrm{d}^n(\alpha)}{\mathrm{d}b^n}\Big|_{b=0} \tag{18}$$

Dividing by $A_0 + 1$ to eliminate the activity coefficient at zero field, we find

$$\frac{A_n}{A_0+1} = \frac{1-Q}{1-2Q}\frac{1}{n!}\frac{\mathrm{d}^n(\alpha)}{\mathrm{d}b^n}\Big|_{b=0} \tag{19}$$

Substituting (11) and (16) into this expression we find the general expression for the n^{th} coefficient of the power series

$$\frac{A_n}{A_0+1} = \frac{1}{2n!}\frac{\mathrm{d}^n}{\mathrm{d}b^n}\left\{\left[F^2(b)\frac{(1-2Q)^2}{(Q)} + 4F(b)\left(\frac{1-Q}{Q}\right)\right]^{1/2} - \left(\frac{1-2Q}{Q}\right)F(b)\right\}\Big|_{b=0} \tag{20}$$

By evaluating this expression we find for the first three coefficients

$$\frac{A_1}{A_0+1} = Q$$

$$\frac{A_2}{A_0+1} = -\frac{2}{3}Q + 2Q^2 - Q^3 \tag{21}$$

$$\frac{A_3}{A_0+1} = \frac{7}{8}Q - \frac{8}{3}Q^2 + \frac{19}{3}Q^3 - 6Q^4 + 2Q^5$$

From the first of these we see that the reduced slope of the linear region of a plot of $\Delta\lambda/\lambda_0$ *versus* b is Q. The function Q is simply related to ρ_0 by equation 17, while by equation 12 $\rho_0 = K(0)/C$. We have therefore a relation between the slope Q and $K(0)/C$. The coefficients A_2 and A_3 are always small and tend to zero as Q tends to zero. Thus by plotting $(\Delta\lambda/\lambda_0 - A_2b^2 - A_3b^3)$ against b, where A_2 and A_3 have been calculated using an approximate value of Q, the curve will be linear throughout the experimental range. The value of the reduced slope, Q, so obtained may be used to recalculate A_2 and A_3. These values are then used in a new plot in order to determine Q. This process of iteration converges rapidly.

Having obtained a value of Q from a series of plots of these coefficients, one can solve equation 22 for a value of $\rho_0 = K(0)/C$. In this particular case, C is the concentration of carbonic acid, H_2CO_3, and $K(0)$ is the first ionization constant of the acid. One may readily show by appropriate substitution in equation 2 that

$$\rho_0 = \frac{K(0)_1}{C} = \frac{[H^+][HCO_3^-]}{C^2} \tag{23}$$

and from equation 3 that

$$C_{\text{total}}\,K(0)_{1(\text{apparent})} = [H^+][HCO_3^-] \tag{24}$$

Substitution of equation 24 into equation 23 yields the relation

$$\rho_0 = \frac{K(0)_{1(\text{apparent})}C_{\text{total}}}{C^2} \tag{25}$$

or

$$K(0)_1 = (\rho_0 K(0)_{1(\text{apparent})}C_{\text{total}})^{1/2} \tag{26}$$

which relates the true ionization constant with the high field conductance results and the analytically determined total concentration of carbon dioxide.

An analysis of the probable error which one may expect in an evaluation of $K(0)/C$ from high field conductance measurements will now be given.

The dissociation constant, $K(0)/C$, is related to the reduced slope, Q, by equation 22. We find by differentiating this equation that

$$\mathrm{d}\left(\frac{K(0)}{C}\right)\Big/\frac{K(0)}{C} = \frac{\mathrm{d}Q}{Q}\frac{1}{(1-Q)(2Q-1)} \tag{27}$$

It may be shown that the probable error, $P(Q)$, in the measurement of a slope Q for a straight line consisting of n evenly spaced points is given by

$$P(Q) = \left(\frac{12n}{n^2-1}\right)^{1/2}\frac{P(\Delta\lambda/\lambda_0)}{B} \tag{28}$$

where $P(\Delta\lambda/\lambda_0)$ is the probable error in $\Delta\lambda/\lambda_0$ and B is the highest value of b at which $\Delta\lambda/\lambda_0$ is measured.[7] The assumptions involved in this expression are that the intercept $A_0 << 1$ and that $A_2b^2 + A_3b^3 << \Delta\lambda/\lambda_0$. Both these assumptions are good.

Combining equations 27 and 28 we have the expression for the relative probable error in the equilibrium constant divided by the concentration

$$P\left(\frac{K(0)}{C}\right)\Big/\frac{K(0)}{C} = \frac{1}{Q(1-Q)(2Q-1)}\left(\frac{12n}{n^2-1}\right)\frac{P(\Delta\lambda/\lambda_0)}{B} \tag{29}$$

This function may be separated into three parts: the

---

[7] See A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 249. These authors show that, in terms of the symbols used in this paper, for a line consisting of n evenly spaced points, the probable error in the slope Q of a $\Delta\lambda/\lambda_0$ *versus* b plot is given by

$$P(Q) = \left(\frac{n}{n\Sigma' b^2 - (\Sigma b)^2}\right)^{1/2} P(\Delta\lambda/\lambda_0)$$

Substituting for the summations the quantities

$$\sum^{n} b^2 = B^2/n^2 \sum^{n} N^2 = \frac{B^2}{n^2}\left(\frac{n(n+1)(2n+1)}{6}\right)$$

$$\sum_{1}^{n} b = \frac{B}{n}\sum_{1}^{n} N = \frac{B}{n}\left(\frac{n(n+1)}{2}\right)$$

(H. B. Dwight, "Tables of Integrals," The Macmillan Co., New York, N. Y., 1949, p. 7) and simplifying, we find for the probable error in the slope Q

$$P(Q) = \left(\frac{12n}{n^2-1}\right)^{1/2}\frac{P(\Delta\lambda/\lambda_0)}{B}$$

which is equation 28.

part depending on Q, the reduced slope, the part depending on n, the number of points, and the part depending on the measuring instrument. Let us call the first factor $F(Q)$; it is defined by

$$F(Q) = \frac{1}{Q(1 - Q)(2Q - 1)}$$

Since ρ_0 is related to the reduced slope by equation 22, then

$$F(Q) = \frac{-(\rho_0 + 4)^{3/2}}{\rho_0^{1/2}}$$

From a plot of log $F(Q)$ against log ρ_0, it is found that the function $F(Q)$ has a minimum value of about ten. The relative probable error in ρ_0 is then at least ten times that in the factors which depend upon the number of points taken and upon the instrument, as will now be indicated.

The error factor which depends upon the number of points measured is given by that portion of equation 29

$$(12n/n^2 - 1)^{1/2}$$

In our measurements it is convenient to obtain about nine points. Hence $n = 9$, and $(12n/n^2 - 1)^{1/2}$ is 1.2. This factor does not vary markedly with n.

The probable error in $\Delta\lambda/\lambda_0$ given with the DPT bridge is less than 0.1. The value of B, the highest value of the parameter b, which is obtainable with the present pulse modulator, cells and accessory equipment is about 0.25 for 1-1 electrolytes in water at 25°. Hence the relative probable error in ρ_0 is given by

$$\frac{P(\rho_0)}{\rho_0} F(Q)(1.2)\left(\frac{0.1}{0.25}\right) \cong 0.5F(Q)[\text{in } \%]$$

Since the function $F(Q)$ is at the minimum equal to ten, the relative probable error in ρ is at the minimum 5%. The minimum relative probable error in ρ_0 is very large for extremely weak electrolytes. Although this degree of precision is the best which this type of measurement can produce, there are many cases where such an estimate may be valuable.

Discussion

Utilizing equation 23, a value of $K(0)_1$ (apparent) equal to 4.45×10^{-7} from ref. 5, and a value of $\rho_0 = 2.247$ obtained as shown in the preceding section, we find the true ionization constant of carbonic acid to be $1.32 \pm 0.05 \times 10^{-4}$ at 25.00°. The fraction of the carbon dioxide present which is hydrated is readily obtained from the ratio of the two ionization constants; it is 0.37%. Other investigators have used spectrophotometric and thermal kinetic methods to obtain the true ionization constant of carbonic acid.[8,9] Of particular interest is the method used by Roughton,[9] who obtained a value $2.4 \pm 0.4 \times 10^{-4}$ at 15°. This quantity is, of course, obtained at a different temperature than that which we report; it is also the result of measurements in a sodium chloride solution, rather than in pure water. Harned and Davies[5] found the apparent ionization constant of carbonic acid to have the values 3.80 and 4.45×10^{-7} at 15 and 25°. It would be expected that the true constants found by Roughton[9] and by the present authors would exhibit the same trend toward a larger value at the higher temperature. Such is not the case, however, nor are the limits of error quoted by each investigator sufficient to account for this lack of agreement. It is our intention to extend these measurements to the range of temperatures from 0 to 50°, for which apparent ionization constant data are available. It will then be possible to check the consistency of the data from another point of view.

The discussion of probable errors above shows that it should be possible to determine ionization constants to better than 10% in the range $0.05 \leq K(0)/C \leq 50$. It is possible to change the cell constant of the high field conductance cells used in order to keep the ratio of $K(0)/C$ equal to or about 2, at which point the measurement of $K(0)/C$, and hence of $K(0)$, is the most accurate. It is fortuitous that the cells presently available and the $K(0)$ of carbonic acid complement each other to yield a result having the maximum accuracy possible with this method. The values of $K(0)$ and C with which we can work are not independent because, as has been mentioned in ref. 3, the high field pulse power supply has a finite internal impedance and requires matching to a similar minimum resistive load for proper operation. If the electrolyte is not such a weak one, C must be made larger and the cell constant must be made smaller in order to maintain this particular minimum, while at the same time satisfying the requirement that $K(0)/C$ be approximately 2. The reverse is true for very weak electrolytes, with an additional limitation that the solvent conductance must not become an undue fraction of the measured conductance.

Acknowledgment.—This work was supported by the Office of Naval Research.

NEW HAVEN, CONN.

---

(8) R. Brinkman, R. Margaria and F. J. W. Roughton, *Phil. Trans. Roy. Soc.*, **A232**, 65 (1933).

(9) F. J. W. Roughton, THIS JOURNAL, **63**, 2930 (1941).