THE EFFECT OF VARIATION IN IONIC STRENGTH ON THE APPARENT FIRST AND SECOND DISSOCIATION CONSTANTS OF CARBONIC ACID.

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The biological and chemical importance of carbonic acid has stimulated much work upon its first dissociation constant with the immediate object of using this constant for the calculation of the hydrogen ion concentration of biological solutions. Fewer investigations have had as their object the determination of the second dissociation constant.

The mathematical treatment of the behavior of solutions of strong electrolytes by Milner (1) and by Debye and Hückel (2) has brought to the empirical results obtained by Lewis (3) and his collaborators, and Brönsted and La Mer (4) a theoretical explanation which seems adequate. Experimental work has indicated that the deviation in the behavior of strong electrolytes in moderately dilute solution from their behavior in infinitely dilute solution can be approximately expressed in the following manner.

If $\alpha =$ the activity
$\gamma =$ " " coefficient, and
$c =$ " molal concentration of an ion, then
$\alpha = \gamma c$. Further, that the activity coefficient is related to the ionic concentration of the solution by the empirical formula
$- \log \gamma = \beta v^2 \sqrt{\mu}$ where
$\beta =$ an empirically determined constant which has a value of approximately 0.50
$v =$ the valence and
$\mu =$ the ionic strength and is defined as $\frac{1}{2} \Sigma z^2$.

The theoretical considerations of Debye and Hückel led to an expression, which under certain limiting conditions, corresponded well with the above empirical equation.
In view of these developments and the desirability of knowing the activity of bicarbonate and carbonate ions for subsequent studies, we have endeavored to determine the effect of varying ionic strength on the apparent dissociation constants of carbonic acid.

**FIRST DISSOCIATION CONSTANT.**

The first dissociation constant of carbonic acid has been accurately determined by numerous investigators. Of the determinations based on conductivity measurements those of Walker and Cormack (5) and of Kendall (6) are probably the most reliable. The results of these workers, recalculated by Warburg (7), give the value for \( K_1 \) as \( 3.11 \times 10^{-7} \) at \( 18^\circ \); \( pK_1 = 6.507 \). Kendall's value for \( pK_1 \) is 6.656 at \( 0^\circ \) and 6.460 at \( 25^\circ \). This represents a change in \( pK_1 \) per degree of 0.0078. Assuming that this temperature coefficient is valid up to \( 38^\circ \), the \( pK_1 \) of carbonic acid would be 6.36 at body temperature. Hasselbalch (8) in 1916, determined \( pK_1' \) electrometrically in bicarbonate solutions ranging in concentration from 0.005 to 0.05 N. The method for measuring electrometric pH in CO2-containing solutions at that time contained certain errors, which Warburg has pointed out in recalculating Hasselbalch's values for \( pK_1' \). These values are consistently about 0.09 lower than Warburg's and about the same amount lower than ours. The reason for the discrepancy apparently lies in the differences in technique employed in the measurement of pH values. The most accurate determinations of the first dissociation constant by electrometric measurement appear to be those of Warburg. These results we have recalculated, using the solubility coefficient for CO2 found in this laboratory, and have included in Fig. 1 with our own results.

The mass law equation for the ionization of carbonic acid in terms of activity is

\[
\frac{a_{H^+} \times a_{HCO_3^-}}{a_{HCO_3^-}} = K_1
\]

In the logarithmic form this becomes

\[
\log a_{H^+} + \log a_{HCO_3^-} - \log a_{HCO_3^-} = \log K_1
\]

where \( \alpha \) represents the activity of each individual component. For \( \alpha_{HCO_3^-} \) one may write \( \gamma_1 [HCO_3^-] \) where \( \gamma_1 \) denotes the activ-
ity coefficient of the HCO₃⁻ ion. Furthermore, in the presence of a relatively large amount of NaHCO₃ one may write γ₁ [NaHCO₃] instead of γ₁ [HCO₃⁻], assuming for the moment, that NaHCO₃ behaves as a strong electrolyte. Since the activity of a gas is proportional to its tension, one may write

\[ \alpha_{HCO_3} = \frac{p_{CO_2}}{760} \times \frac{a_{CO_2}}{0.0224} \]

where \( p_{CO_2} \) denotes the tension of CO₂ with which the solution is in equilibrium and \( a_{CO_2} \) the solubility of CO₂ in the solution at that temperature. In conformity with the recent recommendations of Sörensen and Linderström-Lang (9) we shall write \( p_{\alpha_H} \) for \( - \log \alpha_{H} \). With the above substitutions Equation 1 then becomes

\[ \log K_1 = \log p_{\alpha_H} - \log [\text{NaHCO}_3] - \log p_{CO_2} - \log \frac{a_{CO_2}}{760} \times \frac{0.0224}{0.0224} \]

\[ = \log K_1 - \log \gamma_1 \]

We shall let \( pK_i' = - \log K_i' = pK_1 + \log \gamma_1 \)
Our experiments have been performed with the object of determining the relation between $pK'_1$ (and consequently $\log \gamma_1$) and the ionic strength of the solution.

**EXPERIMENTAL.**

The experiments to be reported here represent the results of the determination of $pK'_1$ in solutions of eight different ionic strengths. Each of these experiments was repeated with a freshly prepared solution.

The sixteen different solutions whose compositions are given in Table I were prepared from NaHCO$_3$ and NaCl of a high degree of purity. Each was rotated for 30 minutes in a water bath at 38° with hydrogen and CO$_2$ at a tension previously calculated to give the desired pH. The saturation was repeated for a second 30 minute period in order to insure equilibrium. The liquid phases were then separated by the technique described in a previous paper (10) and the following analyses were made.

Samples of the gas phase were transferred to the Haldane-Henderson gas apparatus and the tension of CO$_2$ was determined. The liquid phase, which was contained in filled glass bulbs over mercury, was analyzed for its CO$_2$ content in the Van Slyke (11) manometric gas apparatus. The $pH$ was determined electrochemically at 38° in the Clark electrode vessel using the cell

\[
\text{Hg} \mid \text{HgCl} \mid \text{Saturated KCl} \mid \text{Saturated KCl bridge} \mid \text{Unknown solution} \mid \text{H}_2 \mid \text{Pt}
\]

The potential of the cell, with 0.1 M HCl in place of the unknown solution, was determined at the beginning of each day’s experiment. This value of “$e_0$”, calculated on the assumption that the $pH$ of 0.1 M HCl is 1.08, is given in each table. As pointed out by Cullen (12) this procedure serves as a daily calibration of the cell system used. The value 1.08, used as the $pH$ of 0.1 M HCl, is taken from Lewis’ value for the activity of H$^+$ in an HCl solution whose ionic strength is 0.1 $\mu$.

Values of $pH$ are calculated from the equation

\[
pH = \frac{E.M.F. \text{ (corrected to 1 atmosphere dry } H_2)}{0.05916} - e_0
\]

1Lewis and Randall (3), p. 382
### TABLE I.
The pK₁' of Carbonic Acid at 38° in Salt Solutions of Varying Ionic Strength.

| No. | p\textsubscript{CO}_2 | Solubility coefficient of CO\textsubscript{2} | H\textsubscript{2}CO\textsubscript{3} | CO\textsubscript{2} | NaHCO\textsubscript{3} | log
\[
\frac{\text{NaHCO}_3}{\text{H}_2\text{CO}_3}
\] | pH  | pK₁' | NaCl | \(\mu\) | \(\sqrt{\mu}\) |
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In odd numbered experiments \(\varepsilon_0 = 0.2364\); in even numbered experiments \(\varepsilon_0 = 0.2351\).

* Loss of CO\textsubscript{2} from gas phase. Not plotted in Fig. 1.
In Table I are given the results of our analyses. The H$_2$CO$_3$ is calculated from the CO$_2$ tension. This is subtracted from the total CO$_2$ leading to the values for NaHCO$_3$.

In the ninth column are given the values of pK$_1'$ calculated from these data by means of Equation 2. The results of our determinations, together with those found by Warburg, are given in Fig. 1, in which the values pK$_1'$ are plotted as ordinates and the $\sqrt{\mu}$ as abscissae.

It will be seen that most of the points lie on a straight line which intersects the ordinate at 6.33 and has a slope of 0.5. The equation of this line is therefore

$$pK_1' = 6.33 - 0.5 \sqrt{\mu}$$

Combining Equation 3 with this and substituting 6.33 for pK$_1$ we obtain

$$-\log \gamma_1 = 0.5 \sqrt{\mu}$$

This empirical equation apparently fits the experimental data even when the ionic strength of the solution is as great as 0.180. Such correspondence would not have been expected from the theory of Debye and Hückel because it is known that in solutions whose ionic concentration is greater than 0.10 $\mu$, correction should be made for the dimensions of the ions present and for the altered dielectric properties of the solvent. This would cause the theoretical line to bend toward the abscissa and our actual points lie slightly above such a curve. It is shown clearly, however, that the curve relating $-\log \gamma_1$ and $\sqrt{\mu}$ is linear and has a slope of the order of magnitude predicted by the Debye and Hückel theory in the region of moderately dilute solutions.

SECOND DISSOCIATION CONSTANT.

Determinations of the second dissociation constant of carbonic acid have been made by McCoy (13), Seyler and Lloyd (14), Bjerrum and Gjaldbaek (15), and others. McCoy's results, as recalculated by Stieglitz (16), led to a value of $K_2 = 5.4 \times 10^{-11}$ or pK$_2 = 10.27$ at 25°; Seyler and Lloyd found $K_2 = 4.3 \times 10^{-11}$ or pK$_2 = 10.37$; and Bjerrum and Gjaldbaek give $K_2 = 6.0 \times 10^{-11}$ or pK$_2 = 10.22$ at 25°. Although it was recognized by McCoy that the concentration of the solution in which the con-
stant was determined affected the constant obtained, no systematic study of the effect of varying ionic strength on the second dissociation constant has been made.

As in the case of the first dissociation constant we are here concerned with the mass law equation,

\[
\frac{a_{H^+} \times a_{CO_2^-}}{a_{HCO_3^-}} = K_2
\]

which in the logarithmic form becomes

\[
\log a_{H^+} + \log a_{CO_2^-} - \log a_{HCO_3^-} = \log K_2
\]

Substituting \( \gamma_2[CO_2^-] \) and \( \gamma_1[HCO_3^-] \) for \( a_{CO_2^-} \) and \( a_{HCO_3^-} \) respectively,

Equation 5 may be written

\[
\log a_{H^+} + \log \gamma_2[CO_2^-] - \log \gamma_1[HCO_3^-] = \log K_2
\]

We have shown in the previous section that if \( [HCO_3^-] \) be taken equal to \( [NaHCO_3] \) then \( - \log \gamma_1 = 0.5 \sqrt{\mu} \). By making the assumption that \( Na_2CO_3 \) also is a strong electrolyte, so that \( [CO_3^{2-}] = [Na_2CO_3] \), Equation 6 may be rewritten

\[
\log a_{H^+} + \log [Na_2CO_3] + \log \gamma_2 - \log [NaHCO_3] + 0.5 \sqrt{\mu} = \log K_2
\]

Transposing \( \log \gamma_2 \) and \( 0.5 \sqrt{\mu} \) to the right-hand side, dividing through by minus one and substituting \( pX_H \) for \( - \log a_{H^+} \), Equation 7 becomes

\[
pX_H - \log [Na_2CO_3] + \log [NaHCO_3] = - \log K_2 + \log \gamma_2 + 0.5 \sqrt{\mu} = pK_2
\]

Our experimental work has had for its purpose the determination of \( pK_2 \) in solutions of different ionic strengths. From these results we have been able to determine the relation between \( \log \gamma_2 \) and the ionic strength.

**EXPERIMENTAL.**

As in the case of the first dissociation constant, sixteen different solutions were prepared, representing eight different ionic strengths. The \( CO_2 \) of each solution was determined gasometrically and the total alkali (\( NaOH + Na_2CO_3 + NaHCO_3 \)) titri-
TABLE II.

The \( pK_z \) of Carbonic Acid at 38° in Salt Solutions of Varying Ionic Strength.

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<th>No.</th>
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<th>NaCO(_3)</th>
<th>NaHCO(_3)</th>
<th>Total ( CO_3 )</th>
<th>NaCO(_3)</th>
<th>NaHCO(_3)</th>
<th>( \log )</th>
<th>( \sigma )</th>
<th>( \mu )</th>
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In odd numbered experiments \( \varepsilon_0 = 0.2350 \); in even numbered experiments \( \varepsilon_0 = 0.2349 \).
metrical. Using Michaelis' (17) value of 13.475 for $pK_a$ at $38^\circ$, $p\omega\text{OH}^+$ was obtained. From the activity coefficient of $\text{OH}^-$ in solutions of different ionic strength, as given in Lewis and Randall, the NaOH concentration was calculated.

From the ratio of $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$ to total CO$_2$ the $\text{Na}_2\text{CO}_3$ and NaHCO$_3$ were calculated. A ratio of $\text{Na}_2\text{CO}_3$ to NaHCO$_3$ was chosen which gave the maximum accuracy and was sufficiently high so that the H$_2$CO$_3$ concentration could be neglected. The $p\omega_H$ of each solution was determined electrometrically using as $\epsilon_0$ the values found with 0.1 N HCl at the beginning of each experiment.

From these data and Equation 8, we have calculated $pK_a'$ for each solution. Our results are tabulated in Table II and graphically represented in Fig. 2 with $pK_a'$ as ordinates and $\sqrt{\mu}$ as abscissae. The equation which satisfies this line is

$$pK_a' = 10.22 - 1.1 \sqrt{\mu}.$$
Combining with this Equation 8, and putting $pK_2 = 10.22$, we obtain

$$-\log \gamma_2 = 1.6 \sqrt{\mu}.$$  

If the simple relationship $-\log \gamma = 0.5 v^2 \sqrt{\mu}$ held for the carbonate ion one might expect the relation between $-\log \gamma_2$ and the $\sqrt{\mu}$ to be

$$-\log \gamma_2 = 0.5 \times 2^2 \sqrt{\mu} = 2 \sqrt{\mu}$$

It is seen that the slope over the range of concentrations with which we worked is somewhat less than that expected from the theory. In view of the fact that no account has been taken of the dimensions of the ions, or of the change in dielectric constant of the solution at the higher concentrations, it is felt that the correspondence of our results with what might have been anticipated from theoretical considerations is satisfactory. As in the case of $\gamma_1$, the linear relationship between $-\log \gamma_2$ and $\sqrt{\mu}$ appears to hold to a concentration of $\mu = 0.16$.

CONCLUSIONS.

The first and second dissociation constants of carbonic acid have been determined at 38° in solutions of varying ionic strength.

When extrapolated to $\mu = 0.0$, the first dissociation constant was found to be $4.68 \times 10^{-7}$ or $pK_1 = 6.33$. The activity coefficient of the bicarbonate ion, $\gamma_1$, was found to be related to the ionic strength of the solution from $\mu = 0.01$ to $\mu = 0.18$ according to the equation

$$-\log \gamma_1 = 0.5 \sqrt{\mu}$$

The apparent first dissociation constant is related to the ionic strength of the solution according to the equation

$$pK_1' = 6.33 - 0.5 \sqrt{\mu}$$

The second dissociation constant of carbonic acid was found to be $6.03 \times 10^{-11}$ or $pK_2 = 10.22$ at 38°. The activity coefficient of the carbonate ion, $\gamma_2$, was found to be related to the ionic strength of the solution from $\mu = 0.02$ to $\mu = 0.16$ according to the equation

$$-\log \gamma_2 = 1.6 \sqrt{\mu}$$
The apparent second dissociation constant is related to the ionic strength of the solution according to the equation

\[ pK_2' = 10.22 - 1.1 \sqrt{\mu} \]

These results are in harmony with the theory of the behavior of strong electrolytes in dilute solutions as elaborated by G. N. Lewis, Bronsted, and Debye and Hückel.

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