The thermodynamic ionization constants of carbonic acid: Determination of ratio of $K_1$ to $K_2$ from measurements in very dilute aqueous solutions.

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I. INTRODUCTION

As a prelude to measuring the dissociative equilibria of inorganic carbon in sea water, we have redetermined the ratio of thermodynamic dissociation constants of carbonic acid in pure water. Whereas the first dissociation constant, $K_1$, has been repeatedly determined from galvanic and conductance cell measurements with good agreement between different methods and laboratories, the second constant, $K_2$, based solely on galvanic cell measurements, is considerably less well established.

We have devised a gas-solution method of determining $K_1/K_2$ which avoids the use of galvanic or conductance cells and allows accurate measurements in very dilute solution. Since $K_1$ is quite accurately known, our results provide, essentially, a new approach to determining $K_2$. We have employed ionic strengths as low as 0.002 m (molality or mol kg$^{-1}$ of H$_2$O), nearly ten times lower than the minimum of earlier measurements. At this dilution the Debye-Hückel limiting law, expressed unambiguously in terms of fundamental physical constants, differs from the empirical, extended law by only a few percent. Our results, if experimentally correct, should therefore be a more valid basis for establishing $K_2$ than the earlier galvanic cell data.

The work described below was carried out at 20°C. Measurements are feasible for both higher and lower temperatures, and with other salts of sea water replacing those of sodium.

Before discussing our own measurements we will critically review
the most important earlier studies of carbonic acid equilibria in dilute solutions. In spite of the considerable attention these studies have already received, we will point out some previously overlooked aspects of the measurements and their significance.
II. THE FIRST DISSOCIATION CONSTANT

The dissociative equilibrium:

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \]

is governed by the equilibrium quotient:

\[ K_1 = \frac{a_{\text{H}^+}a_{\text{HCO}_3^-}}{a_{\text{CO}_2}a_{\text{H}_2\text{O}}} = \frac{m_{\text{H}_2\text{CO}_3}^m}{m_{\text{CO}_2}^m m_{\text{H}_2\text{O}}^m} \cdot \frac{\gamma_{\text{H}^+}\gamma_{\text{HCO}_3^-}}{\gamma_{\text{CO}_2}\gamma_{\text{H}_2\text{O}}} \]

(1)

where \( a, m, \) and \( \gamma \) refer to the activity, molality, and activity coefficients, respectively, of the subscripted chemical species, written without their charges, if any.

As a reference state, the condition is chosen that:

\[ \gamma_\text{H} = \gamma_{\text{HCO}_3^-} = \gamma_{\text{CO}_2} = a_{\text{H}_2\text{O}} = 1 \]

in pure water at every temperature and at a total pressure of 1 atmosphere. \( K_1 \) is, thus, a constant at all salt concentrations but varies with temperature and pressure. For pressures up to 1 atmosphere, the influence of pressure is, however, slight.

Hastings and Sendroy [1925] employed the galvanic cell:

\[ \text{Pt} \mid \text{H}_2, \text{CO}_2 \mid \text{NaHCO}_3(m_1), \text{NaCl}(m_2), \text{CO}_2(m_3) \parallel \text{saturated KCl bridge} \parallel \text{saturated KCl} \mid \text{HgCl} ; \text{Hg} \]

(1)
A semicolon here denotes a metallic contact at an electrode. A single bar refers to a nonmetallic phase boundary, a double bar to a liquid junction.

The \( H_2, CO_2 \) gas mixture at the platinum electrode was held at ambient pressure while the mole fraction of \( CO_2 \) was varied from 8 to 24\%. The molar ionic strength (mol \( \ell^{-1} \) of solution) was varied from .01 to .18. Below .02 mol \( \ell^{-1} \) the solutions contained no NaCl. It was feasible to omit the use of a chloride salt in the test solution because a salt bridge provided chloride at the reference electrode irrespective of the composition of the test solution. Measurements were made only at 38°C, approximately the temperature of human blood.

MacInnes and Belcher [1933, 1935] employed the cell:

\[
\text{Glass Electrode} \mid \text{MHCO}_3(m_1), \text{MCl}(m_2), \text{CO}_3(m_3) \mid \text{AgCl} ; \text{Ag} \quad (\text{II})
\]

where \( M \) refers to Na or K. The concentration of \( CO_2 \) was controlled by passing a current of pure \( CO_2 \) gas or mixture of \( CO_2 \) and \( N_2 \) gas (range 0.5 to 31\% \( CO_2 \)) at ambient pressure over the solution. Extrapolations to infinite dilution were found to be independent of salt cation and \( CO_2 \) partial pressure. The molar ionic strength was varied from .002 and .25. Measurements were made at 25\° and 38\°C.

Harned and Davis [1943] employed the cell:

\[
\text{Pt} ; \text{H}_2, \text{CO}_2 \mid \text{NaHCO}_3(m_1), \text{NaCl}(m_2), \text{CO}_2(m_3) \mid \text{AgCl} ; \text{Ag} \quad (\text{III})
\]

The \( H_2, CO_2 \) gas mixture at the platinum electrode was held at ambient
pressure while the mole fraction of CO\textsubscript{2} was varied from 14 to 85\%. The molal ionic strength was varied from .004 to .21. Measurements were made in 5°C intervals from 0° to 50°C. All series of observations began at 25°. The temperature was then varied between 0° and 25° or 25° and 50°. The temperature was finally readjusted to 25° and the series deemed satisfactory only if good agreement was obtained with the initial readings. Thus, four times as many measurements were made at 25°C as at the other temperatures. Altogether eight sets of data, each at various ionic strengths, were obtained at 25°C; truly a comprehensive body of experimental data.

Nansten [1947] carried out a limited series of measurements from 5 to 45°C in 10°C intervals. He probably used the same type of cell as Harned and Davis, although he does not describe details of his experiment. He used a single gas mixture with 16% CO\textsubscript{2} and varied the molal ionic strength from .003 to 3.1. Only three solutions were in the dilute range (.14m or less).

No further direct measurements of the first dissociation of carbonic acid have been reported since Nansten's study of nearly 20 years ago. Earlier measurements, summarized by MacInnes and Belcher [1933, pp. 2637-2639] need not be reviewed here since they are almost surely less reliable than the four studies discussed above.

In all these studies except MacInnes and Belcher [1933, 1935], the concentration m\textsubscript{CO\textsubscript{2}} was calculated from the CO\textsubscript{2} partial pressure,
$P_{CO_2}$, by the expression:

$$m_{CO_2} = S_{\mu} P_{CO_2}$$  \hspace{1cm} (2)

where $S_{\mu}$ denotes the Henry's Law coefficient, a quantity which varies both with temperature and ionic strength.

MacInnes and Belcher [1933, 1935] employed Henry's Law, expressed in terms of the $CO_2$ activity in solutions, i.e.:

$$a_{CO_2} = SF_{CO_2}$$  \hspace{1cm} (3)

where $S$ is equal to the solubility of $CO_2$ at zero concentration in pure water. At pressures below one atmosphere, departures of $CO_2$ gas from ideality are very small (Weiss, 1974) and were, with one exception, ignored by all investigators: i.e. the fugacity of $CO_2$ was assumed equal to the $CO_2$ pressure.

Except for Näsänen, who accepted the solubility measurements of Harned and Davis, all investigators used different values of $S_{\mu}$ or $S$ to calculate $m_{CO_2}$ or $a_{CO_2}$. Because the electrometric experiments described above actually yield values of the product $SK_1$ on extrapolation, unnecessary uncertainty is introduced if solubility coefficients of one investigation are combined with $K_1$ values of another. This fact should not be overlooked because in many practical applications it is the relation between $P_{CO_2}$ and salt concentrations which is sought, a relation which depends on the product $SK_1$ and not on $K_1$ itself.
The results of the four investigations are summarized for 20°, 25°, and 38°C in Tables 1 through 3. A very careful set of direct determinations of $K_1$ by the conductivity method (Shedlovski and MacInnes [1935]) are also listed. Molar quotients reported in the original articles have been converted to molal quotients in the tables. Quotients in some cases were obtained by interpolation using equations for the temperature dependence as cited by the original authors. In one case the original solubility data at finite ionic strength were extrapolated to zero salt concentration.

The reconstructed values of $SK_1$ in Table 3 offer a direct comparison of the various electromotive force data for the first dissociation of carbonic acid. At 25°C, where Harned and Davis carried out many measurements, the agreement of their results with the two independent determination of MacInnes and Belcher, and of Näsänen is very close. With respect to MacInnes and Belcher's value for $SK_1$ the agreement is indeed considerably closer than for $K_1$ alone, suggesting that the errors in $S$ were larger than in the product $SK_1$. With respect to Näsänen's results, since the same values of $S$ were used, the degree of agreement in $SK_1$ is the same as for $K_1$. The results at 38°C are only slightly less concordant.

Further support that the results shown in Table 3 closely reflect the true equilibrium quotients is given by the direct evaluations of $K_1$ of Shedlovski and MacInnes [1935]. When these data are combined with the most recent determinations of the solubility, $S$, reported
by Weiss [1974], the resulting product, $SK_1$, at all three temperatures, agrees with the electromotive force data within the range of disagreement of the solubility data of Table 2. Thus, the correct values of $-\log SK_1$ between 20° and 38°C are probably within .02 of the values of Harned and Davis.

III. THE SECOND DISSOCIATION CONSTANT

The equilibrium condition:

$$\text{HCO}_3^- \rightleftharpoons H^+ + \text{CO}_3^{2-}$$

is governed by the equilibrium quotient:

$$K_2 = \frac{a_{H^3\text{CO}_3}}{a_{\text{HCO}_3}} = \frac{m_{H^3\text{CO}_3}}{m_{\text{HCO}_3}} \cdot \frac{\gamma_{H^3\text{CO}_3}}{\gamma_{\text{HCO}_3}}$$

with reference state conditions analogous to those for $K_1$.

Hastings and Sendroy [1925] employed cell (I) again except that $Na_2\text{CO}_3(m_3)$ replaced $CO_2(m_3)$. The concentration ratio of $Na_2\text{CO}_3$ to $Na\text{HCO}_3$ was made high enough that the solution exerted very little pressure of $CO_2$. They thus dispensed with adding $CO_2$ to the hydrogen gas used at the hydrogen electrode. They varied the molar ionic strength from .02 to .21. Below .08 molar their solutions contained no NaCl.

To calculate $m_{H\text{CO}_3}$ and $m_{\text{CO}_3}$ they considered the hydrolysis equilibrium:

$$\text{CO}_3^{2-} + H_2O \rightleftharpoons \text{HCO}_3^- + OH^-$$
where, for the ion product of water, they employed the value of Michaelis [1922] expressed as an activity product. They did not furnish details of their calculations.

MacInnes and Belcher [1933, 1935] employed the cell:

\[
\text{Pt ; } H_2, CO_2 \mid KHCO_3(m_1), K_2CO_3(m_2), KCl(m_3) \mid AgCl ; Ag \quad (IV)
\]

which is basically the same cell as cell III. They reported that their solutions exerted an appreciable equilibrium pressure of CO$_2$. Consequently they passed pure H$_2$ gas at ambient pressure through a saturator containing a solution of the same composition as the cell. The molar ionic strength was varied between .01 and .22. Measurements were made at 25° and 38°C. Hydrolysis of CO$_3^{2-}$ was considered using values of the ionic concentration product of water as reported by Harned [1925] at 25°C and Harned and Hamer [1933] at 38°C.

Harned and Scholes [1941] employed the same cell and temperatures as for $K_1$ except that Na$_2$CO$_3(m_3)$ replaced CO$_2(m_3)$. The H$_2$ gas at ambient pressure was pumped in a closed circuit which included a "saturator" not otherwise described. The molal ionic strength was varied from .02 to .16. A correction was made for hydrolysis of CO$_3^{2-}$ by a different method than MacInnes and Belcher used, but with very nearly the same results at 25°C where the methods could be crosschecked.
Näsanen [1946] carried out measurements at 25°C in the molal ionic strength range .02 to 2.0. Only three solutions were as dilute as .26. Few experimental details were given.

The results are summarized in Table 4.

IV. RATIO OF THE DISSOCIATION CONSTANTS

An important check on the consistency of the data for $K_1$ and $K_2$ is given by evaluating the quotient:

$$\frac{SK_1}{K_2} = \frac{a_{HCO_3}}{P_{CO_2}} \frac{m_{HCO_3}}{a_{H_2}O} \frac{\gamma_{HCO_3}}{m_{CO_3}} \frac{\gamma_{HCO_3}}{a_{H_2}O}$$

(5)

Because the hydrogen activity, $a_H$, does not contribute, this quotient is independent of any inconsistencies in the manner of computing $a_H$. Table 5 lists values of $\log SK_1/K_2$ based on the data of Tables 3 and 4. The value of Hastings and Sendroy at 38° agrees well with that of MacInnes and Belcher, while that of Harned and co-workers at 25°C agrees well with Näsanen's result. The earlier pair of studies, however, yields values considerably lower than the latter pair. As is discussed further in the next section, this discrepancy is more probably related to the method of extrapolation rather than to systematic differences in the experimental results.

Also listed in Table 5 are data of Walker et al. [1927], obtained by a single gas-solution equilibration experiment without the use of electrodes. These results, based on a method similar to ours, are discussed in section VI, below; they lie between the results of
Hastings, MacInnes, and coworkers and those of Niesen, Harned, and coworkers.

V. EXTRAPOLATION TO ZERO CONCENTRATION

The electromotive force measurements discussed above actually refer to variations in the mean ionic activity of hydrochloric acid as a function of total salt concentration. Thermodynamic dissociation constants can be derived from these measurements only by extrapolation to zero concentration. No entirely satisfactory means of extrapolation is recognized, and it is worthwhile to review the various techniques used.

Hasting and Sendroy [1925] employed their apparatus essentially as a pH meter which they calibrated daily with 0.1 N HCl. They calculated the hydrogen ion activity, \( a_H \), of each test solution by the relation:

\[
\log a_H = (\xi - \xi_0) k
\]

where \( \xi \) denotes the observed electromotive force of their cell expressed in international volts. The constant \( \xi_0 \) was chosen so that for 0.1 N HCl, \( \log a_H = -1.08 \), consistent with the value of Lewis and Randall [1923, p. 382]. The factor, \( k \), represents a universal constant at a given absolute temperature, \( T \) and one atmosphere pressure (see, e.g., column 4 of Tables 5-1-2 in Harned and Owen, 1958, p. 160).
To evaluate $K_1$ Hastings and Sendroy wrote an expression equivalent to:

$$
\log K_1 - \log \frac{\gamma_{HCO_3}}{a_{H_2O}\gamma_{CO_2}} = \log a_{H_2O}^{m_{HCO_3}} - \log S_P^{m_{CO_2}} \tag{7}
$$

consistent with equations (1) and (2). The small differences arising from substituting molal for molar units of concentration in the dilute concentration range may here be disregarded. See e.g. MacInnes [1939, footnotes to p. 209.]

The authors plotted values of the right side of equation (7) versus the square root of the ionic strength, $\mu$. Disregarding the small dependency of $a_{H_2O}$ and $\gamma_{CO_2}$ on $\mu$, they found from their data that:

$$
\log \gamma_{HCO_3} = -0.5 \sqrt{\mu} \tag{8}
$$

which agrees closely with the prediction of the Debye-Hückel limiting law. See, e.g., MacInnes [1939, pp. 143-147] and Harned and Owen [1958, p. 165].

For $K_2$ they wrote an expression equivalent to:

$$
\log K_2 - \log \frac{\gamma_{CO_3}}{\gamma_{HCO_3}} = \log \frac{a_{HCO_3}^{m_{CO_3}}}{m_{HCO_3}} \tag{9}
$$

consistent with equation (4). They plotted the right side of
equation (9) versus \( \sqrt{\mu} \) and found:

\[
\log \frac{\gamma_{\text{CO}_3}}{\gamma_{\text{HCO}_3}} = -1.1 \sqrt{\mu}
\]  

(10)

This result agrees poorly with the Debye–Hückel limiting law which predicts a proportionality with \(-1.6 \sqrt{\mu}\).

From equations (7) through (10) it follows that:

\[
\log \frac{m_{\text{HCO}_3}^2}{m_{\text{CO}_2} m_{\text{CO}_3}} = \log (SK_1/K_2) - 0.6 \sqrt{\mu}
\]  

(11)

where the dependencies of the activity of water and carbonic acid on ionic strength have again been disregarded.

MacInnes and Belcher [1933, 1935] wrote for \( K_1 \) an expression equivalent to:

\[
\log K_1 = \log \frac{\gamma_{\text{CO}_3}}{a_{\text{H}_2\text{O}} \gamma_{\text{Cl}}} - (\xi - \xi^o) k + \log \frac{m_{\text{HCO}_3}}{m_{\text{Cl}}} - \log S\text{PCO}_2
\]  

(12)

which can be derived from equations (1) and (3) with \( a_\text{H} \) replaced according to the relation:

\[
(\xi - \xi^o)k = \log a_\text{H} + \log \gamma_{\text{Cl}}^w \gamma_{\text{Cl}}
\]  

(13)

See, e.g., MacInnes and Belcher [1933, equation (2) p. 2631] where
\( \xi \) denotes the electromotive force of cell II. The constant \( \xi_o \) was obtained from that for cell III corrected for the difference arising from substituting a glass electrode for a hydrogen electrode. Equation (12) differs significantly from equation (7) because the electromotive force of cell II varied in response to changes in chloride ion activity, an unavoidable consequence of using a chloride reference electrode without liquid junction.

The Debye-Hückel limiting law predicts that \( \gamma_{HCO_3} = \gamma_{Cl} \) and indeed a plot of the right side of equation (12) versus \( \mu \) supports this prediction since only a slight dependence on ionic strength \( \mu \) was found:

\[
\log \frac{\gamma_{HCO_3}}{\gamma_{Cl}} = -0.03 \sqrt{\mu} \text{ at } 25^\circ C
\]
\[
\log \frac{\gamma_{HCO_3}}{\gamma_{Cl}} = -0.02 \sqrt{\mu} \text{ at } 38^\circ C
\]

(The dependence is here expressed versus \( \sqrt{\mu} \) so that the results can be compared with those of Hasting and Sendroy [1925].)

For \( K_2 \) MacInnes and Belcher [1933, 1935] wrote an expression equivalent to:

\[
\log K_2 - \log \frac{\gamma_{CO_3}}{\gamma_{HCO_3} \gamma_{Cl}} = - (\xi - \xi_o) k + \log \frac{m_{CO_3}}{m_{HCO_3} m_{Cl}}
\]

consistent with equations (4) and (13).
They plotted the right side of equation (15) versus $\sqrt{\mu}$ and found:

$$\log \frac{\gamma_{CO_3}}{\gamma_{HCO_3} \gamma_{Cl}} \begin{cases} = -.38 \sqrt{\mu} \text{ at } 25^\circ C \\ = -.56 \sqrt{\mu} \text{ at } 38^\circ C \end{cases}$$ (16)

If this relation is combined with equation (14) to eliminate reference to the chloride ion activity we obtain:

$$\log \frac{m_{HCO_3}}{p_{CO_2} m_{CO_3}} \begin{cases} = \log (SK_1 / K_2) - .35 \sqrt{\mu} \text{ at } 25^\circ C \\ = \log (SK_1 / K_2) - .54 \sqrt{\mu} \text{ at } 38^\circ C \end{cases}$$ (17)

similar at $38^\circ C$ to the results of Hasting and Sendroy [1925], and thus in poor agreement with the Debye-Hückel limiting law.

Harned and Davis [1943] wrote for $K_1$ an expression equivalent to:

$$\log K_1 - \log \frac{\gamma_{HCO_3}}{a_{H_2O} \gamma_{CO_2} \gamma_{Cl}} = -(\xi - \xi_0) k + \log \frac{m_{HCO_3}}{m_{Cl}} - \log S \mu P_{CO_2}$$ (18)

which differs from equation (12) by the substitution of $S_\mu$ for $S$ in the last term and the consequent appearance of $-\log \gamma_{CO_2}$ in the extrapolation function represented by the left side of the equation. (This treatment of the solubility is not obvious from a reading of their article but can be verified by comparing their plotted data with their original measurements.)
We have not attempted to determine the dependency of $\mu$ from the data of Harned and Davis [1943] at all temperatures reported, but for $25^\circ$ we find from their figure 3 that:

$$\log K_1 - \log \frac{\gamma_{\text{HCO}_3}}{a_{\text{H}_2\text{O}}^\gamma \gamma_{\text{CO}_2} \gamma_{\text{Cl}}} = .141 \; \mu$$

(19)

Since at $25^\circ$ the data of Harned and Bonner [1945, p. 1029] indicate that:

$$\log a_{\text{H}_2\text{O}} = -.015 \; \mu$$
$$\log \gamma_{\text{CO}_2} = .102 \; \mu$$

it follows that:

$$\log K_1 - \log \frac{\gamma_{\text{HCO}_3}}{\gamma_{\text{Cl}}} = .054 \; \mu$$

(2C)

In comparison, Harned and Bonner [1945] over a wider range in $\mu$ experimentally found a dependency for the left side of equation (20) of only .016 $\mu$. (See their equations (18), (21), (28) and (30).) The data of Harned and Bonner indicate a similarly small dependency at $20^\circ$ and $38^\circ$. Therefore, we conclude that most of the dependency on $\mu$ which Harned and Davis found in their extrapolation functions (approximately .14 $\mu$) was a result of their employing the solubility relation in the form of equation (2) rather than as equation (3).
If this conclusion is correct, the Debye-Hückel prediction, 
\[ \gamma_{\text{HCO}_3} \approx \gamma_{\text{Cl}} \], is very closely fulfilled over an extended range in ionic strength.

For \( K_2 \) Harned and Scholes [1941] adopted a less direct approach than previous investigators. They compared their data to the Debye-Hückel prediction:

\[
\log \frac{\gamma_{\text{HCO}_3} \gamma_{\text{Cl}}}{\gamma_{\text{CO}_3}} = \frac{\zeta \sqrt{\mu}}{1 + A \sqrt{\mu}} + B_\mu
\]  

(21)

where \( \zeta \) is the Debye-Hückel limiting law factor [Harned and Owen, 1958, p 165, Table 5-2-1, column 3] and \( A \) is an empirical factor which varies from ion to ion. A second empirical factor, \( B \), was added to give a better fit to the right side of equation (15). The constant, \( A \), they set equal to 1.414. This value, according to theory, corresponds to a mean distance of approach of ions of 4.3 Å; it arises as the best fit of the Debye-Hückel expression for the mean ionic activity coefficient of HCl [Harned and Owen, 1958, p. 469].

From figure 1 of Harned and Scholes [1941], we find that

\[ B = -0.16 \mu \]

This dependency on \( \mu \) is several fold that found for \( \log \left( \frac{\gamma_{\text{HCO}_3}}{\gamma_{\text{Cl}}} \right) \) and accords with a general finding that the Debye-Hückel
theory is more successful for solutions containing singly charged ions than multiply charged ions. In spite of this uncertain applicability of the Debye-Hückel formulation, Harned and Scholes stated (p. 1708) that they "seriously doubt the correctness" of the direct extrapolation used by MacInnes and Belcher.

The Harned and Scholes data (see our figure 1) are not a strong basis for rejecting that extrapolation, however. Indeed, the two measurements of Harned and Scholes at lowest ionic strength agree closely with the extrapolation curve of MacInnes and Belcher. These measurements were rejected by the authors as belonging to a "first series" for which "less consistent results were obtained" at ionic strengths below 0.018. Since the "second series" did not extend below an ionic strengths of 0.02, the accepted data provide no experimental verification of the Debye-Hückel formula in the concentration range most critical to the extrapolation. Thus, it is not obvious that the data and extrapolation of Harned and Scholes are to be preferred to those of Hasting and Sendroy or MacInnes and Belcher. The measurements of Näsänen are too few and poorly described to be of use in resolving this controversy. Another set of data, however, tend to support the validity of the extrapolation used by the Harned group. These data will now be described.
Figure 1. Extrapolation Function for the second dissociation of carbonic acid recopied from Harned and Scholes [1941, p. 1708, figure 2]. X, first series; O, second series. Straight line: best fit of second series data.

Data of MacInnes and Belcher [1933] (symbol •) shown for comparison.
VI. GAS-SOLUTION EQUILIBRIUM

The equilibrium:

$$\text{CO}_2 + \text{H}_2\text{O} + \text{N}_2\text{CO}_3 \rightleftharpoons 2 \text{MHCO}_3$$

was studied directly by Walker, Bray, and Johnson [1927] by means of the equilibration cell:

$$\text{CO}_2 \text{(gas)} \mid \text{MHCO}_3(m_1), \text{M}_2\text{CO}_3(m_2), \text{MCl}(m_3)$$

where $M$ refers to Li, Na, or K. This cell contains no electrodes; its results lead to a determination of the quotient $SK_1/K_2$.

To achieve equilibrium, streams of air containing a constant proportion of $\text{CO}_2$ were passed through solutions of bicarbonate or carbonate salt for four to five days. The $\text{CO}_2$ content of the air was determined to an accuracy of about 5 ppm (parts per million by volume) for air containing 260 to 400 ppm of $\text{CO}_2$ but typically about 330 ppm. The total carbon concentration, $m_1 + m_2$, of an aliquot of the equilibrated solution was found by precipitation with $\text{Ba}_2\text{CO}_3$. A second aliquot was titrated with $\text{HCl}$ to the methyl orange end point to determine the carbonate alkalinity, $m_1 + 2m_2$. The ratio of $m_2$ to $m_1$ ranged from about 9% for the most dilute solutions to near unity in the more concentrated solutions. Measurements were carried out at 25°C and 37°C in the molal ionic strength range 0.1 to 3.1 with and without neutral salt ($m_3$) added. On the basis of values of Henry's law coefficient, $S^H$, taken from the data of Bohr [1899], the ratio $K_1/K_2$ was also calculated.
Although it may not appear immediately obvious, this experiment differs essentially in only one particular from the electromotive force studies discussed above: substitution of a total carbon assay for an estimation of hydrogen ion concentration.

In order to extrapolate their experimental data to zero concentration, the authors wrote an expression equivalent to equation (5) which they rearranged in the form:

\[
\phi = \frac{SK_1}{K_2} \left( \frac{\gamma_{CO_2} a_{H_2O}}{\gamma_{HCO_3}^2} \right) = \frac{m_{HCO_3}^2}{P_{CO_2} m_{CO_3}}
\]  

(22)

Following these authors, we will denote the quotient \( m_{HCO_3}^2 (P_{CO_2} m_{CO_3}) \) by the symbol \( \phi \). To evaluate \( \phi \), they assumed that \( m_{HCO_3} = m_1 \) and \( m_{CO_3} = m_2 \). Plots of \( \log \left[ \frac{m_1^2}{(P_{CO_2} m_2)} \right] \) versus \( \sqrt{\mu} \) at low ionic strength agreed closely with the Debye–Hückel limiting law:

\[
\log \phi = \log (SK_1/K_2) - 1.02 \sqrt{\mu}
\]  

(23)

contrary to the results of Hasting and Sendroy, and MacInnes and Belcher (equations 11 and 17), but in support of results of Harned and coworkers.
By graphic extrapolation of $\phi$ to $\mu = 0$ Walker et al. [1927] found that $\log SK_1/K_2$ was equal to 2.491 at 25°C and 2.296 at 37°C. The latter value is equivalent to 2.309 at 38°C if we accept the temperature coefficients of Harned and coworkers to make the small one degree temperature adjustment. The results of Walker et al. thus agree within about 0.02 of a log K unit with those of the Harned laboratory (see Table 5). Even closer agreement is found if the value of $\log K_1$, of Shedlovski and MacInnes [1935], based on conductivity data, is combined with recent solubility data reported by Weiss [1974] and the $\log K_2$ values of Harned and Scholes [1974] (2.497 at 25°C and 2.315 at 38°C).

Surprisingly little attention has been given to these equilibration cell data. MacInnes and Belcher [1933] noted merely that the $\log K_1/K_2$ value of Walker et al. [1927] at 25°C was in "very rough agreement" with their value. Actually, the disagreement was only 0.05 when allowance is made for the use of different values of the solubility coefficient $S_\mu$. Harned and coworkers do not discuss the work at all, although both studies were done in the Chemistry Department of Yale University. The work has rarely been cited in recent years.

VII. RECOMPUTATION OF GAS SOLUTION DATA

Since our experiments involve measurements of the same quantities as were determined by Walker et al., [1927] it is worthwhile to investigate the computation of $\phi$ in light of modern theory. In particular we will avoid the approximations that $m_{HCO_3^-}$ and $m_{CO_3^2-}$ are equal respectively to $m_1$ and $m_2$ by employing stoichiometric relation-
ships which connect $m_1$, $m_2$, and $m_3$ with the molal concentrations of all the most important chemical species actually present in solution. This approach would be rigorous if we could with certainty specify all of these species and the equilibrium quotients which connect them. In practice, we hypothesize which species are important and we estimate the implied equilibrium quotients using available, often insufficient, experimental data.

Under these circumstances, it is not surprising that the existence of some species is still controversial. For example, it is not easy to decide from available experimental data whether the ion pairs $\text{NaHCO}_3^0$ and $\text{NaCO}_3^-$ exist and, along with the other ions present, obey the Debye-Hückel theory, or whether the behavior of the ionic medium as a whole departs in some regular way from the predictions of that theory with no such ion pairs involved. We will therefore only tentatively postulate, in consonance with recent evidence of Butler and Huston [1970] and Nakayama [1971], that the sodium and potassium salt solutions of Walker et al. [1927] are best described on the molecular scale if we include, in addition to the species already discussed, the ion pairs $\text{NaHCO}_3^0$, $\text{NaCO}_3^-$, $\text{KHCO}_3^0$, and $\text{KCO}_3^-$. The total molal concentration of carbon in sodium salt solution is then given by:

$$m_1 + m_2 = m_{\text{CO}_2} + m_{\text{HCO}_3} + m_{\text{NaHCO}_3} + m_{\text{CO}_3} + m_{\text{NaCO}_3}$$ (24)

while the total for sodium is:

$$m_1 + 2m_2 + m_3 = m_{\text{Na}} + m_{\text{NaHCO}_3} + m_{\text{NaCO}_3}$$ (25)
and the total chloride:

\[ m_3 = m_{\text{Cl}} \]  

(26)

In addition to these stoichiometric constraints, the electrical charge of the ions must sum to zero, i.e.:

\[ m_{\text{Na}} + m_H - m_{\text{HCO}_3} - 2m_{\text{CO}_3} - m_{\text{OH}} - m_{\text{NaCO}_3} - m_{\text{Cl}} = 0 \]  

(27)

From these four equations it follows that the stoichiometric concentrations \( m_1 \) and \( m_2 \) are given in terms of individual species by the relations:

\[ m_1 = 2m_{\text{CO}_2} + m_{\text{HCO}_3} + m_{\text{NaHCO}_3} + m_H - m_{\text{OH}} \]  

(28)

\[ m_2 = m_{\text{CO}_2} + m_{\text{CO}_3} + m_{\text{NaCO}_3} - m_H + m_{\text{OH}} \]  

(29)

Similar equations apply to the potassium salt solutions.

The thermodynamic constraints between these species are expressed by stoichiometric or (so-called "apparent") quotients, defined by the expressions:

\[ k_1 = \frac{\frac{m_{\text{HCO}_3}}{m_{\text{CO}_2}}}{\frac{\gamma_{\text{HCO}_3}}{\gamma_{\text{CO}_2}}} = k_1 \frac{a_{\text{H}_2\text{O}}}{\gamma_{\text{HCO}_3}} \]  

(30)

\[ k_2 = \frac{\frac{m_{\text{CO}_3}}{m_{\text{HCO}_3}}}{\frac{\gamma_{\text{CO}_3}}{\gamma_{\text{HCO}_3}}} = k_2 \frac{\gamma_{\text{CO}_3}}{\gamma_{\text{HCO}_3}} \]  

(31)
Similarly, for sodium (and analogously for potassium):

\[ k_{Al} = \frac{m_{Na}m_{HCO_3}}{m_{NaHCO_3}} = K_{Al} \frac{\gamma_{NaHCO_3}}{\gamma_{Na}^\gamma_{HCO_3}} \]  
\[ k_{A2} = \frac{m_{Na}m_{CO_3}}{m_{NaCO_3}} = K_{A2} \frac{\gamma_{NaCO_3}}{\gamma_{Na}^\gamma_{CO_3}} \]

The solubility, \( S_\mu \), as defined by equation (2) is also an apparent quotient, or at least partially so.

Expressions for these quotients versus temperature and ionic strength are given in Table 6. In the case of \( k_{Al} \) and \( k_{A2} \) the values are only approximate. Their dependence on ionic strength is hardly known and even the thermodynamic quotients \( K_{Al} \) and \( K_{A2} \) are quite uncertain.

From the set of nine equations, (26) through (34), the molal concentrations of the nine species, \( CO_2 \), \( HCO^- \), \( CO^- \), \( NaHCO^0 \), \( NaCO^- \), \( Na^+ \), \( Cl^- \), \( H^+ \), and \( OH^- \) may be found in terms of the five stoichiometric quotients and \( m_1 \), \( m_2 \) and \( m_3 \). If this is done, the \( CO_2 \) partial pressure, \( P_{CO_2} \), is, however, a dependent variable contrary to the experimental conditions. Since \( \phi \) is predicted by equation (22) to depend on the ratio \( S_\mu K_1/K_2 \), it is possible to obtain agreement between the observed and predicted \( P_{CO_2} \) by making either \( S_\mu k_1 \) or \( k_2 \) a dependent variable to be evaluated in terms of the experimental data. Since the product \( S_\mu k_1 \) is better known,
as discussed above, we have chosen that equation (2) replace equation (31) in the set of nine equations. Thus the apparent quotient, \( k_2 \), becomes a dependent variable in the calculation and the solubility, \( S_\mu \), is added to the set of known apparent quotients.

The formal, or stoichiometric, ionic strength:

\[
\mu_S = m_1 + 3m_2 + m_3
\]  

(35)

differs appreciably from the ionic strength calculated on the previous assumption of ion association. For sodium salt solutions:

\[
\mu = \frac{1}{2}(m_{Na} + m_H + m_{HCO_3} + 4m_{CO_3} + m_{OH} + m_{NaCO_3} + m_{Cl})
\]  

(36)

In order to compute consistent values of the molal concentrations of the sodium salt solutions in terms of the stoichiometric quotients as functions of \( \mu \), we adopted an iterative procedure. Initially assuming \( \mu = \mu_S \), we estimated values of all of the apparent quotients, except \( k_2 \), from the equations of Table 6. Then we solved equations (28) and (29) for the bicarbonate and carbonate molalities, using equations (33) and (34) to eliminate reference to the ion pairs \( NaHCO_3^0 \) and \( NaCO_3^- \), i.e.:

\[
m_{HCO_3} = \frac{(m_1 - 2m_{CO_2} - m_H + m_{OH})(1 + m_{Na}/k_{A1})^{-1}}{1 + m_{Na}/k_{A1}}
\]  

(37)

\[
m_{CO_3} = \frac{(m_2m_{CO_2} + m_H - m_{OH})(1 + m_{Na}/k_{A2})^{-1}}{1 + m_{Na}/k_{A2}}
\]  

(38)

The approximations used by Walker et al. [1927] were equivalent to setting \( m_{CO_2} \), \( m_H \), \( m_{OH} \), \( k_{A1}^{-1} \) and \( k_{A2}^{-1} \) all equal to zero in these expressions. Their approximations can be immediately improved on, since \( m_{CO_2} \) may be directly calculated from the observed value of \( P_{CO_2} \) via equation (2),
and since the degree of association of sodium ion is so small that we obtain very close estimates of $1 + \frac{m_{Na}}{k_{A1}}$ and $1 + \frac{m_{Na}}{k_{A2}}$ by initially setting $m_{Na}$ equal to the total molality of sodium: $m_1 + 2m_2 + m_3$. With this latter approximation and by initially setting the small quantities $m_H$ and $m_{OH}$ equal to zero, both the bicarbonate and carbonate concentrations are closely estimated by equations (37) and (38). Based upon these estimates of $m_{HCO_3}$ and $m_{CO_3}$, the molalities $m_H$ and $m_{OH}$ are estimated via equations (30) and (32), and $m_{NaHCO_3}$ and $m_{NaCO_3}$ via equations (33) and (34). Lastly, the molality $m_{Na}$ and ionic strength are recomputed using equations (25) and (36). In the iterative procedure which we adopted the whole sequence of calculations was repeated several times, beginning the second iteration with a recomputation of the apparent quotients based on the new estimate of $\mu$. After the iteration was repeated until the value of $\mu$ converged to better than $1 \times 10^{-6}$, a quantity:

$$\phi_{\mu} = \frac{m_{HCO_3}^2}{p_{CO_2} m_{CO_3}}$$

(39)

was calculated where the subscript on $\phi$ emphasizes that the computations of $m_{HCO_3}$ and $m_{CO_3}$ were carried out assuming free ions (and free ion ionic strength, $\mu$) rather than by the approximate method used by Walker et al. [1927]. Results of such recalculation for solutions of Walker et al. [1927] involving sodium and potassium
salts at ionic strengths below .16 molal are listed in Table 7 and plotted in Figure 2.

If ion pairs with Na and K are ignored, $\phi_{\mu}$, calculated by the method we have just described, agrees in all cases within 1% with $\phi$, calculated by Walker et al. as equal to $m_1^2/(m_2^2 P_{CO_2})$. This agreement is well within the experimental error, and lends support to the view of Walker et al. [1927, p. 1245] that $\phi$ is an experimental quantity which may be applies directly to actual cases without the necessity of any assumptions as to the extent of ionization or the solubility of carbon dioxide in the particular solution.

This agreement, which also applies to the potassium salt solutions, would not be found for solutions near the bicarbonate equivalence point where $m_2$ approaches zero, but for such solutions $P_{CO_2}$ is, of course, much higher than in any of the experiments of Walker et al. These authors, indeed, note that $\phi$ may be regarded as constant only over a limited range of $P_{CO_2}$, although they don't specify that range.

A further test of the significance of $\phi_{\mu}$, calculated on the basis of free ions and apparent quotients, is to compare the computed values with the prediction of the Debye-Hückel theory:

$$\log \phi_{\mu} = \log \phi_0 - 2\zeta\sqrt{2\rho \mu/(1 + A\sqrt{\mu})}$$

where $\zeta$, $\rho$, and $A (=1.414)$ are to be evaluated according to Table 6.
Figure 2. The function, $\phi_{\mu}$, recomputed from the data of Walker et al. [1927, pp. 1240-1242, Tables I and IV] $\triangle$, NaHCO$_3$ – Na$_2$CO$_3$ solutions; $\triangledown$, KHCO$_3$ – K$_2$CO$_3$ solutions. The smooth curves are drawn through "best" estimates of the function, $\phi$, as determined by the authors [ibid, p. 1245, Table IX].
and where \( \phi_0 \) denotes the value of \( \phi_\mu \) at zero ionic strength. From this point on in our discussion \( \phi_\mu \) and \( \phi_0 \) will denote computed values assuming no ion pairing with Na or K, whereas \( \phi_\mu', \phi_0' \) will denote corresponding values with ion pairing.

The agreement of the experimental data with prediction is readily discerned by comparing values of \( \phi_0 \) and \( \phi_0' \) as computed from individual experimental runs or groups of runs of nearly the same ionic strength. Computed values of \( \log \phi_0 \), listed in Table 7, are practically constant for solutions below .05m in ionic strength. Average values for sodium and potassium, 2.490 and 2.497, respectively, are in close agreement with a value of 2.491 which Walker et al. [1927] found by extrapolating graphically plots of \( \log \phi \) versus \( \sqrt{\mu} \) both for salts of sodium and of potassium. If, however, the data are included up to ionic strength of .16m the value of \( \log \phi_0 \) for potassium rises with ionic strength to near 2.520 while that for sodium falls to near 2.485. The difference in behavior of sodium and potassium salts at ionic strengths above .05m can also be seen in figure 2. This difference is consistent with evidence that potassium ions have less tendency than sodium ions to form ion pairs in sea water (See e.g. Disteche [1974] p. 97).

The values of \( \phi_0' \) assuming ion pairing for both potassium and sodium can be brought into close agreement with the Debye-Hückel formulation, at ionic strength up to .16m and even higher, but not with \( k_{A1} \) and \( k_{A2} \) based on the experimental measurement of the mean ionic activity of NaCl of Butler and Huston [1970] as listed in Table 6. These values produce estimates of \( \log \phi_0' \) which rise steadily with increasing
ionic strength even in the most dilute solutions (See Table 7). Because
the formation of NaHCO$_3^0$ and KHCO$_3^0$ in general decreases HCO$_3^-$ and thus
lowers the calculated value of $\phi'_\mu$, whereas the formation of NaCO$_3^-$
and KCO$_3^-$ decreases CO$_3^{2-}$ and thus raises $\phi'_\mu$, it is not possible to pre-
dict in advance whether invoking ion pairing will raise or lower $\phi'_\mu$. The
separate influences of $k_{A1}$ and $k_{A2}$ might be distinguished in a carefully
controlled series of experiments in which the proportions of
bicarbonate and carbonate were varied widely, but in the narrow
range in bicarbonate-carbonate ratios of the data of Walker et al.
[1927] the influences of the individual ion pairs cannot be resolved.

The experiments of Harned and coworkers did involve a wide
range of bicarbonate-carbonate ratio. Nevertheless, since the
data very nearly obey the Debye-Hückel theory without invoking ion
pairing, the experimental uncertainties in estimating $k_{A1}$ and $k_{A2}$
are large. Thus the estimates of ion pairing by Nakayama [1970]
based on these data, although not inconsistent with the experimental
observations, do not conclusively prove ion-pairing.

The values of $\phi_0$ from potassium and sodium begin to diverge only
at ionic strengths above the range of validity of the Debye-Hückel formu-
lation. Thus, it is probably impossible to establish the validity of
both ion pairing and the Debye-Hückel theory with any combination of
experiments: We are confronted with too many parameters to evaluate.

From the point of view of our own experiments, to be described next,
the most important conclusion we draw from the data of Walker et al. [1927]
in dilute solution is that these data very nearly obey the Debye-Hückel
prediction without postulating the existance of NaHCO$_3^0$ and NaCO$_3^-$. Thus
we will discuss our own results without reference to such ion pairing.
Returning to the question of the correctness of the various extrapolation procedures used to establish $K_2$ in dilute solution, the agreement of $\phi_\mu$ with the Debye-Hückel prediction (assuming no ion pairing with Na or K) lends support to the procedure of Harned and Scholes [1941]. Before concluding, however, that the procedures of MacInnes and Belcher [1933, 1935] and Hasting and Sendroy [1925] are clearly wrong, it is worthwhile to look carefully once more at the ionic strength dependence of all of the data bearing on the second dissociation of carbonic acid.

Because the Harned and MacInnes groups both used Ag-AgCl reference electrode without liquid junction, their extrapolation functions for $K_1$ (or $SK_1$) are nearly independent of ionic strength, as discussed earlier. Their extrapolations to derive $K_2$ thus involved almost the same $\mu$ dependency as that for $\phi_\mu$.

We have taken advantage of this fact to devise an indirect extrapolation function for $K_2$ at 25° based on the results of Walker et al. [1927] for $\phi_\mu$. Specifically we have calculated values of the function $-\log(SK_1/\phi_\mu)$ where $-\log SK_1$ is set equal to 7.815 in agreement both with Harned and coworkers and with MacInnes and Belcher, as shown in Table 3. A plot of $-\log(SK_1/\phi_\mu)$ and the Harned school extrapolation function for $K_2$ based on equation (21) is shown in Figure 3. We have recomputed values of the latter function from the original tabulated data of Harned and Scholes and of MacInnes and Belcher because, in several instances, the values we compute differ from the plotted
Figure 3. Extrapolation Function, $-\log K_2'$, for the second dissociation of carbonic acid, recomputed from original experimental data. X, O, and straight line have same meaning as in Figure 1. △, ▽ refer, respectively, to sodium and potassium salt solutions of Walker et al. [1927]. The dashed curve shows the interpolation versus $\sqrt{\mu}$ of MacInnes and Belcher [1933].
data of the original publications, and we place more reliance on the original tabulated data. Within the scatter of the data points of each investigation, there is no significant difference between the three sets of data. The extrapolation of MacInnes and Belcher, based on equation (15) and shown as a dotted line, satisfies the data as closely as does the function of Harned and Scholes. Clearly, the results of Walker et al. [1927] do not settle the question of which extrapolation to use. Additional data at lower ionic strength are needed.

VIII. THE EXPERIMENT

Materials Used

Anhydrous sodium carbonate of high purity was obtained commercially (Baker "Ultrex"). Portions from 0.2 to 1.9 g were brought to constant weight by repeated heating in a sand bath at 270 ± 10°C.

Concentrated phosphoric acid (Allied Chemical, Reagent Grade, 85%) was diluted to 0.4 m with CO₂-free distilled water obtained as described below. The dilute solution was found by the method of Wong [1970, p. 11] to contain no detectable CO₂.

Water free of CO₂ was prepared from commercially available de-ionized water, first distilled in a quartz still, and then transferred to a 5-liter spherical pyrex flask where it was boiled for 2 to 4 hours. The flask was then immediately sealed from the atmosphere with a waxed ground glass cap assembly which included a viton double O-ring 8 mm bore greaseless stopcock and a 14/35 standard
taper joint for attachment to a vacuum system. Apiezon W wax was used. After the flask had cooled, it was inverted and attached, via the tapered joint using the same wax sealant, to the vacuum line so that the water could be dispensed by gravity flow.

**Apparatus**

Equilibrations were performed in an assembly consisting of 1-liter spherical pyrex bulbs connected with a wide standard taper joint and an 8 mm bore viton O-ring greaseless stopcock (Figure 4). An entrance cap and an additional greaseless stopcock attached to the upper bulb permitted dry salts, stirring bars and CO₂-free water to be placed in either bulb. A short side arm on the upper bulb provided means for transferring CO₂ gas into the bulb by cooling the arm with liquid nitrogen. The entire assembly was attached to a vacuum line as shown in Figure 5. The volumes of the two bulbs were precisely determined from their weights filled with water.

Manometric determinations of CO₂ gas were performed in a multiple chamber constant volume manometric system in which gas samples of a wide range in sizes (.02 to 5000 cc STP) can be measured to a precision of 1 part in 3000 or better.

A microbalance (Mettler H5), a semi-microbalance (Mettler H51), and a 10 kg solution balance (Seederer-Kohlbusch) were used to carry out the gravimetric measurements.
Figure 4. Equilibration vessel.
Figure 5. Vacuum system to process samples.
Procedure

Enough anhydrous Na₂CO₃ to prepare a solution of a desired carbonate alkalinity was transferred from a glass weighing bottle, previously brought to constant weight, directly to the dry lower bulb of the equilibration apparatus. The bottle was reweighed and the weight of sample obtained by difference.

The upper bulb was attached using a wax sealant and the entire equilibration apparatus was evacuated. Next, approximately 350 cc of CO₂-free water was admitted to the lower bulb by gravity flow through both bulbs. The stopcock between the bulbs was closed and residual water in the upper bulb removed by vacuum pumping. The apparatus, previously evacuated and weighed with the Na₂CO₃ in the lower bulb, was reweighed and the weight of water obtained by difference. In this manner, exclusively by gravimetric procedures, a solution of Na₂CO₃ of known concentration was obtained in the lower bulb.

To convert this solution to an acidity roughly equivalent to a NaHCO₃ solution of the same carbonate alkalinity, pure CO₂ gas was prepared from a second portion of anhydrous Na₂CO₃. This portion, about 3 percent larger than the first, was transferred from the same weighing bottle to a CO₂ extraction apparatus as described by Wong [1970]. The weight of salt was again determined by difference. The salt was acidified with approximately 50 cc
of 0.4 M H₃PO₄ solution and the evolved CO₂ collected in a trap at liquid N₂ temperature. Water was removed by an intervening trap at dry ice temperature. The CO₂ was sublimed several times to free it from traces of residual water vapor and of noncondensible gas and then was transferred by sublimation to the manometer where the amount of CO₂ gas was determined. This procedure provided a carbon assay of the Na₂CO₃ and insured that the amount of CO₂ gas was accurately determined, irrespective of the salt purity.

This gas was then transferred to the equilibration apparatus by sublimation into the short side arm provided for this purpose in the upper bulb. With the connecting stopcock open, the apparatus was placed horizontally in a constant temperature water bath regulated to 20 ± 0.01°C. Magnetic stirring was commenced, and the solution and gas phase were brought to equilibrium overnight. The apparatus was handled carefully so that no solution splashed into the second bulb.

After equilibration the stopcock between the bulbs was closed and the CO₂ gas and water in the upper bulb transferred to the manometer after removal of the water and traces of noncondensible gas. The water was frozen into a sample tube and its amount found gravimetrically. The connecting stopcock was reopened and another equilibration made overnight. This process was continued until a suitable series of equilibrations had been completed.
Calculation of Assay

The equation of state used to calculate the amount, \( n \), in moles of CO\(_2\) gas from the manometric data is expressed in the implicit form.

\[
P V = n R T (1 + \frac{n}{V} B(T) + \ldots) \tag{41}
\]

where \( P, V \) and \( T \) denote the measured pressure, volume, and absolute temperature, \( R \) is the gas constant, and \( B(T) \) is the temperature dependent second virial coefficient in the expansion of the compressibility factor, \( PV \), in powers of the density \( 1/V \). Higher order terms in \( 1/V \) are neglected. Equation (41), when solved for \( n \), reads:

\[
n = -\frac{V}{2B} \left( 1 - \sqrt{1 + \frac{4PB}{RT}} \right) \tag{42}
\]

where specifically:

1. \( P \) and \( T \) are expressed in dynes cm\(^{-2}\) and °K, respectively.
2. \( V \) is the calibrated volume of the manometric chamber, in cm\(^3\).
3. \( B \) is the value of the second virial coefficient for CO\(_2\) gas at temperature \( T \), in cm\(^3\)/mol, as calculated with the following interpolation function from values tabulated by Sengers et al. [1971]:
   \[
   B = 442.002 - \frac{125548}{T} - 0.483343T
   \]
4. \( R \) is the gas constant, taken as 8.31436 \times 10\(^7\) ergs mol\(^{-1}\) °K\(^{-1}\).

The pressure \( P \) is calculated from the difference between two
measured heights of mercury by the equation:

\[ P = \Delta h \cdot \rho_{Hg}(T) \cdot g \]  (43)

where:

1. \( \Delta h \) is the observed mercury height difference in cm
2. \( \rho_{Hg}(T) \) is the density of mercury at temperature \( T \) in g/cm\(^3\) (g/ml = 1.000027)
3. \( g \) is the acceleration of gravity at 32° 52' N taken to be 979.558 cm sec\(^{-2}\)

The number of moles of \( \text{CO}_2 \) gas obtained from the manometric measurement was divided by the number of moles of sodium carbonate to obtain the percent assay.

The method outlined above was also used to calculate the amount of \( \text{CO}_2 \) gas contained in the upper bulb after equilibration and transfer to the manometer.
IX. RESULTS

Eleven aqueous solutions, prepared as described above, were used to carry out 32 equilibrations. The experimental and derived data are listed in Tables 8, 9, and 10.

Since the assays of sodium carbonate (Table 8) indicate negligible impurity, we assumed an assay of 100% in the calculations and thus disregarded the individual assays, i.e., we calculated the amount of \( \text{CO}_2 \) gas added to the carbonate solution directly from the observed weight of the sodium carbonate from which it was derived. Because this \( \text{CO}_2 \) gas was combined in solution with a second portion of sodium carbonate taken from the same supply, we assumed that the two portions had the same purity. If this assumption is correct the uncertainty in purity, (as long as it is small), contributes little error because the determination of \( \phi \) depends essentially on the ratio of the amounts of \( \text{CO}_2 \) gas and sodium carbonate combined to make up the bicarbonate solution.

The computations of \( \phi \) and \( \phi_0 \) made use of the iterative procedure described in section VI, above. Ion pairing with sodium was neglected by setting \( k_{A1}^{-1} \) and \( k_{A2}^{-2} \) equal to zero.

Because the first equilibration of each series began with a large excess of \( \text{CO}_2 \) in the gas phase while the succeeding equilibrations began with a small deficit, the concordance of the
first equilibrations of each series with succeeding equili-
brations indicates that equilibrium was very nearly achieved.
As can be seen from Table 9, there is a small, and only Table 9
possibly s ignificant, difference between initial and succeeding runs: 9 initial runs yield an average value of 2.572 for \( \log \phi_0 \), while 23 succeeding runs yield 2.581. If the above difference in average values does reflect lack of equilibrium, the first runs should be contributing virtually all of the error. For this reason, the results of the initial runs were omitted in further treatment of the data.

The computed values of \( \log \psi \), omitting first runs, are plotted in Figure 6. The results of Walker et al. [1927] are also plotted for comparison. We have adjusted the latter data to 20° assuming the temperature variation in \( \log (SK_1/K_2) \) obtained from the data of Harned and coworkers (see Table 5) i.e., we have raised the values of Walker et al. by .076. These latter data show a slightly lesser dependence on ionic strength and thus fit less well to the Debye-Hückel predic-
tion than our data, but the agreement is quite satisfactory.

Since the choice of the parameter \( A \) of equation (40) is to some degree arbitrary [Hamer, 1959] we have examined the difference in curve fit using two values:
Figure 6. Our new determination of $\phi_\mu$ compared with results of Walker et al. [1927]. Smooth curve: best fit of new data to Debye–Hückel formulation with $A = 1.414$. Dashed curve: same except $A = 1.000$.

○, SI0 data

△, ▼ refer respectively to the sodium and potassium salt solutions of Walker et al. [1927].
For $A = 1.414$, $\log \phi_0 = 2.581 \pm 0.0089$

For $A = 1.000$, $\log \phi_0 = 2.584 \pm 0.0095$

The uncertainties refer to one standard deviation in the individual runs. The first value of $A$ was chosen by Harned and Scholes [1941] in connection with the extrapolation for $K_2$, while Harned and Bonner used the second value in connection with the apparent quotient, $k_1$. In the concentration range .001 to .01 molal the average values of $\log \phi_0$, varying $A$ from 1 to 1.414, agree to .003, well below the standard deviation of the data points (.009). Clearly, either extrapolation is satisfactory as a predictor of $\phi_\mu$. Conversely, it is impossible to establish a best value of $A$ to a high degree of precision from our results. Over a wider range in ionic strength $A$ could be better established, but this would not add greatly to our confidence in its estimation because equation (40) is no longer expected to be valid at higher salt concentrations.

We have further challenged the appropriateness of the Debye-Hückel extrapolation by comparing values of the extrapolation function $\log \phi_\mu / S K_1$, derived from our experimental data for $\phi_\mu$, with the data of Harned and Scholes and of MacInnes and Belcher expressed in the same manner as for Figure 3. We have adjusted our data to 25°C by lowering all values in $\log \phi_\mu$ by .076. Our results agree better (Table 10 and Figure 7) with the extrapolation of Harned and Scholes...
Figure 7. Extrapolation Function for the second dissociation of carbonic acid. Selected data, reproduced from figure 3, are compared with averages of the new determinations, denoted by error bars representing plus and minus two times the standard deviations of the averages in Table 10.
than with that of MacInnes and Belcher. This statement is qualified, however, because of the possibility of systematic errors arising from the different methods used, and the temperature adjustment to our data. Nevertheless, the sharp fall in the extrapolation function toward zero ionic strength indicated by the data of MacInnes and Belcher and the first series of Harned and Scholes, is clearly not found in our data.

Our data tend to corroborate the second series of Harned and Scholes. It thus seems likely that Harned and Scholes used good judgment in rejecting their first series.

At 20°C the only direct comparison we can make between our data and earlier investigations is with that of the Harned school. Our value of log $SK_1/K_2$ is .009 lower than theirs using essentially the same method of extrapolation.

If we adjust our data to 25°C we can compare our average value of log $\phi_0$ with the data of five other investigations:

<table>
<thead>
<tr>
<th>Investigation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MacInnes and Belcher</td>
<td>2.435</td>
</tr>
<tr>
<td>Walker et al.</td>
<td>2.491</td>
</tr>
<tr>
<td>Shedlovski and MacInnes for $K_1$</td>
<td></td>
</tr>
<tr>
<td>Murray and Riley for $S$, and Harned</td>
<td></td>
</tr>
<tr>
<td>and Scholes for $K_2$</td>
<td>2.497</td>
</tr>
<tr>
<td>Our work</td>
<td>2.505</td>
</tr>
<tr>
<td>Nässänen</td>
<td>2.508</td>
</tr>
<tr>
<td>Harned and coworkers</td>
<td>2.514</td>
</tr>
</tbody>
</table>
We conclude that the MacInnes and Belcher value is incorrect because of experimental errors at lower concentrations, reinforced by a questionable extrapolation procedure. Among the other investigations there is little basis to prefer one value over another. The range is .023 units from the lowest to the highest value. Our value is close to the mean of the other four. We conclude that our equilibration procedure is as reliable as previous methods.

Furthermore, the individual analytical errors which contribute to the uncertainty in our method are so low that we are optimistic that, with further work, we can reduce the scatter found in our present result. Systematic errors such as arise in preparing the solutions or failing to reach equilibrium ought to be reducible, and the equilibration method we have devised should, if carefully pursued, yield a value of log $\phi_0$ which is accurate to better than 0.01. As can be seen from Table 9, the imprecision (1 σ) in calculating log $\phi_0$ from our 22 post-initial equilibrations is only .002. Much of this scatter is associated with differences between series, not individual runs. For the longest series, at an ionic strength of .008 molal, the imprecision of a single run is .004. If this low imprecision could be maintained between runs by practically eliminating errors in preparing solutions, we could, indeed, achieve an accuracy to .001 with only 16 runs. This goal is perhaps more than can be hoped for, but we intend to pursue it in further experiments.
<table>
<thead>
<tr>
<th>Source</th>
<th>$-\log K_1$ at 20°C</th>
<th>$-\log K_1$ at 25°C</th>
<th>$-\log K_1$ at 38°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastings and Sendroy [1925]$^a$</td>
<td>-</td>
<td>-</td>
<td>6.327</td>
</tr>
<tr>
<td>MacInnes and Belcher [1933, 1935]$^a$</td>
<td>-</td>
<td>6.342</td>
<td>6.306</td>
</tr>
<tr>
<td>Harned and Davis [1943]</td>
<td>6.381</td>
<td>6.352</td>
<td>6.300$^b$</td>
</tr>
<tr>
<td>NisMnen [1947]</td>
<td>6.382$^b$</td>
<td>6.349</td>
<td>6.302$^b$</td>
</tr>
</tbody>
</table>

$^a$ Original data in moles dm$^{-3}$ were converted to moles kg$^{-1}$ by the formula $-\log K_1$ (molal) = $-\log K_1$ (molar) + log $\rho$, where $\rho$, the density of water, is .99823, .99708, and .99297 at 20, 25 and 38° respectively (Harned and Owen, 1958 p. 161).

$^b$ Interpolation based on equation of $-\log K_1$ versus temperature given in the original article.
TABLE 2. Values of Henry's Law Constant Used by Original Investigators to Compute $K_1$

<table>
<thead>
<tr>
<th>Investigators</th>
<th>$S \left( \text{Moles kg}^{-1}\text{-atm}^{-1} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$20^\circ \text{C}$</td>
</tr>
<tr>
<td>Hastings and Sendroy [1925]</td>
<td>-</td>
</tr>
<tr>
<td>MacInnes and Belcher [1933, 1935]</td>
<td>-</td>
</tr>
<tr>
<td>Shedlowski and MacInnes [1935]</td>
<td>-</td>
</tr>
<tr>
<td>Harned and Davis [1943]</td>
<td>0.03924</td>
</tr>
<tr>
<td>Murray and Riley [1971]$^d$</td>
<td>0.03916</td>
</tr>
</tbody>
</table>

$^a$ Original data expressed as a Solubility Coefficient (equal to $S \times 22.4 \text{ dm}^3\text{mole}^{-1}$) were extrapolated to zero ionic strength using the Setchenow equation: $\log S/S_\mu = kc$ [see Harned and Owen 1958, p. 531] where $k$ is a constant and $c$ is the molar concentration.

$^b$ Based on various earlier investigations of Findlay, Kunerth, Van Slyke and their associates as cited by MacInnes and Belcher.

Value at $38^\circ \text{C}$ was corrected for the deviation of the equation of state of CO$_2$ from that of a perfect gas by an unspecified method.

$^c$ Not used to compute $SK_1$ in Table 3.

$^d$ As interpreted by Weiss [1974].
### TABLE 3. Computed Values of $-\log SK_1$ based on Data of Tables 1 and 2

<table>
<thead>
<tr>
<th></th>
<th>$-\log SK_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
</tr>
<tr>
<td>Hastings and Sendroy [1925]</td>
<td>-</td>
</tr>
<tr>
<td>MacInnes and Belcher [1933, 1935]</td>
<td>-</td>
</tr>
<tr>
<td>Harned and Davis [1943]</td>
<td>7.787</td>
</tr>
<tr>
<td>Näsänen [1947]$^a$</td>
<td>7.788</td>
</tr>
<tr>
<td>Shedlovski and MacInnes [1935]$^b$</td>
<td>7.800</td>
</tr>
</tbody>
</table>

$^a$ Employing the solubility data of Harned and Davis [1943], listed in Table 2.

$^b$ Employing the solubility data of Murray and Riley [1971], listed in Table 2.
<table>
<thead>
<tr>
<th>Source</th>
<th>20°C</th>
<th>25°C</th>
<th>38°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastings and Sendroy [1925]a</td>
<td></td>
<td>-</td>
<td>10.217</td>
</tr>
<tr>
<td>MacInnes and Belcher [1933, 1935]a</td>
<td>-</td>
<td>10.250</td>
<td>10.201</td>
</tr>
<tr>
<td>Näsänen [1946]a</td>
<td>-</td>
<td>10.319</td>
<td></td>
</tr>
<tr>
<td>Harned and Scholes [1941]</td>
<td>10.377</td>
<td>10.329</td>
<td>10.232b</td>
</tr>
</tbody>
</table>

*aOriginal data in moles dm⁻³ were corrected to moles kg⁻¹ by the same method as for K₁ in Table 1.*

*bInterpolation based on equation for -log K₂ versus temperature given in the original article.*
### TABLE 5. Computed Values of $\log(\frac{SK_1}{K_2})$ Based on Data of Tables 3 and 4

<table>
<thead>
<tr>
<th></th>
<th>$20^\circ C$</th>
<th>$25^\circ C$</th>
<th>$38^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastings and Sendroy [1925]</td>
<td>--</td>
<td>--</td>
<td>2.286</td>
</tr>
<tr>
<td>MacInnes and Belcher [1933, 1935]</td>
<td>--</td>
<td>2.435</td>
<td>2.286</td>
</tr>
<tr>
<td>Harned and Coworkers [1941, 1943]</td>
<td>2.590</td>
<td>2.514</td>
<td>2.330</td>
</tr>
<tr>
<td>Niisänen [1946, 1947]</td>
<td>--</td>
<td>2.508</td>
<td>--</td>
</tr>
<tr>
<td>Walker, Bray and Johnston [1927]</td>
<td>--</td>
<td>2.491</td>
<td>2.309</td>
</tr>
</tbody>
</table>
TABLE 6. Equations to Calculate Apparent Quotients of the Carbonic Acid System, Sodium Chloride, and Water as Functions of Absolute Temperature, T, and Molal Ionic Strength, \( \mu \)

**Solubility of CO\(_2\)**

\[
-\log S = -2388.016 \ T^{-1} + 14.03059 - 0.0152799 \ T \\
+ 171.5303 \ \mu T^{-1} - 0.9071009 \ \mu + 0.0014512024 \ \mu T
\]

**First Dissociation of Carbonic Acid**

\[
-\log k_1 = -D_1 = 3386.2013 \ T^{-1} - 14.701034 + 0.03251536 \ T \\
- 552.09225 \ T^{-1} + 3.4311775 \ \mu - 0.0051149412 \ \mu T
\]

where:

\[
D_1 \equiv D_1(\mu, t) = (14883 + 0.75545 \times 10^{-3} t + 0.1743 \times 10^{-5} t^2 \\
+ 0.11665 \times 10^{-7} t^3) \sqrt{8\mu}/(1 + \sqrt{\mu})
\]

\( t = T + 273.16 \)

**Second Dissociation of Carbonic Acid**

\[
-\log k_2 = -D_2 = 2902.39 \ T^{-1} - 6.4980 + 0.02379 \ T
\]

where:

\[
D_2 \equiv D_2(\mu, t) = 4 \ \zeta \sqrt{2\mu}/(1 - \sqrt{2\mu})
\]

\( \zeta \) is as quoted below under General Functions

**Ionization of Water**

\[
-\log k_w = -D_w = 4470.99 \ T^{-1} - 6.0875 + 0.017060 \ T
\]

where:

\[
D_w \equiv D_w(\mu, t) = \frac{2\ \zeta \sqrt{2\mu}}{1 + A\ \sqrt{\mu}} + B\ \mu + C\ \mu^{3/2}
\]
\[ A' = 3.6(50.30)(DT)^{3/2} \]
\[ B = 0.198 + 0.2 \times 10^{-3}t \]
\[ C = -0.0085 - 0.2 \times 10^{-3}t \]
\[ t = T + 273.16 \]

\[ \zeta \text{ and } D \text{ are as quoted below under General Functions} \]

**Dissociation of Sodium Bicarbonate and Carbonate Ion Pairs**

We assume:

\[ k_{A1} = K_{A1} k_1 / K_1 \]
\[ k_{A2} = K_{A2} k_2 / K_2 \]

where \( K_1 \) refers to the value of the corresponding \( k_1 \) at \( \mu = 0 \).

The thermodynamic quotients \( K_{A1} \) and \( K_{A2} \) at 25°C are averages of the estimates of recent measurements of Butler and Huston:

\[ -\log K_{A1} = -0.20 \]
\[ -\log K_{A2} = 1.00 \]

**General Functions**

**Debye-Hückel Limiting Slope Function:**

\[ \zeta = 1.290 \times 10^{-6} (D(t)T)^{-3/2} \]

**Dielectric Constant of Water:**

\[ D = D(t) = 78.54[1 - 0.4579 \times 10^{-2}(t - 25) + 0.119 \times 10^{-4}(t - 25)^2 \]
\[ + 0.28 \times 10^{-7}(t - 25)^3 \]

**Density of Water:**

\[ \rho(t) = \frac{1 - (t - 3.39863)^2(t + 288.9414)}{508929.2(t + 68.12963)} \]
Based on our simultaneous least squares fit of $S_{\mu}$ versus $\mu$ and $T$ from smoothed observations of Harned and Davis [1943, Table II, p. 2033]. Data at 2M and 3M were excluded in making the fit.

Our simultaneous least square fit of $-\log k_1 + D_1(\mu,t)$ from smoothed observations of Harned and Bonner [1945, Table II, p. 1028]. The function $D_1(\mu,t)$ is as expressed in the original article (equations 19, 22, and 23) and differs analytically from the Debye-Hückel term quoted by Harned and Owen [1958, equation 3-4-8, p. 164] and used below in the formulation of $K_2$ and $k_w$.

In agreement with formulation by Harned and Scholes [1941, equations 4 and 9] except that $\mu$ is replaced by $\xi/\rho^2$. $\phi\mu$ and the limiting slope, $\xi$, are expressed as described by note g below. An error in sign of the second term in the authors' equation 9 has been corrected. The formulation is applicable only in dilute solutions because it lacks extended terms. This computation of $k_2$ has been included here for completeness, but has not been used in the calculations described in sections VII and IX.

Consistent with Harned and Owen [1958, equation 15-3-7a, p. 645, and equation 15-2-3, p. 641] except that "$\xi(f)$" of the original formulation (see equation 15-2-4, p. 642) is replaced by $\xi\sqrt{2}$ to be consistent with the above formulation for $k_2$.

Because the variation in degree of ion pairing with ionic strength is not well established, we assume that the substitution of one Na$^+$ for one H$^+$ in the species $H_2CO_3^-$, HCO$_3^-$, will not alter
the activity coefficient ratios appearing in equations (33) and (34), i.e.

\[
\frac{\gamma_{Na} \gamma_{HCO_3}}{\gamma_{NaHCO_3}} = \frac{\gamma_{H} \gamma_{HCO_3}}{\gamma_{H_2CO_3}}
\]

\[
\frac{\gamma_{Na} \gamma_{CO_3}}{\gamma_{NaCO_3}} = \frac{\gamma_{H} \gamma_{CO_3}}{\gamma_{HCO_3}}
\]

where \(\gamma_{H_2CO_3} = \gamma_{CO_3} a_{H_2O}\)

The formulations of \(K_{Al}\) and \(K_{A2}\) are consistent with this hypothesis.

\[\text{f Butler and Huston [1970, Table V, p. 2982] report for log } K_{Al}, \]
\[-.30 \text{ and -.08, and for log } K_{A2}, -.97, .96, .77 \text{ based on experiments with the cell:}\]

\[
\text{Na(Hg)|NaHCO_3(m_1) or Na}_2\text{CO}_3(m_2), \text{NaCl(m_3)|AgCl:Ag} (V)
\]

Their table quotes values of the reciprocals of \(K_{Al}\) and \(K_{A2}\), which they denote, respectively, by the symbols \(K_1''\), and \(K_1'\).

\[\text{g The limiting slope, } \xi, \text{ is as expressed by Harned and Owen [1958,}
\]
equation 3-4-8, p. 164]. The dielectric constant and density are from the same reference, equations (5-1-1, p. 159, and 5-1-5, p. 163.) Variations in dielectric constant and density with ionic strength have been neglected in the formulation of \(k_2\), but are allowed for indirectly by special extended terms in the formulation of \(k_1\) and \(k_w\).
### TABLE 7. Analyses of Equilibrated Carbonate-Bicarbonate Solutions

at 25°C Derived from Data of Walker et al. [1927]

<table>
<thead>
<tr>
<th>No. of runs averaged(^a)</th>
<th>(m_1) (mmol/Kg)</th>
<th>(m_2) (mmol/Kg)</th>
<th>(P_{CO_2}) (atm x 10(^6))</th>
<th>(\mu) (mmol/Kg)</th>
<th>(\sqrt{\mu}) ((mol/Kg)^{1/2})</th>
<th>log (\phi)</th>
<th>log (\phi_m)</th>
<th>log (\phi_0)</th>
<th>log (\phi_0')</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na HCO(_3) - Na(_2)CO(_3) Solutions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>7.86</td>
<td>.69</td>
<td>360</td>
<td>9.93</td>
<td>.100</td>
<td>2.396</td>
<td>2.396</td>
<td>2.4385</td>
<td>2.506</td>
</tr>
<tr>
<td>5</td>
<td>9.04</td>
<td>.97</td>
<td>347</td>
<td>11.94</td>
<td>.109</td>
<td>2.388</td>
<td>2.389</td>
<td>2.4386</td>
<td>2.510</td>
</tr>
<tr>
<td>1</td>
<td>10.80</td>
<td>1.33</td>
<td>360</td>
<td>14.78</td>
<td>.122</td>
<td>2.386</td>
<td>2.389</td>
<td>2.494</td>
<td>2.523</td>
</tr>
<tr>
<td>1</td>
<td>16.29</td>
<td>3.72</td>
<td>312</td>
<td>27.43</td>
<td>.166</td>
<td>2.360</td>
<td>2.363</td>
<td>2.499</td>
<td>2.541</td>
</tr>
<tr>
<td>1</td>
<td>23.55</td>
<td>7.51</td>
<td>343</td>
<td>46.05</td>
<td>.215</td>
<td>2.332</td>
<td>2.336</td>
<td>2.503</td>
<td>2.559</td>
</tr>
<tr>
<td>2</td>
<td>28.38</td>
<td>12.14</td>
<td>325</td>
<td>64.76</td>
<td>.254</td>
<td>2.310</td>
<td>2.312</td>
<td>2.502</td>
<td>2.568</td>
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<tr>
<td>3</td>
<td>41.90</td>
<td>29.09</td>
<td>350</td>
<td>129.11</td>
<td>.359</td>
<td>2.236</td>
<td>2.240</td>
<td>2.482</td>
<td>2.572</td>
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<tr>
<td>2</td>
<td>42.26</td>
<td>30.98</td>
<td>332</td>
<td>135.13</td>
<td>.368</td>
<td>2.239</td>
<td>2.242</td>
<td>2.488</td>
<td>2.580</td>
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<tr>
<td>1</td>
<td>43.93</td>
<td>34.11</td>
<td>332</td>
<td>146.19</td>
<td>.382</td>
<td>2.233</td>
<td>2.234</td>
<td>2.486</td>
<td>2.581</td>
</tr>
<tr>
<td>wt. av. (17 runs)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.490</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Calculations were carried out first on the individual runs and then the computed values of \(\mu\), log \(\phi\), etc. were averaged.
TABLE 7. Analyses of Equilibrated Carbonate-Bicarbonate Solutions
at 25°C Derived from Data of Walker et al. [1927] (cont')

<table>
<thead>
<tr>
<th>No. of runs averaged&lt;sup&gt;a&lt;/sup&gt;</th>
<th>( m_1 ) (mmol/Kg)</th>
<th>( m_2 ) (mmol/Kg)</th>
<th>( P_{CO_2} ) (atm x 10&lt;sup&gt;6&lt;/sup&gt;)</th>
<th>( \mu ) (mmol/Kg)</th>
<th>( \sqrt{\mu} ) (mol/Kg)&lt;sup&gt;1/2&lt;/sup&gt;</th>
<th>log ( \phi )</th>
<th>log ( \phi_\mu )</th>
<th>log ( \phi_0 )</th>
<th>log ( \phi_0' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{KHCO}_3 - \text{K}_2\text{CO}_3 ) Solutions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>8.87</td>
<td>.94</td>
<td>345</td>
<td>11.68</td>
<td>.108</td>
<td>2.392</td>
<td>2.392</td>
<td>2.487</td>
<td>2.511</td>
</tr>
<tr>
<td>1</td>
<td>10.09</td>
<td>1.22</td>
<td>342</td>
<td>13.74</td>
<td>.117</td>
<td>2.387</td>
<td>2.390</td>
<td>2.492</td>
<td>2.519</td>
</tr>
<tr>
<td>5</td>
<td>19.48</td>
<td>5.28</td>
<td>324</td>
<td>35.29</td>
<td>.188</td>
<td>2.347</td>
<td>2.350</td>
<td>2.501</td>
<td>2.549</td>
</tr>
<tr>
<td>1</td>
<td>22.89</td>
<td>6.85</td>
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<td>43.41</td>
<td>.208</td>
<td>2.348</td>
<td>2.351</td>
<td>2.515</td>
<td>2.569</td>
</tr>
<tr>
<td>1</td>
<td>27.56</td>
<td>10.85</td>
<td>325</td>
<td>60.07</td>
<td>.245</td>
<td>2.332</td>
<td>2.336</td>
<td>2.521</td>
<td>2.585</td>
</tr>
<tr>
<td>4</td>
<td>30.67</td>
<td>14.60</td>
<td>332</td>
<td>74.42</td>
<td>.273</td>
<td>2.289</td>
<td>2.290</td>
<td>2.490</td>
<td>2.561</td>
</tr>
<tr>
<td>1</td>
<td>41.03</td>
<td>25.69</td>
<td>350</td>
<td>118.04</td>
<td>.344</td>
<td>2.272</td>
<td>2.275</td>
<td>2.510</td>
<td>2.597</td>
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<tr>
<td>1</td>
<td>41.57</td>
<td>29.50</td>
<td>320</td>
<td>130.00</td>
<td>.361</td>
<td>2.262</td>
<td>2.265</td>
<td>2.508</td>
<td>2.599</td>
</tr>
<tr>
<td>4</td>
<td>45.80</td>
<td>36.69</td>
<td>316</td>
<td>155.79</td>
<td>.395</td>
<td>2.259</td>
<td>2.261</td>
<td>2.519</td>
<td>2.617</td>
</tr>
<tr>
<td>wt. av. (21 runs)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.502</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculations were carried out first on the individual runs and then the computed values of \( \mu \), log \( \phi \), etc. were arranged.
### TABLE 8. Carbon Assays of Anhydrous Sodium Carbonate.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Weight of Na₂CO₃ (g)</th>
<th>Manometric Data</th>
<th>Assay %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pressure (mm Hg)</td>
<td>Volume (cc)</td>
</tr>
<tr>
<td>29</td>
<td>0.137912</td>
<td>376.132</td>
<td>63.277</td>
</tr>
<tr>
<td></td>
<td></td>
<td>73.773</td>
<td>323.795</td>
</tr>
<tr>
<td>30</td>
<td>0.075075</td>
<td>205.899</td>
<td>63.277</td>
</tr>
<tr>
<td>31</td>
<td>0.073369</td>
<td>201.050</td>
<td>63.277</td>
</tr>
<tr>
<td>32</td>
<td>0.384310</td>
<td>205.254</td>
<td>63.277</td>
</tr>
<tr>
<td>33</td>
<td>0.729802</td>
<td>389.550</td>
<td>63.277</td>
</tr>
<tr>
<td>34</td>
<td>0.039384</td>
<td>426.679</td>
<td>15.973</td>
</tr>
<tr>
<td>35</td>
<td>0.022335</td>
<td>242.129</td>
<td>15.973</td>
</tr>
<tr>
<td>36</td>
<td>0.016410</td>
<td>179.068</td>
<td>15.973</td>
</tr>
<tr>
<td>37</td>
<td>0.332855</td>
<td>178.321</td>
<td>323.795</td>
</tr>
<tr>
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Average of 10 assays: 100.01 \( \sigma = 0.10 \)

* Omitted from average
### TABLE 9. Analysis of Equilibrated Sodium Carbonate-Carbon Dioxide Solutions at 20° - New Results

<table>
<thead>
<tr>
<th>Run. No.</th>
<th>wt Na₂CO₃ (mg.)</th>
<th>wt H₂O (g.)</th>
<th>amt. CO₂ (m mol)</th>
<th>m₁ (m mol/Kg)</th>
<th>m₂ (m mol/Kg)</th>
<th>P&lt;sub&gt;CO₂&lt;/sub&gt; (atm x 10&lt;sup&gt;6&lt;/sup&gt;)</th>
<th>μ</th>
<th>log φ&lt;sub&gt;μ&lt;/sub&gt;</th>
<th>log φ&lt;sub&gt;0&lt;/sub&gt;</th>
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<td>1.290</td>
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TABLE 9. Analysis of Equilibrated Sodium Carbonate-Carbonate-Dioxide Solutions at 20° - New Results (con't 2)

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<tr>
<th>Run. No.</th>
<th>wt Na₂CO₃ (mg.)</th>
<th>wt H₂O (g.)</th>
<th>wt CO₂ (m mol)</th>
<th>m₁ (m mol/Kg)</th>
<th>m₂ (m mol/Kg)</th>
<th>PCO₂ (atm × 10⁶)</th>
<th>μ (m mol/Kg)</th>
<th>log φ_μ</th>
<th>log φ₀</th>
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TABLE 9. Analysis of Equilibrated Sodium Carbonate-Carbon

Dioxide Solutions at 20° - New Results (cont 3)

<table>
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<th>Run.</th>
<th>wt</th>
<th>wt</th>
<th>amt.</th>
<th>$m_1$</th>
<th>$m_2$</th>
<th>$P_{CO_2}$</th>
<th>$\mu$</th>
<th>$\log{\phi_\mu}$</th>
<th>$\log{\phi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>Na$_2$CO$_3$ (mg.)</td>
<td>H$_2$O (g.)</td>
<td>CO$_2$ (m mol)</td>
<td>(m mol/Kg)</td>
<td>(m mol/Kg)</td>
<td>(atm x 10$^6$)</td>
<td>(m mol/Kg)</td>
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<tr>
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<td>376.51</td>
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<td>1544.3</td>
<td>21.353</td>
<td>2.464</td>
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</table>

SERIES 4

| 33.0 | 719.22 | 322.607 | 6.88557 | 40.1907 | .9411 | 5435.1 | 43.222 | 2.403 | 2.565 |
| .1   | " | 322.582 | 6.63790 | 39.3531 | 1.3610 | 3922.8 | 43.585 | 2.411 | 2.573 |
| .2   | " | 322.566 | 6.45915 | 38.6395 | 1.7191 | 3070.1 | 43.911 | 2.418 | 2.582 |

Average excluding first runs (23 equilibrations) 2.581± .0089
Average including first runs (32 equilibrations) 2.578± .0103

Footnotes
a Omitted because of poor assay
b Omitted because of stirrer malfunction.


**TABLE 10. Extrapolation Function for Second Dissociation Derived from Data of Table 9.**

<table>
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<tr>
<th>Series No.</th>
<th>No. of runs averaged</th>
<th>$\sqrt{\mu}$ (mol/Kg)$^{1/2}$</th>
<th>log $\phi_0$ at 20°C</th>
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<td>10.317</td>
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\(^{a}\) All first runs (e.g. 30.0) omitted from averages.
REFERENCES


Harned, H.S. and Hamer, W.J. 1933. The ionization constant of water and the dissociation of water in potassium chloride solutions from electromotive forces of cells without liquid junction. 


