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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 0.002m (molality or mol kg^{-1} of H_2O), 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:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

is governed by the equilibrium quotient:

$$K_1 = \frac{a_H a_{HCO_3}}{a_{CO_2} a_{H_2O}} = \frac{m_H m_{HCO_3}}{m_{CO_2} m_{H_2O}} \cdot \frac{\gamma_H \gamma_{HCO_3}}{\gamma_{CO_2} \gamma_{H_2O}} \qquad (1)$$

where a, m, and γ 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:

$$\gamma_H = \gamma_{HCO_3} = \gamma_{CO_2} = a_{H_2O} = 1$$

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:

$$\text{Pt ; } H_2, CO_2 \;\Big|\; NaHCO_3(m_1),\ NaCl(m_2),\ CO_2(m_3) \;\Big\|\; \begin{matrix}\text{saturated}\\ \text{KCl bridge}\end{matrix} \;\Big|\; \begin{matrix}\text{saturated}\\ \text{KCl}\end{matrix} \;\Big|\; \text{HgCl ; Hg} \qquad (I)$$

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 ℓ^{-1} of solution) was varied from .01 to .18. Below .02 mol ℓ^{-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:

$$\begin{array}{c} \text{Glass} \\ \text{Electrode} \end{array} \Big| \; MHCO_3(m_1),\ MCl(m_2),\ CO_2(m_3) \; \Big| \; AgCl\ ;\ Ag \qquad \text{(II)}$$

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:

$$Pt\ ;\ H_2,\ CO_2 \; \Big| \; NaHCO_3(m_1),\ NaCl(m_2),\ CO_2(m_3) \; \Big| \; AgCl\ ;\ Ag \qquad \text{(III)}$$

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 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.

Näsänen [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_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 Näsänen'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_{CO_2} was calculated from the CO_2 partial pressure,

P_{CO_2}, by the expression:

$$m_{CO_2} = S_\mu P_{CO_2} \tag{2}$$

where S_μ 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.:

$$a_{CO_2} = SP_{CO_2} \tag{3}$$

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_μ 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.

Table 1
Table 2
Table 3

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:

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

is governed by the equilibrium quotient:

$$K_2 = \frac{a_H a_{CO_3}}{a_{HCO_3}} = \frac{m_H m_{CO_3}}{m_{HCO_3}} \cdot \frac{\gamma_H \gamma_{CO_3}}{\gamma_{HCO_3}} \qquad (4)$$

with reference state conditions analogous to those for K_1.

Hastings and Sendroy [1925] employed cell (I) again except that $Na_2CO_3(m_3)$ replaced $CO_2(m_3)$. The concentration ratio of Na_2CO_3 to $NaHCO_3$ 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_{HCO_3} and m_{CO_3} they considered the hydrolysis equilibrium:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

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:

$$\mathrm{Pt}\ ;\ H_2,\ CO_2\ \mid KHCO_3(m_1),\ K_2CO_3(m_2),\ KCl(m_3)\ \mid AgCl\ ;\ Ag \qquad \text{(IV)}$$

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 $Na_2CO_3(m_3)$ 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.

Näsänen [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. 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:

$$\frac{SK_1}{K_2} = \frac{a_{HCO_3}^{2}}{P_{CO_2} a_{CO_3} a_{H_2O}} = \frac{m_{HCO_3}^{2}}{P_{CO_2} m_{CO_3}} \cdot \frac{\gamma_{HCO_3}^{2}}{\gamma_{CO_3} a_{H_2O}} \qquad (5)$$

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 Näsänen'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. Table 5

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 Näsänen, 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:

$$\log a_H = (\xi - \xi_o)\ k \tag{6}$$

where ξ denotes the observed electromotive force of their cell expressed in international volts. The constant ξ_o 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:

$$\log K_1 - \log \frac{\gamma_{HCO_3}}{a_{H_2O}\gamma_{CO_2}} = \log a_H m_{HCO_3} - \log S_\mu P_{CO_2} \qquad (7)$$

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, footnote to p. 209.]

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

$$\log \gamma_{HCO_3} = -0.5 \sqrt{\mu} \qquad (8)$$

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:

$$\log K_2 - \log \frac{\gamma_{CO_3}}{\gamma_{HCO_3}} = \log \frac{a_H m_{CO_3}}{m_{HCO_3}} \qquad (9)$$

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

$$\log \frac{\gamma_{CO_3}}{\gamma_{HCO_3}} = -1.1 \sqrt{\mu} \tag{10}$$

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:

$$\log \frac{m_{HCO_3}^2}{P_{CO_2} m_{CO_3}} = \log (SK_1/K_2) - 0.6 \sqrt{\mu} \tag{11}$$

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:

$$\log K_1 - \log \frac{\gamma_{HCO_3}}{a_{H_2O}\gamma_{Cl}} = -(\xi - \xi_o)k + \log \frac{m_{HCO_3}}{m_{Cl}} - \log SP_{CO_2} \tag{12}$$

which can be derived from equations (1) and (3) with a_H replaced according to the relation:

$$(\xi - \xi°)k = \log a_H + \log \gamma_{Cl} m_{Cl} \tag{13}$$

See, e.g., MacInnes and Belcher [1933, equation (2) p. 2631] where

ξ denotes the electromotive force of cell II. The constant ξ_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 μ supports this prediction since only a slight dependence on ionic strength μ was found:

$$\log \frac{\gamma_{HCO_3}}{\gamma_{Cl}} \begin{array}{l} = -.03\sqrt{\mu} \text{ at } 25°\text{C} \\ = -.02\sqrt{\mu} \text{ at } 38°\text{C} \end{array} \qquad (14)$$

(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:

$$\log K_2 - \log \frac{\gamma_{CO_3}}{\gamma_{HCO_3}\gamma_{Cl}} = -(\xi - \xi_o)k + \log \frac{m_{CO_3}}{m_{HCO_3}m_{Cl}} \qquad (15)$$

consistent with equations (4) and (13).

They plotted the right side of equation (15) versus $\sqrt{\mu}$ and found:

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

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

$$\log \frac{m_{HCO_3}^2}{P_{CO_2} m_{CO_3}} \begin{cases} = \log (SK_1/K_2) - .35\ \sqrt{\mu} \text{ at } 25°C \\ = \log (SK_1/K_2) - .54\ \sqrt{\mu} \text{ at } 38°C \end{cases} \qquad (17)$$

similar at 38°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:

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

which differs from equation (12) by the substitution of S_μ 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 μ from the data of Harned and Davis [1943] at all temperatures reported, but for 25° we find from their figure 3 that:

$$\log K_1 - \log \frac{\gamma_{HCO_3}}{a_{H_2O}\gamma_{CO_2}\gamma_{Cl}} = .141\ \mu \tag{19}$$

Since at 25° the data of Harned and Bonner [1945, p. 1029] indicate that:

$$\log a_{H_2O} = -.015\ \mu$$

$$\log \gamma_{CO_2} = .102\ \mu$$

it follows that:

$$\log K_1 - \log \frac{\gamma_{HCO_3}}{\gamma_{Cl}} = .054\ \mu \tag{20}$$

In comparison, Harned and Bonner [1945] over a wider range in μ experimentally found a dependency for the left side of equation (20) of only .016 μ. (See their equations (18), (21), (28) and (30).) The data of Harned and Bonner indicate a similarly small dependency at 20° and 38°. Therefore, we conclude that most of the dependency on μ which Harned and Davis found in their extrapolation functions (approximately .14 μ) 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, $\gamma_{HCO_3} = \gamma_{Cl}$, 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:

$$\log \frac{\gamma_{HCO_3}\gamma_{Cl}}{\gamma_{CO_3}} = \frac{\zeta \sqrt{\mu}}{1 + A \sqrt{\mu}} + B\mu \qquad (21)$$

where ζ 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

$$B = -.16\ \mu$$

This dependency on μ is several fold that found for $\log (\gamma_{HCO_3}/\gamma_{Cl})$ 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

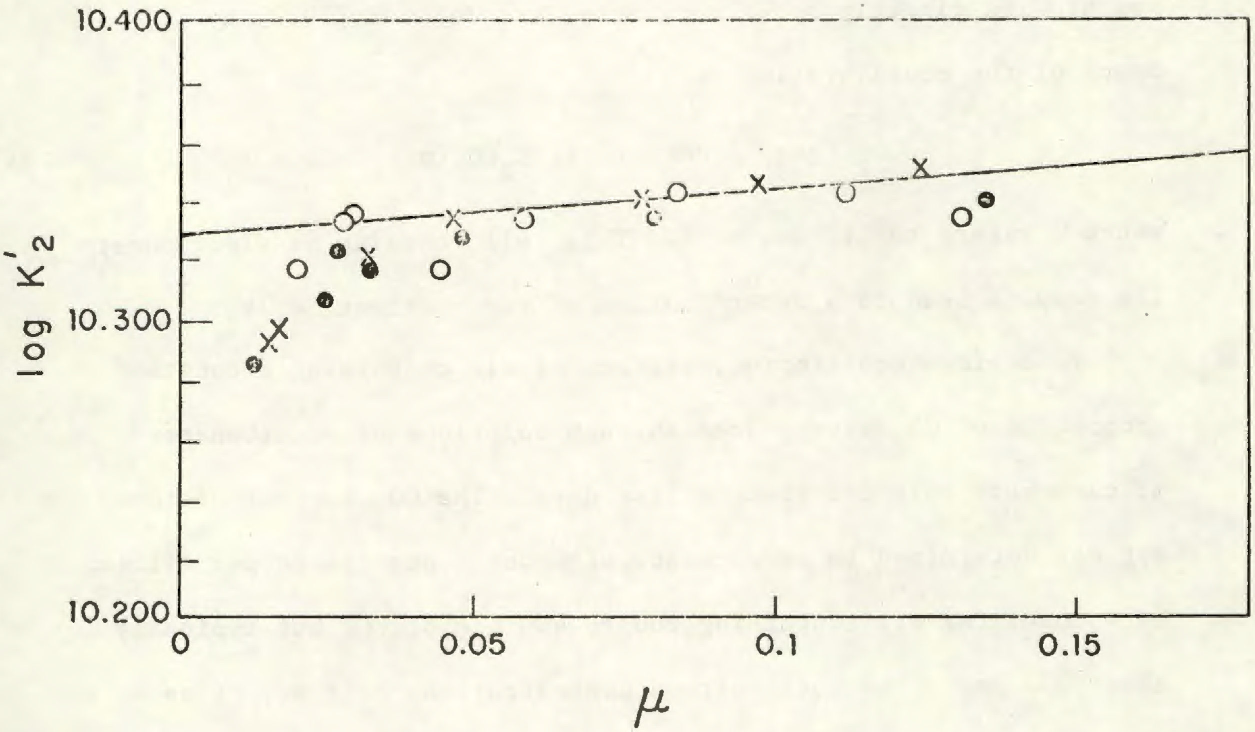

Figure 1. Extrapolation Function for the second dissociation of carbonic acid recopied from Harned and Scholes [1941, p. 1708, figure 2]. X, first series; O, second series. Straight line: best fit of second series data.

Data of MacInnes and Belcher [1933] (symbol ●) shown for comparison.

VI. GAS-SOLUTION EQUILIBRIUM

The equilibrium:

$$CO_2 + H_2O + M_2CO_3 \rightleftharpoons 2\ MHCO_3$$

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

$$CO_2\ (gas)\ |\ MHCO_3(m_1),\ M_2CO_3(m_2),\ MCl(m_3) \qquad (V)$$

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 CO_2 were passed through solutions of bicarbonate or carbonate salt for four to five days. The 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 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 Ba_2CO_3. A second aliquot was titrated with 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° and 37°C in the molal ionic strength range .01 to 3.1 with and without neutral salt (m_3) added. On the basis of values of Henry's law coefficient, S_μ, 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:

$$\phi = \frac{SK_1}{K_2}\left(\frac{\gamma_{CO_3} a_{H_2O}}{\gamma_{HCO_3}^2}\right) = \frac{m_{HCO_3}^2}{P_{CO_2} m_{CO_3}} \tag{22}$$

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

$$\log \phi = \log (SK_1/K_2) - 1.02 \sqrt{\mu} \tag{23}$$

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 ϕ 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 .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 .05 when allowance is made for the use of different values of the solubility coefficient S_μ. 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 ϕ in light of modern theory. In particular we will avoid the approximations that m_{HCO_3} and m_{CO_3} are equal respectively to m_1 and m_2 by employing stoichiometric relationships 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 existance of some species is still controversial. For example, it is not easy to decide from available experimental data whether the ion pairs $NaHCO_3^0$ and $NaCO_3^-$ 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 [1970], 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 $NaHCO_3^0$, $NaCO_3^-$, $KHCO_3^0$, and KCO_3^-.

The total molal concentration of carbon in sodium salt solution is then given by:

$$m_1 + m_2 = m_{CO_2} + m_{HCO_3} + m_{NaHCO_3} + m_{CO_3} + m_{NaCO_3} \tag{24}$$

while the total for sodium is:

$$m_1 + 2m_2 + m_3 = m_{Na} + m_{NaHCO_3} + m_{NaCO_3} \tag{25}$$

and the total chloride:

$$m_3 = m_{Cl} \tag{26}$$

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

$$m_{Na} + m_H - m_{HCO_3} - 2m_{CO_3} - m_{OH} - m_{NaCO_3} - m_{Cl} = 0 \tag{27}$$

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:

$$m_1 = 2m_{CO_2} + m_{HCO_3} + m_{NaHCO_3} + m_H - m_{OH} \tag{28}$$

$$m_2 = m_{CO_2} + m_{CO_3} + m_{NaCO_3} - m_H + m_{OH} \tag{29}$$

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:

$$k_1 = \frac{m_H m_{HCO_3}}{m_{CO_2}} = K_1 \frac{\gamma_{CO_2} a_{H_2O}}{\gamma_H \gamma_{HCO_3}} \tag{30}$$

$$k_2 = \frac{m_H m_{CO_3}}{m_{HCO_3}} = K_2 \frac{\gamma_{HCO_3}}{\gamma_H \gamma_{CO_3}} \tag{31}$$

$$k_w = m_H m_{OH} = \frac{K_w a_{H_2O}}{\gamma_H \gamma_{OH}} \tag{32}$$

Similarly, for sodium (and analogously for potassium):

$$k_{A1} = \frac{m_{Na} m_{HCO_3}}{m_{NaHCO_3}} = K_{A1} \frac{\gamma_{NaHCO_3}}{\gamma_{Na} \gamma_{HCO_3}} \tag{33}$$

$$k_{A2} = \frac{m_{Na} m_{CO_3}}{m_{NaCO_3}} = K_{A2} \frac{\gamma_{NaCO_3}}{\gamma_{Na} \gamma_{CO_3}} \tag{34}$$

The solubility, S_μ, 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_{A1} and k_{A2} the values are only approximate. Their dependence on ionic strength is hardly known and even the thermodynamic quotients K_{A1} and K_{A2} are quite uncertain.

Table 6

From the set of nine equations, (26) through (34), the molal concentrations of the nine species, CO_2, HCO_3^-, CO_3^{2-}, $NaHCO_3^0$, $NaCO_3^-$, 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 ϕ is predicted by equation (22) to depend on the ratio SK_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_μ, is added to the set of known apparent quotients.

The formal, or stoichiometric, ionic strength:

$$\mu_S = m_1 + 3m_2 + m_3 \tag{35}$$

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

$$\mu = \frac{1}{2}(m_{Na} + m_H + m_{HCO_3} + 4m_{CO_3} + m_{OH} + m_{NaCO_3} + m_{Cl}) \tag{36}$$

In order to compute consistant values of the molal concentrations of the sodium salt solutions in terms of the stoichiometric quotients as functions of μ, 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.:

$$m_{HCO_3} = (m_1 - 2m_{CO_2} - m_H + m_{OH})(1 + m_{Na}/k_{A1})^{-1} \tag{37}$$

$$m_{CO_3} = (m_2 m_{CO_2} + m_H - m_{OH})(1 + m_{Na}/k_{A2})^{-1} \tag{38}$$

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 $1 + m_{Na}/k_{A1}$ and $1 + m_{Na}/k_{A2}$ 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 μ. After the iteration was repeated until the value of μ converged to better than $1 \times 10^{-6}\mu$, a quantity:

$$\phi_\mu = \frac{m_{HCO_3}^{2}}{P_{CO_2} m_{CO_3}} \tag{39}$$

was calculated where the subscript on ϕ emphasizes that the computations of m_{HCO_3} and m_{CO_3} were carried out assuming free ions (and free ion ionic strength, μ) 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. Table 7 Figure 2

If ion pairs with Na and K are ignored, ϕ_μ, calculated by the method we have just described, agrees in all cases within 1% with ϕ, calculated by Walker et al. as equal to $m_1^2/(m_2 P_{CO_2})$. This agreement is well within the experimental error, and lends support to the view of Walker et al. [1927, p. 1245] that ϕ 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 ϕ 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 ϕ_μ, calculated on the basis of free ions and apparent quotients, is to compare the computed values with the prediction of the Debye-Hückel theory:

$$\log \phi_\mu = \log \phi_0 - 2\zeta\sqrt{2\rho\mu}/(1 + A\sqrt{\rho\mu}) \qquad (40)$$

where ζ, ρ and A (=1.414) are to be evaluated according to Table 6.

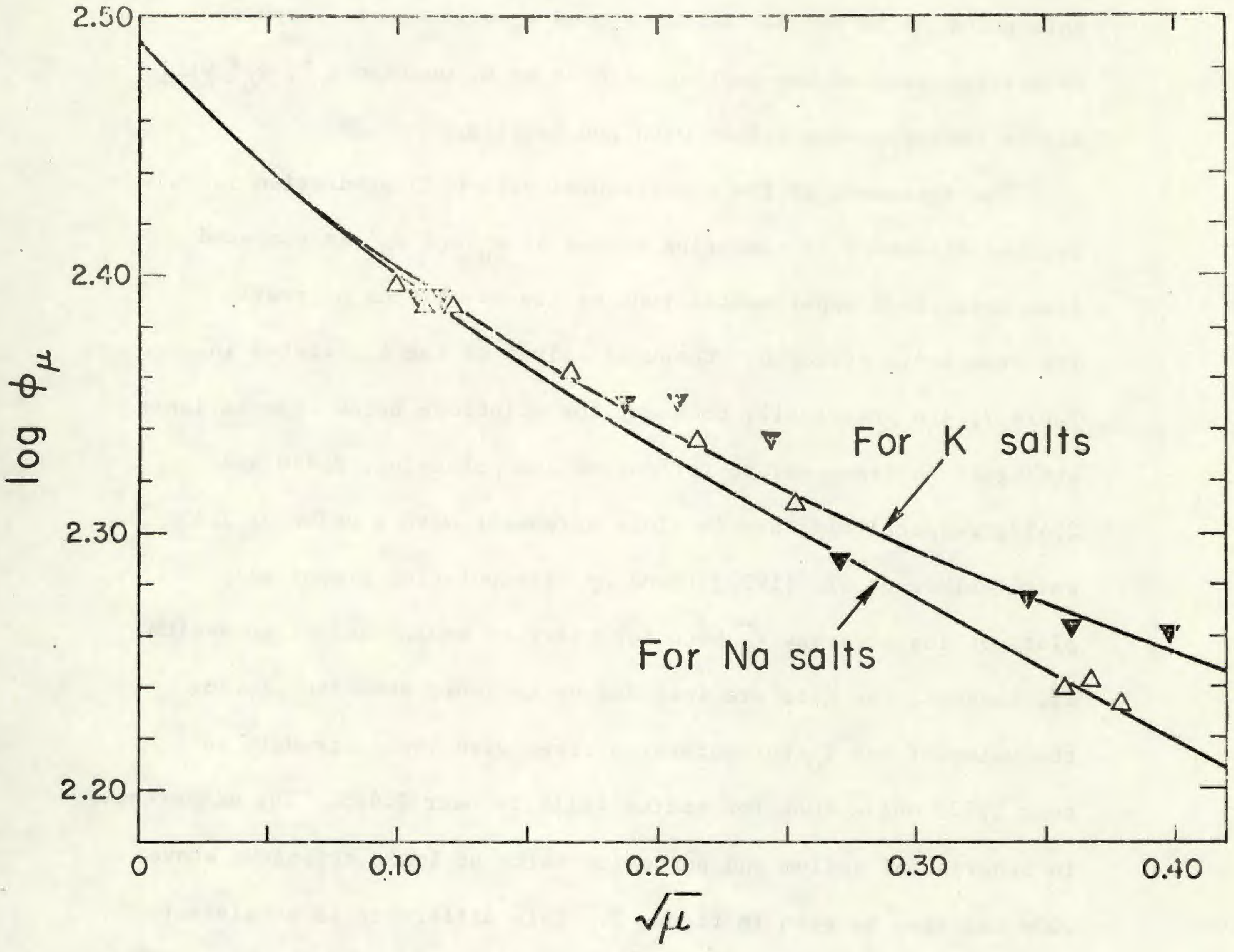

Figure 2. The function, ϕ_μ, recomputed from the data of Walker et al. [1927, pp. 1240-1242, Tables I and IV] Δ, $NaHCO_3$ - Na_2CO_3 solutions; ▼, $KHCO_3$ - K_2CO_3 solutions. The smooth curves are drawn through "best" estimates of the function, ϕ, as determined by the authors [ibid, p. 1245, Table IX].

and where ϕ_0 denotes the value of ϕ_μ at zero ionic strength. From this point on in our discussion ϕ_μ and ϕ_0 will denote computed values assuming no ion pairing with Na or K, whereas ϕ_μ', ϕ_0' will denote corresponding values with ion pairing.

The agreement of the experimental data with prediction is readily discerned by comparing values of ϕ_0 and ϕ_0' as computed from individual experimental runs or groups of runs of nearly the same ionic strength. Computed values of log ϕ_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 ϕ 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 ϕ_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 ϕ_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 ϕ_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 ϕ_μ', whereas the formation of $NaCO_3^-$ and $K_{CO_3}^-$ decreases CO_3^{2-} and thus raises ϕ_μ', it is not possible to predict in advance whether invoking ion pairing will raise or lower ϕ_μ'. 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 ϕ_0 from potassium and sodium begin to diverge only at ionic strengths above the range of validity of the Debye-Hückel formulation. 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 ϕ_μ 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 μ dependency as that for ϕ_μ.

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 ϕ_μ. 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

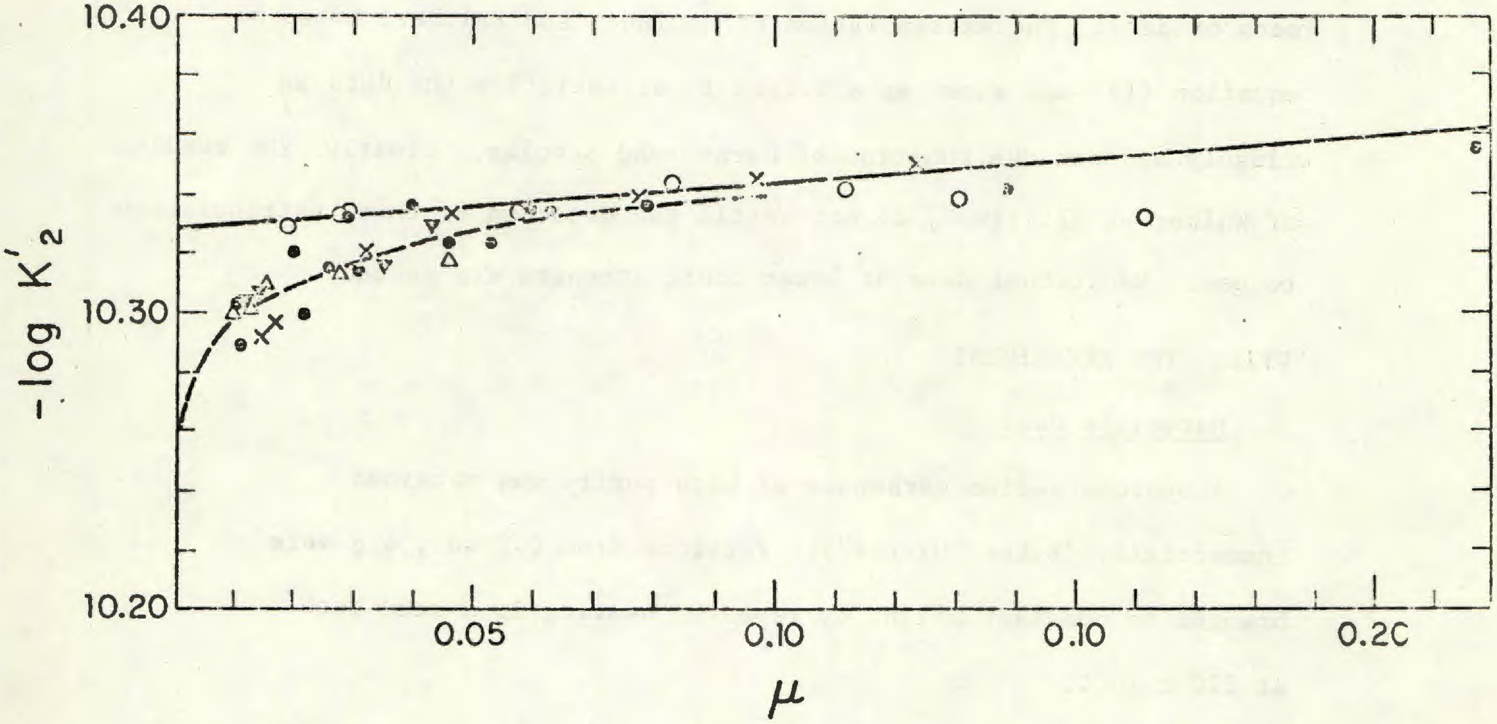

Figure 3. Extrapolation Function, $-\log K_2'$, for the second dissociation of carbonic acid, recomputed from original experimental data. X, O, and straight line have same meaning as in Figure 1. Δ, ▼ refer, respectively, to sodium and potassium salt solutions of Walker et al. [1927]. The dashed curve 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 CO_2-free distilled water obtained as described below. The dilute solution was found by the method of Wong [1970, p. 11] to contain no detectable CO_2.

Water free of CO_2 was prepared from commercially available deionized 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). Fig. 4
An entrance cap and an additional greaseless stopcock attached to the upper bulb permitted dry salts, stirring bars and CO_2-free water to be placed in either bulb. A short side arm on the upper bulb provided means for transferring CO_2 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 Fig. 5
were precisely determined from their weights filled with water.

Manometric determinations of CO_2 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 M5), a semi-microbalance (Mettler H51), and a 10 kg solution balance (Seederer-Kohlbusch) were used to carry out the gravimetric measurements.

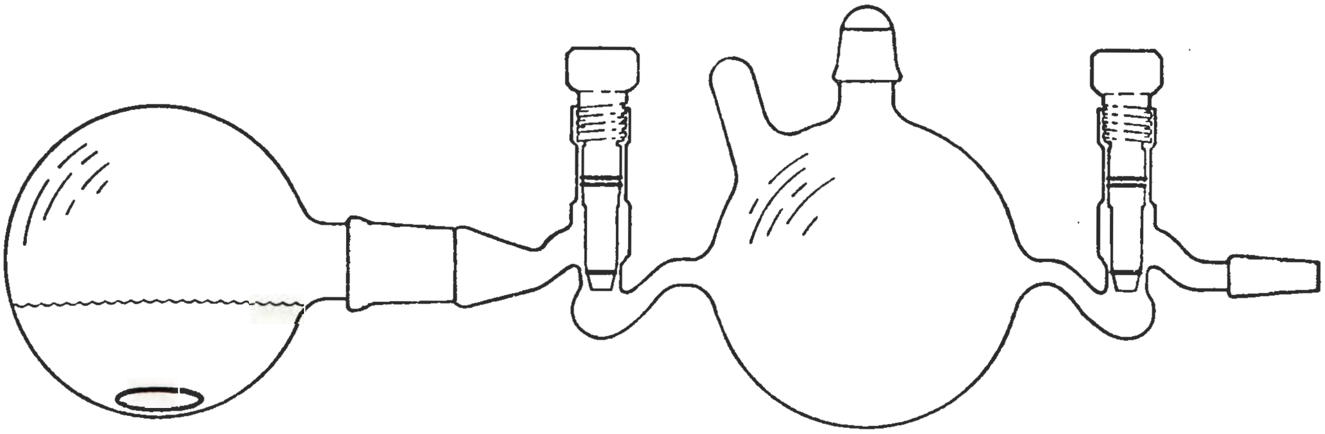

Figure 4. Equilibration vessel.

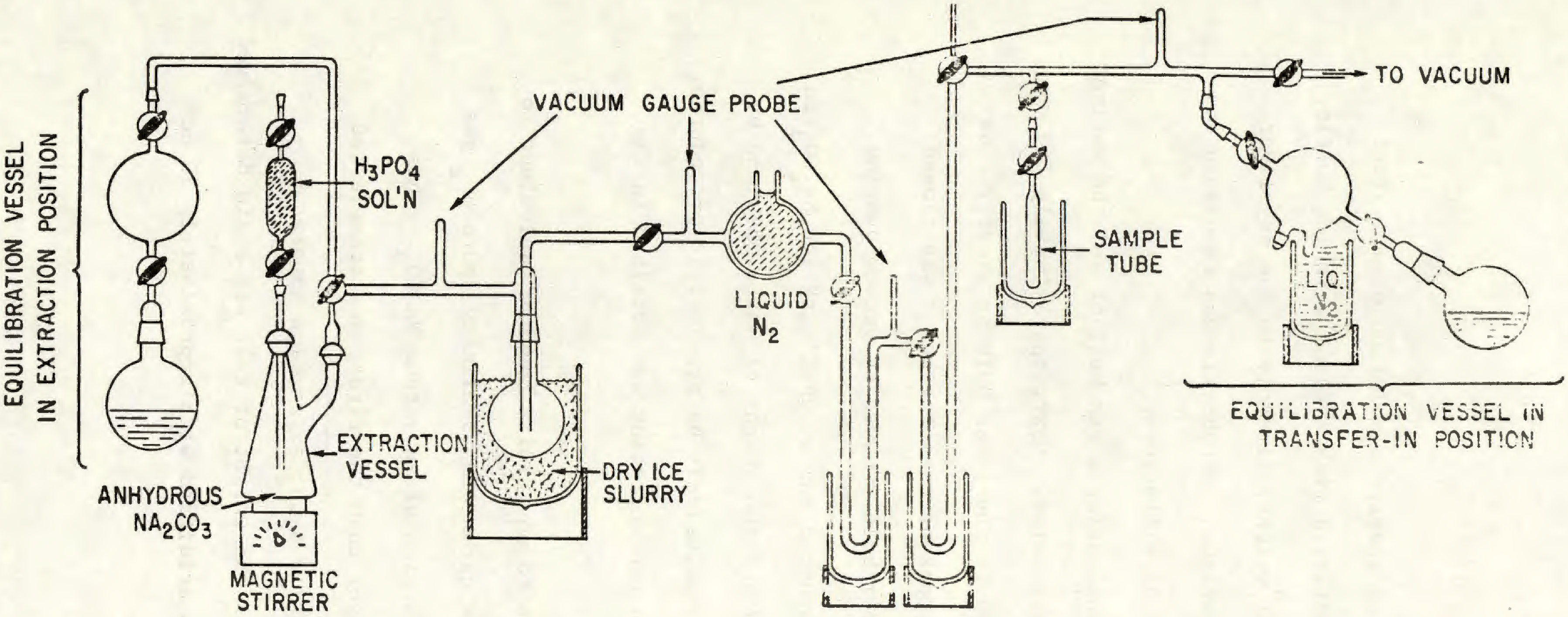

Figure 5. Vacuum system to process samples.

Procedure

Enough anhydrous Na_2CO_3 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 CO_2-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 Na_2CO_3 in the lower bulb, was reweighed and the weight of water obtained by difference. In this manner, exclusively by gravimetric procedures, a solution of Na_2CO_3 of known concentration was obtained in the lower bulb.

To convert this solution to an acidity roughly equivalent to a $NaHCO_3$ solution of the same carbonate alkalinity, pure CO_2 gas was prepared from a second portion of anhydrous Na_2CO_3. This portion, about 3 percent larger than the first, was transferred from the same weighing bottle to a CO_2 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 H_3PO_4 solution and the evolved CO_2 collected in a trap at liquid N_2 temperature. Water was removed by an intervening trap at dry ice temperature. The CO_2 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 CO_2 gas was determined. This procedure provided a carbon assay of the Na_2CO_3 and insured that the amount of CO_2 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 CO_2 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.

$$PV = nRT(1 + \frac{n}{V} B(T) + \ldots.) \tag{41}$$

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:

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

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]: $B = 442.002 - \frac{125548.}{T} - .483343T$

(4) R is the gas constant, taken as 8.31436×10^7 ergs mol^{-1} $°K^{-1}$.

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

$$P = \Delta h \cdot \rho_{Hg}(T) \cdot g \tag{43}$$

where:

(1) Δh 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 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 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.

Table 8
Table 9
Table 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 CO_2 gas added to the carbonate solution directly from the observed weight of the sodium carbonate from which it was derived. Because this 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 ϕ_μ depends essentially on the ratio of the amounts of CO_2 gas and sodium carbonate combined to make up the bicarbonate solution.

The computations of ϕ_μ and ϕ_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 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 equilibrations indicates that equilibrium was very nearly achieved. As can be seen from Table 9, there is a small, and only possibly significant, difference between initial and succeeding runs: 9 initial runs yield an average value of 2.572 for log ϕ_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. Table 9

The computed values of log ϕ_μ, 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 prediction than our data, but the agreement is quite satisfactory. Figure 6

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:

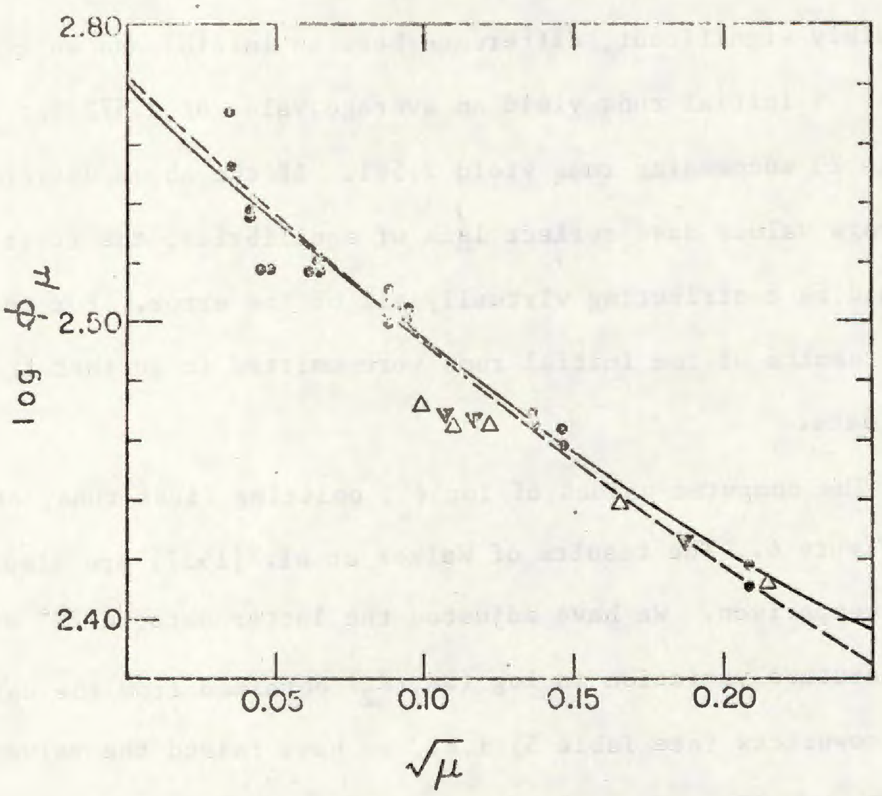

Figure 6. Our new determination of ϕ_μ compared with results of Walker et al. [1927]. Smooth curve: best fit of new data to Debye-Hückel formulation with A = 1.414. Dashed curve: same except A = 1.000.

●, SIO data

Δ, ▼ refer respectively to the sodium and potassium salt solutions of Walker et al. [1927].

For A = 1.414, log ϕ_0 = 2.581 ± .0089

For A = 1.000, log ϕ_0 = 2.584 ± .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 ϕ_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 ϕ_μ. 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 ϕ_μ / SK_1, derived from our experimental data for ϕ_μ, 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 ϕ_μ by .076. Our results agree better (Table 10 and Figure 7) with the extrapolation of Harned and Scholes

Table 10
Figure 7

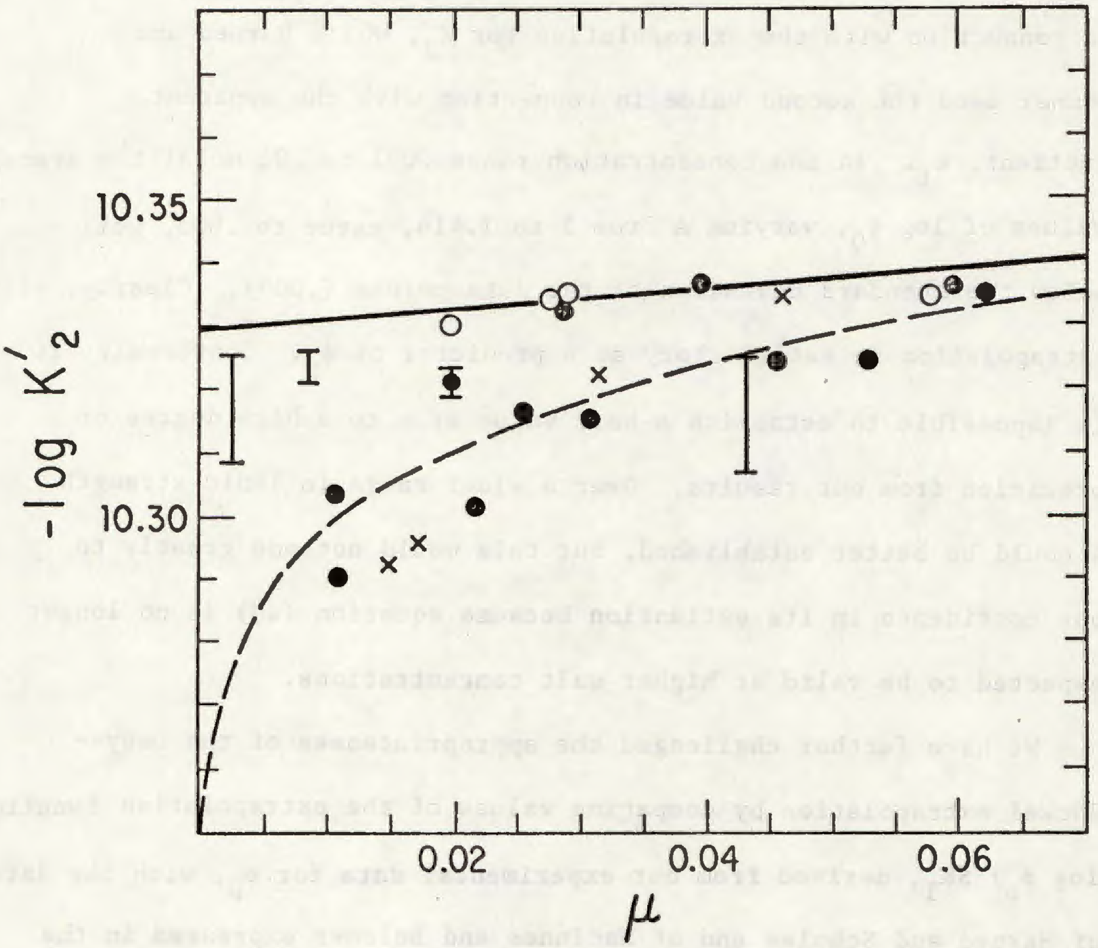

Figure 7. Extrapolation Function for the second dissociation of carbonic acid. Selected data, reproduced from figure 3, are compared with averages of the new determinations, denoted by error bars representing plus and minus two times the standard deviations of the averages in Table 10.

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° we can compare our average value of log ϕ_0 with the data of five other investigations:

MacInnes and Belcher:	2.435
Walker et al.:	2.491
Shedlovski and MacInnes for K_1, Murray and Riley for S, and Harned and Scholes for K_2:	2.497
Our work:	2.505
Näsänen:	2.508
Harned and coworkers:	2.514

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 ϕ_0 which is accurate to better than 0.01. As can be seen from Table 9, the imprecision (1σ) in calculating log ϕ_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 1. Reported Values of the First Dissociation Constant of Carbonic Acid

	$-\log K_1$		
	20°C	25°C	38°C
Hastings and Sendroy [1925][a]	-	-	6.327
MacInnes and Belcher [1933, 1935][a]	-	6.342	6.306
Shedlovski and MacInnes [1935][a]	6.393[b]	6.364	6.314
Harned and Davis [1943]	6.381	6.352	6.300[b]
Näsänen [1947]	6.382[b]	6.349	6.302[b]

[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 ρ, 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

	S(Moles kg^{-1}-atm^{-1})		
	20°C	25°C	38°C
Hastings and Sendroy [1925]	-	-	.02486[a]
MacInnes and Belcher [1933, 1935]	-	.03363[b]	.02460[b]
Shedlowski and MacInnes [1935]	-	.03382[c]	-
Harned and Davis [1943]	.03924	.03440	.02503
Murray and Riley [1971][d]	.03916	.03405	.02492

[a] Original data expressed as a Solubility Coefficient (equal to $S \times 22.4\ dm^3 mole^{-1}$) 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°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 $-\text{Log } SK_1$ based on Data of Tables 1 and 2

	$-\text{Log } SK_1$		
	20°C	25°C	38°C
Hastings and Sendroy [1925]	-	-	7.932
MacInnes and Belcher [1933, 1935]	-	7.815	7.915
Harned and Davis [1943]	7.787	7.815	7.902
Näsänen [1947] [a]	7.788	7.812	7.904
Shedlovski and MacInnes [1935] [b]	7.800	7.832	7.917

[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 4. Reported Values of the Second Dissociation Constant of Carbonic Acid

	$-\log K_2$		
	20°C	25°C	38°C
Hastings and Sendroy [1925][a]	-	-	10.217
MacInnes and Belcher [1933, 1935][a]	-	10.250	10.201
Näsänen [1946][a]	-	10.319	-
Harned and Scholes [1941]	10.377	10.329	10.232[b]

[a] Original data in moles dm^{-3} were corrected to moles kg^{-1} by the same method as for K_1 in Table 1.

[b] Interpolation based on equation for $-\log K_2$ versus temperature given in the original article.

TABLE 5. Computed Values of $\log(SK_1/K_2)$ Based on Data of Tables 3 and 4

	$\log(SK_1/K_2)$		
	20°C	25°C	38°C
Hastings and Sendroy [1925]	-	-	2.286
MacInnes and Belcher [1933, 1935]	-	2.435	2.286
Harned and Coworkers [1941, 1943]	2.590	2.514	2.330
Näsänen [1946, 1947]	-	2.508	-
Walker, Bray and Johnston [1927]	-	2.491	2.309

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, μ

Solubility of CO_2[a]

$$-\log S_\mu = -\,2388.016\ T^{-1} + 14.03059 - .0152799\ T + 171.5303\ \mu T^{-1} - .9071009\ \mu + .0014512024\ \mu T$$

First Dissociation of Carbonic Acid[b]

$$-\log k_1 = -\,D_1 + 3386.2013\ T^{-1} - 14.701034 + .03251536\ T - 552.09225\ T^{-1} + 3.4311775\ \mu - \ 0051149412\ \mu T$$

where:

$$D_1 \equiv D_1(\mu,t) = (14883 + .75545 \times 10^{-3} t + .1743 \times 10^{-5} t^2 + .11665 \times 10^{-7} t^3)\ \sqrt{8\mu}/(1 + \sqrt{\mu})$$

$$t = T + 273.16$$

Second Dissociation of Carbonic Acid[c]

$$-\log k_2 = -\,D_2 + 2902.39\ T^{-1} - 6.4980 + 0.02379\ T$$

where:

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

ζ is as quoted below under General Functions

Ionization of Water[d]

$$-\log k_w = -\,D_w + 4470.99\ T^{-1} - 6.0875 + .017060\ T$$

where:

$$D_w \equiv D_w(\mu,t) = \frac{2\zeta\sqrt{2\mu}}{1+A'\sqrt{\mu}} + B\mu + C\mu^{3/2}$$

$A' = 3.6(50.30)(DT)^{3/2}$

$B = .198 + .2 \times 10^{-3}t$

$C = - .0085 - .2 \times 10^{-3}t$

$t = T + 273.16$

ζ and D are as quoted below under General Functions

Dissociation of Sodium Bicarbonate and Carbonate Ion Pairs[e]

We assume:

$$k_{A1} = K_{A1}k_1/K_1$$
$$k_{A2} = K_{A2}k_2/K_2$$

where K_i refers to the value of the corresponding k_i 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[f]:

$$-\log K_{A1} = - .20$$
$$-\log K_{A2} = 1.00$$

General Functions[g]

Debye-Huckel Limiting Slope Function:

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

Dielectric Constant of Water:

$$D \equiv D(t) = 78.54[1 - .4579 \times 10^{-2}(t - 25) + .119 \times 10^{-4}(t - 25)^2 + .28 \times 10^{-7}(t - 25)^3$$

Density of Water:

$$\rho(t) = \frac{1 - (t - 3.39863)^2(t + 288.9414)}{508929.2(t + 68.12963)}$$

[a] Based on our simultaneous least squares fit of S_μ versus μ 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.

[b] 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.

[c] In agreement with formulation by Harned and Scholes [1941, equations 4 and 9] except that μ is replaced by $\zeta\sqrt{\rho 2}$. $\rho\mu$ and the limiting slope, ζ, 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.

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

[e] 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 $\gamma_{H_2CO_3} \equiv \gamma_{CO_2} a_{H_2O}$

The formulations of K_{A1} and K_{A2} are consistent with this hypothesis.

[f] Butler and Huston [1970, Table V, p. 2982] report for log K_{A1}, -.30 and -.08, and for log K_{A2}, -.97, .96, .77 based on experiments with the cell:

$$Na(Hg)|NaHCO_3(m_1) \text{ or } Na_2CO_3(m_2),\ NaCl(m_3)|AgCl{:}Ag \qquad (V)$$

Their table quotes values of the reciprocals of K_{A1} and K_{A2}, which they denote, respectively, by the symbols K_1'', and K_1'.

[g] The limiting slope, ζ, 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]

No. of runs averaged[a]	m_1 (mmol/Kg)	m_2 (mmol/Kg)	P_{CO_2} (atm x 10^6)	μ (mmol/Kg)	$\sqrt{\mu}$ $(mol/Kg)^{1/2}$	log ϕ	log ϕ_μ	log ϕ_0	log ϕ_0'
<u>Na HCO_3 - Na_2CO_3 Solutions</u>									
1	7.86	.69	360	9.93	.100	2.396	2.396	2.485	2.506
5	9.04	.97	347	11.94	.109	2.388	2.389	2.486	2.510
1	10.80	1.33	360	14.78	.122	2.386	2.389	2.494	2.523
1	16.29	3.72	312	27.43	.166	2.360	2.363	2.499	2.541
1	23.55	7.51	343	46.05	.215	2.332	2.336	2.503	2.559
2	28.38	12.14	325	64.76	.254	2.310	2.312	2.502	2.568
3	41.90	29.09	350	129.11	.359	2.236	2.240	2.482	2.572
2	42.26	30.98	332	135.13	.368	2.239	2.242	2.488	2.580
1	43.93	34.11	332	146.19	.382	2.233	2.234	2.486	2.581
	wt. av. (17 runs)							2.490	

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[a] Calculations were carried out first on the individual runs and then the computed values of μ, log ϕ, etc. were averaged.

TABLE 7. Analyses of Equilibrated Carbonate-Bicarbonate Solutions at 25°C Derived from Data of Walker et al. [1927] (con't)

No. of runs averaged[a]	m_1 (mmol/Kg)	m_2 (mmol/Kg)	P_{CO_2} (atm x 10^6)	μ (mmol/Kg)	$\sqrt{\mu}$ $(\mathrm{mol/Kg})^{1/2}$	log ϕ	log ϕ_μ	log ϕ_0	log ϕ_0'
$\underline{KHCO_3 - K_2CO_3}$ Solutions									
3	8.87	.94	345	11.68	.108	2.392	2.392	2.487	2.511
1	10.09	1.22	342	13.74	.117	2.387	2.390	2.492	2.519
5	19.48	5.28	324	35.29	.188	2.347	2.350	2.501	2.549
1	22.89	6.85	343	43.41	.208	2.348	2.351	2.515	2.569
1	27.56	10.85	325	60.07	.245	2.332	2.336	2.521	2.585
4	30.67	14.60	332	74.42	.273	2.289	2.290	2.490	2.561
1	41.03	25.69	350	118.04	.344	2.272	2.275	2.510	2.597
1	41.57	29.50	320	130.00	.361	2.262	2.265	2.508	2.599
4	45.80	36.69	316	155.79	.395	2.259	2.261	2.519	2.617
	wt. av. (21 runs)							2.502	

[a] Calculations were carried out first on the individual runs and then the computed values of μ, log ϕ, etc. were arranged.

TABLE 8. Carbon Assays of Anhydrous Sodium Carbonate.

		Manometric Data			Assay %	
Experiment No.	Weight of Na_2CO_3(g)	Pressure (mm Hg)	Volume (cc)	Temperature (°C)	Single Determination	Average
29	.137912	376.132	63.277	19.60	99.98	
		73.773	323.795	19.96	100.00	99.99
30	.075075	205.899	63.277	20.58	100.07	
		40.328	323.795	20.48	100.21	100.14
31	.073369	201.050	63.277	20.47	100.02	
		39.363	323.795	20.38	100.13	100.07
32	.384310	205.254	323.795	19.91	99.96	99.96
33	.729802	389.550	323.795	20.12	99.95	99.95
34	.039384	426.679	15.973	20.05	100.13	
		108.015	63.277	20.20	100.14	100.13
35	.022335	242.129	15.973	19.92	100.11	100.11
36	.016410	179.068	15.973	20.83	100.40*	
		45.292	63.277	20.83	100.50*	100.45*
37	.332855	178.321	323.795	20.86	99.90	99.90
38	.156150	429.546	63.277	22.10	99.98	
		84.260	323.795	22.26	100.06	100.02
39	.031260	338.946	15.973	20.94	99.83	
		85.915	63.277	21.41	99.90	99.86
		Average of 10 assays				100.01 σ = .10

* Omitted from average

TABLE 9. Analysis of Equilibrated Sodium Carbonate-Carbon Dioxide Solutions at 20° - New Results

Run. No.	wt Na_2CO_3 (mg.)	wt H_2O (g.)	amt. CO_2 (m mol)	m_1 (m mol/Kg)	m_2 (m mol/Kg)	P_{CO_2} (atm x 10^6)	μ (m mol/Kg)	log ϕ_μ	log ϕ_0
SERIES 1									
36.0	16.46	378.671	.15483	.7812	.0197	96.4	.841	2.493[a]	2.521[a]
35.0	21.76	333.308	.21073	1.1360	.0481	290.4	1.290	1.869[b]	1.903[b]
.1	"	333.283	.19750	1.1469	.0427	86.8	1.273	2.571	2.605
.2	"	333.258	.19354	1.1288	.0518	74.1	1.281	2.552	2.586
39.0	30.35	336.355	.29493	1.6496	.0266	238.1	1.736	2.530	2.570
.1	"	336.329	.28408	1.6170	.0430	165.6	1.748	2.536	2.576
.2	"	336.309	.27654	1.5888	.0571	127.7	1.760	2.538	2.578
34.0	38.28	337.613	.37158	2.0708	.03447	299.5	2.183	2.510	2.554
.1	"	337.596	.35793	2.0298	.05507	208.5	2.199	2.518	2.562
.2	"	337.567	.34843	1.9941	.07297	161.5	2.214	2.518	2.562
30.0	71.53	353.696	.70832	3.7338	.04132	659.3	3.881	2.501	2.559
.1	"	353.673	.67828	3.6580	.07933	431.7	3.909	2.517	2.575
31.0	72.70	355.994	.69223	3.7030	.0754	455.3	3.944	2.517	2.575
.1	"	355.970	.67148	3.6354	.1094	366.3	3.972	2.517	2.575
.2	"	355.947	.65615	3.5777	.1383	267.5	3.998	2.520	2.579

TABLE 9. Analysis of Equilibrated Sodium Carbonate-Carbon Dioxide Solutions at 20° - New Results (con't 2)

Run. No.	wt Na_2CO_3 (mg.)	wt H_2O (g.)	amt. CO_2 (m mol)	m_1 (m mol/Kg)	m_2 (m mol/Kg)	P_{CO_2} (atm x 10^6)	μ (m mol/Kg)	log ϕ_μ	log ϕ_0
SERIES 2									
29.0	141.75	352.087	1.30118	7.1354	.2310	618.6	7.848	2.511	2.591
.1	"	352.068	1.27299	7.0207	.2886	509.9	7.901	2.500	2.579
.2	"	352.047	1.24976	6.9232	.3376	427.9	7.946	2.505	2.585
.3	"	352.025	1.23026	6.8361	.3814	372.1	7.987	2.507	2.587
.4	"	351.998	1.21330	6.7576	.4210	330.3	8.025	2.510	2.590
.5	"	351.969	1.19826	6.6837	.4582	303.7	8.061	2.502	2.582
.6	"	351.941	1.18442	6.6162	.4923	277.9	8.094	2.503	2.583
38.0	151.249	331.532	1.47325	8.3433	.1331	1223.5	8.788	2.494	2.578
.1	"	331.511	1.41750	8.1768	.2166	843.4	8.856	2.502	2.586
.2	"	331.489	1.37907	8.0471	.2818	615.5	8.911	2.540[b]	2.624[b]
.3	"	331.463	1.35102	7.9132	.3490	537.5	8.975	2.501	2.586
SERIES 3									
37.0	326.154	339.055	3.14044	17.4802	.3366	2411.9	18.582	2.462	2.577
.1	"	339.034	3.03054	17.1350	.5098	1715.5	18.727	2.469	2.584
.2	"	339.013	2.95237	16.8324	.6617	1352.7	18.866	2.465	2.581

TABLE 9. Analysis of Equilibrated Sodium Carbonate–Carbon Dioxide Solutions at 20° - New Results (con't 3)

Run. No.	wt Na_2CO_3 (mg.)	wt H_2O (g.)	amt. CO_2 (m mol)	m_1 (m mol/Kg)	m_2 (m mol/Kg)	P_{CO_2} (atm x 10^6)	μ (m mol/Kg)	$\log \phi_\mu$	$\log \phi$
32.0	376.51	345.736	3.62591	19.7971	.3771	2784.0	21.034	2.455	2.576
.1	"	345.715	3.49905	19.4019	.5754	1987.9	21.202	2.458	2.580
.2	"	345.691	3.40847	19.0672	.7435	1544.3	21.353	2.464	2.586
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.[a]

Series No.	No. of runs averaged	$\sqrt{\mu}$ (mol/Kg)$^{1/2}$	log ϕ_0 at 20°C	$-\log K_2$ at 25°C
1	9	.050	2.578	10.317
2	8	.089	2.585	10.324
3	4	.142	2.583	10.322
4	2	.209	2.578	10.317

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[a] All first runs (e.g. 30.0) omitted from averages.

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