

AN ABSTRACT OF THE THESIS OF

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Title THE PARTIAL EQUIVALENT VOLUMES OF SALTS IN
SEA WATER

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The partial equivalent volumes (\bar{V}_s) of the major salts in sea-water have been measured over the salinity range from 30 to 40‰ and a temperature range from 0°C to 25°C. The following table presents the results of this work.

$$\bar{V}_{Bc} = \bar{V}_{NaCl} + \bar{V}_{(B - Na^+)} + \bar{V}_{(c - Cl^-)}$$

$$\bar{V}_s(S^{\circ}/\text{oo}, t^{\circ}\text{C}) = a_{00} + a_{01}t + a_{02}t^2 + (a_{10} + a_{11}t)S \pm \epsilon \text{ ml/eq}$$

| \bar{V}_s | a_{00} ml/eq | $a_{01} \times 10^2$ | $a_{02} \times 10^2$ | $a_{10} \times 10^2$ | $a_{11} \times 10^2$ | ϵ ml/eq |
|-------------------------------|-------------------|----------------------|----------------------|----------------------|----------------------|---------------------|
| \bar{V}_{NaCl} | 15.54 | 16.0 | -0.289 | 1.16 | 0.086 | ±0.08 |
| $\bar{V}_{(K^+ - Na^+)}$ | 11.33 | -5.66 | 0.125 | -1.85 | 0.029 | ±0.12 |
| $\bar{V}_{(Mg^{++} - Na^+)}$ | -6.16 | -14.9 | 0.207 | -4.16 | 0.110 | ±0.20 |
| $\bar{V}_{(Ca^{++} - Na^+)}$ | -6.03 | 1.41 | -0.231 | -2.21 | 0.0 | ±0.27 |
| $\bar{V}_{(SO_4^{=} - Cl^-)}$ | -11.09 | 5.78 | 0.0057 | 6.23 | -0.109 | ±0.12 |
| $\bar{V}_{(HCO_3^- - Cl^-)}$ | 5.98 | 10.4 | -0.199 | 2.40 | 0.0 | ±0.26 |
| $\bar{V}_{(NO_3^- - Cl^-)}$ | 9.44 | 0.448 | 0.255 | 1.19 | 0.0 | ±0.15 |
| $\bar{V}_{\text{sea salt}}$ | 13.42 | 13.9 | -0.254 | 0.924 | 0.093 | ±0.09 |

The partial equivalent volume of sea salt has been computed from the partial volumes of the major salts in seawater. At $S = 34.46^{\circ}/\text{oo}$ and $t = 24.5^{\circ}\text{C}$, $\bar{V}_{\text{sea salt}} = 16.35 \pm 0.09 \text{ ml/eq}$. This value agrees closely with $\bar{V}_{\text{sea salt}}$ computed from density data in Knudsen's Hydrographical Tables.

THE PARTIAL EQUIVALENT VOLUMES
OF SALTS IN SEAWATER

by

IVER WARREN DUEDALL

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THE PARTIAL EQUIVALENT VOLUMES OF SALTS IN SEAWATER

INTRODUCTION

The purpose of this investigation is to determine the partial equivalent volumes of the major salts in seawater at temperatures and salinities commonly observed in the World Ocean. The partial equivalent volume (\bar{V}_1) of a salt in seawater is defined as

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1} \right)_{T, P, n_2, \dots}$$

where \bar{V}_1 is the increase in volume (V) of an infinitely large volume of seawater due to the addition of one equivalent of the salt 1.

A knowledge of the partial equivalent volumes of the major salts in seawater will lead to a better understanding of the physical chemistry of seawater. For instance, the effect of the ionic environment of seawater on the major constituents can be evaluated by comparing the partial equivalent volumes in seawater with those at infinite dilution. Also, since the ionic strength is a measure of the interactions of all the ions in solution, comparisons of the partial equivalent volumes of salts in seawater with those in a sodium chloride solution of the same ionic strength as seawater tests how well the ionic strength concept holds for seawater.

To study the effect of pressure on ionic equilibria, the partial

equivalent volumes must be known. At constant temperature, the pressure coefficient of the solubility of a salt in aqueous solutions depends upon the difference between the partial volumes of the products and reactants.

Physical oceanographers are interested in determining the density of seawater with high accuracy in order to compute ocean current velocities using the geostrophic approximations. The results of this thesis can be used to construct a density model of seawater by considering seawater a two-component system comprised of sea salt and water, where sea salt is an appropriate mixture of the major salts in seawater. Lyman and Fleming's (1940) formula for artificial seawater is one example of sea salt. It is of particular interest to compare the partial equivalent volume of sea salt derived from the density of seawater with the value determined from a summation of the partial equivalent volumes of the individual salts.

Probably the most important application of the results will be in using these data plus specific conductance data to compute the partial equivalent conductances of the major salts in seawater. This information is needed to gain a better understanding of the density-conductance correlation of seawater that is being investigated by Cox et al. (1962). However, to estimate how this correlation is altered by slight changes in the relative composition of seawater, the partial equivalent volumes and partial equivalent conductances

of the major salts in seawater must be known.

Review of Literature

Many investigators have determined partial equivalent volumes of various salts in pure water and in aqueous solutions of strong electrolytes (i. e. , NaCl soln); however, no data exist in the literature on the determination of partial equivalent volumes of salts in seawater.

Wirth (1940a) discussed the partial molar volumes^{1/} of the various salts in seawater and their relation to the problem of the density of seawater. His approach was to first define the apparent molar volume^{2/} (\bar{v}) of a salt as

$$\bar{v} = M/d_o - \frac{1000(d_1 - d_o)}{C d_o}$$

where M is the molecular weight of the salt, d_o is the density of the pure solvent, d_1 is the density of the solution, and C is the concentration expressed as moles per liter.

1/ The partial molar volume (ml/mole) is the volume change referred to one mole of solute. For a divalent salt, the partial molar volume is twice the partial equivalent volume.

2/ The apparent molar volume of the solute in solution is determined by assuming that the volume of the solvent is not changed when the solution is formed.

Next, he used an equation for the apparent equivalent volume of a "theoretical salt" as a function of chlorosity. The equation was $\bar{v} = A + B Cl^{\frac{1}{2}}$, where A and B are parameters to be evaluated. The constant A is a summation of the partial equivalent volumes of the major ions in seawater at infinite dilution (pure water). The partial volumes of the ions are determined by assuming that the volume of the potassium ion equals the volume of the fluoride ion. Hence, a knowledge of the partial equivalent volume of potassium fluoride at infinite dilution makes it possible to estimate the volumes of all other ions. The constant B, which is a slope term, was determined using the same technique as was used to evaluate A.

By equating the "theoretical salt" equation with the above apparent volume-density relation, Wirth obtained an equation for the density of seawater in terms of chlorosity. At the chlorinities of Knudsen's density determinations, a tabulation of the computed densities showed that Wirth's computed density was uniformly higher than actual observations reported by Knudsen. The greatest difference in density was 28 parts per million at a chlorinity of 19.584^o/oo.

Wirth's basic idea of considering the density of seawater as an additive property of partial equivalent volumes is sound; however, he was limited to the data then available. The data reported in this thesis allows a more realistic computation of the partial equivalent volume since the data presented here refers to seawater rather than

distilled water.

Owen and Brinkley (1941) have calculated the effect of pressure upon ionic equilibria in pure water and in salt solutions. To give their results oceanographic interest, partial molar volumes and pressure coefficients for various salts in "salt water" (0.725 molal NaCl) were computed from data appearing in the literature. The partial molar volume estimates made by Owen and Brinkley will later be compared with the results of this thesis.

Zen (1957) has tabulated, at various temperatures, the partial molar volumes of several single salts in aqueous solutions as functions of temperature and concentration. The partial volumes were computed from density data appearing in the International Critical Tables. He shows how this information can be used to solve geochemical problems such as the solubility of calcium carbonate as a function of pressure. Zen did not estimate the partial molar volumes of salts in seawater.

EXPERIMENTAL METHOD

The apparatus used to determine the partial equivalent volumes of salts in seawater was a specially designed dilatometer. The procedure and details of the apparatus have been recently described by Duedall and Weyl (1965). A reprint of the paper is appended as Appendix I. By using a dilatometer, the change in volume of a solution due to the addition of a small increment of salt is measured directly. The main steps in the method are the following: (a) the dilatometer is filled with seawater and placed into a constant temperature bath; (b) known weights of salt are introduced into the dilatometer by means of a salt dispenser, and the change in position of the menisci is measured with a cathetometer; (c) for each salt addition, the cumulative volume change (ΔV) divided by the cumulative equivalents (Δn_1) of salt added is computed; and (d) the ratio, $\Delta V / \Delta n_1$, is plotted as a function of mass added and the data extrapolated to zero^{3/} salt addition to determine the partial equivalent volume of the salt.

The error in each cumulative addition comes from two sources: (1) the error in the volumetric calibration factor of the

^{3/} The limit, as Δn_1 approaches zero, of $\Delta V / \Delta n_1$ is \bar{V}_1 , i. e.,

$$\lim_{\Delta n_1 \rightarrow 0} \Delta V / \Delta n_1 = \partial V / \partial n_1.$$

dilatometer and (2) the error inherent in the manipulation of the dilatometer, which decreases as the number of salt additions increases. The error in the weight of salt added is considered negligible since weighings were made to an accuracy of ± 0.00005 gm. To avoid error due to a loss of salt from the salt dispenser, duplicate runs were made. A thorough discussion of the errors in this method can be found in Appendix I. The absolute error in the partial equivalent volumes of the salts investigated ranged from ± 0.07 to ± 0.33 ml/eq.

Salts Investigated

The partial volumes of the following salts were measured at various temperatures and salinities:

| | |
|---|--|
| NaCl | $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ |
| KCl | NaNO_3 |
| Na_2SO_4 | KNO_3 |
| K_2SO_4 | Mg-acetate $\cdot 4\text{H}_2\text{O}$ |
| $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ | Na-acetate $\cdot 3\text{H}_2\text{O}$ |
| KHCO_3 | |

The choice of the above salts was based on the following:

- (a) the salts can be weighed with precision and accuracy on an analytical balance; (b) the transfer of known increments of salt to the dilatometer by means of a salt dispenser is quantitative; (c) the salts

contain at least one of the major ions found in seawater; and (d) most of them can be arranged into groups of four salts of similar anion and cation pair to provide a check on the experimental method.

The salts used were Baker and Adamson reagent grade quality^{4/} and were not further purified. Potassium bicarbonate and the hydrated salts were not dried before using because of the uncertainty in the composition and stability of the dried form. The remaining salts were dried at 150°C for at least two hours.

The non-dryable salts did not show noticeable deliquescence under laboratory conditions; therefore, the error introduced into the results due to non-drying was estimated from the percent of water, as an impurity, present in the salt when purchased from the manufacturer. The significance of this error is illustrated for magnesium sulfate: At $S = 34.46^{\circ}/\text{oo}$, $t = 24.5^{\circ}\text{C}$, the partial molar volume of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is 128.85 ± 0.40 ml/mole. Magnesium sulfate shipped from the manufacturer contains a maximum of 0.5 percent water. Since the partial molar volume of water in seawater is approximately 18 ml/mole, a 0.5 percent correction will lower the partial molar volume of the salt by 0.09 ml/mole. This represents a non-drying error of slightly less than 0.1 percent in the final result and is only one-fourth of the estimated experimental

^{4/} Baker and Adamson Quality, Allied Chemical, General Chemical Division, Morristown, N. J.

error (± 0.40 ml/mole). The same analysis applied to the other non-dryable salts gives similar results. The error due to non-drying of potassium bicarbonate and the hydrated salts can be ignored since it is small compared to the experimental error in the actual measurement.

Preparation of Seawater

Artificial seawater was used throughout because natural seawater contains small amounts of organic matter, nutrients, and trace elements that enhance biological activity. The absence of these materials from artificial seawater will not affect the partial equivalent volumes since it is mainly the abundance and interactions of the major ions in solution that influence the value of \bar{V}_s .

The recipe of Lyman and Fleming (1940) was used for the preparation of artificial seawater and represents only the major ions found in natural seawater. However, the reagent grade salts used in the preparation of the seawater were not further purified; hence, small amounts of impurities were present in the artificial seawater.

Three separate batches, approximately 20 kg each, of seawater of different salinities were prepared using the method described in Appendix II. The salinity of each batch of seawater was

determined using an inductive salinometer^{5/} that had been calibrated with standard Copenhagen seawater. The uncertainty in the salinity determination was estimated to be slightly less than $\pm 0.01^\circ/\text{oo}$. Each batch of seawater was equilibrated with laboratory air; the pH of each seawater was about 8.15 and remained essentially constant during storage.

Salinities and Temperatures of Partial Equivalent
Volume Measurements

The objective of this investigation was to determine the partial volumes of the major salts in seawater at temperatures and salinities characteristic of the World Ocean. The variation of the partial volumes at constant temperature (24.5°C) with salinity was determined by making measurements at salinities 30.13, 34.46, and $40.07^\circ/\text{oo}$. The variation of \bar{V}_s with temperature was obtained at a salinity of $34.46^\circ/\text{oo}$ and temperatures of 0° , 10° , and 24.5°C . Some additional partial volume measurements were made at $S = 30.13^\circ/\text{oo}$ and $t = 0^\circ\text{C}$.

Plot of Data - Example

The partial equivalent volume of a particular salt in seawater is defined as the limit, as Δn_1 approaches zero, of the rate of

^{5/} Hytech Inductive Salinity and Conductivity Meter, Model 621.

change in volume (V) of seawater with respect to equivalents of salt added:

$$\bar{V}_1 = \lim_{\Delta n_1 \rightarrow 0} \Delta V / \Delta n_1$$

The uncertainty in \bar{V}_1 increases as Δn_1 approaches zero; therefore, the partial equivalent volume is determined by making a series of salt additions, plotting the ratio of the cumulative volume change to cumulative equivalents of salt added, and extrapolating to zero salt addition.

A plot of duplicate runs for potassium sulfate ($S = 34.46^\circ/\text{oo}$, $t = 24.5^\circ\text{C}$) is shown in Figure 1. The partial equivalent volume, obtained by extrapolation, was found to be 20.77 ± 0.09 ml/eq.

The method used to determine the position of the solid line (Figure 1) was first to estimate the limits of uncertainty of the extrapolated result (indicated by the dashed lines in Figure 1) from the experimental error, indicated by vertical bars in Figure 1, in each measurement and then to fit a straight line between the dashed lines. The data reduction used for this determination is found in Table I.

For a hydrated salt such as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, the partial equivalent volume of MgSO_4 , excluding the water of hydration, is determined by first evaluating the partial volume of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and then subtracting from it the partial volume of the water. The partial volume of water in seawater is computed (see Appendix III)

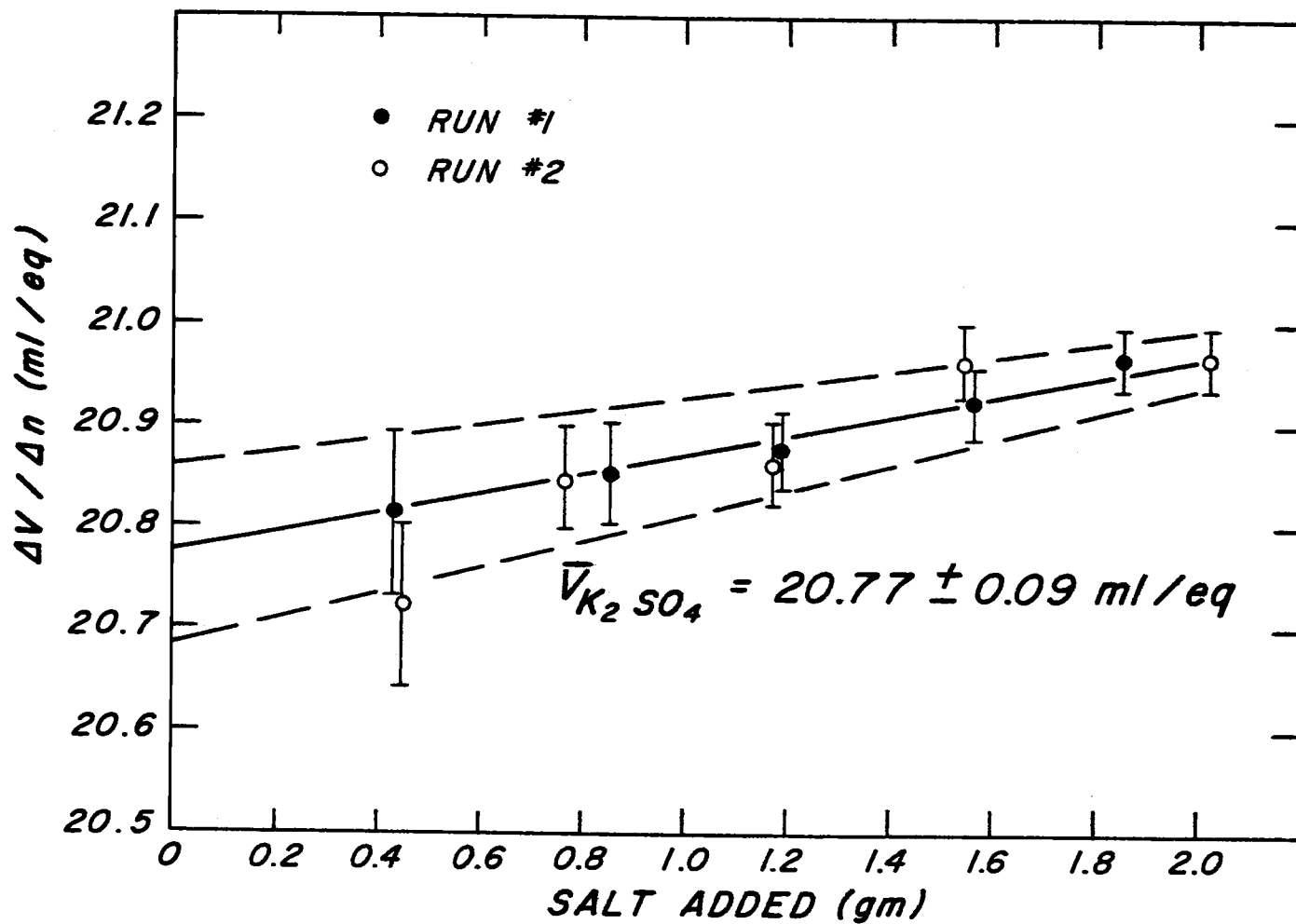


Figure 1. Data from duplicate runs to determine the partial equivalent volume of potassium sulfate in seawater ($S = 34.46^\circ/\text{oo}$) at 24.5°C .

Table I. Data reduction of potassium sulfate run (see Figure 1): $S = 34.46^{\circ}/\infty$, $t = 24.5^{\circ}C$.

| | a | b | c ^{a/} | b/ d ^{b/} | e ^{c/} | f | g |
|-------|--------------------------|--------------------------------|-----------------|-------------------------------------|-----------------|-------------------------|-------------------------------------|
| | Cumulative mass gm | Cumulative ΔH cm | Ab/a ml/eq | Manip error $0.75/\Delta H$ % | Cal error % | $\sqrt{d^2 + e^2}$ % | Absolute error fc/(100) ml/eq |
| Run 1 | | | | | | | |
| 1 | 0.43219 | 2.0474 | 20.81 | ± 0.366 | ± 0.13 | ± 0.39 | ± 0.08 |
| 2 | 0.85265 | 4.0469 | 20.85 | ± 0.185 | ± 0.13 | ± 0.23 | ± 0.05 |
| 3 | 1.18754 | 5.6432 | 20.88 | ± 0.133 | ± 0.13 | ± 0.19 | ± 0.04 |
| 4 | 1.56043 | 7.4303 | 20.92 | ± 0.101 | ± 0.13 | ± 0.16 | ± 0.03 |
| 5 | 1.85319 | 8.8440 | 20.97 | ± 0.085 | ± 0.13 | ± 0.15 | ± 0.03 |
| Run 2 | | | | | | | |
| 1 | 0.44866 | 2.1162 | 20.72 | ± 0.354 | ± 0.13 | ± 0.38 | ± 0.08 |
| 2 | 0.76003 | 3.6065 | 20.85 | ± 0.208 | ± 0.13 | ± 0.25 | ± 0.05 |
| 3 | 1.17521 | 5.5810 | 20.86 | ± 0.134 | ± 0.13 | ± 0.19 | ± 0.04 |
| 4 | 1.54594 | 7.3760 | 20.96 | ± 0.102 | ± 0.13 | ± 0.16 | ± 0.03 |
| 5 | 2.02682 | 9.6711 | 20.97 | ± 0.078 | ± 0.13 | ± 0.15 | ± 0.03 |

^{a/} A = conversion factor: product of dilatometer capillary volume calibration and equivalent weight of the salt.

^{b/} Manipulation error, see Appendix I for discussion.

^{c/} Calibration error, see Appendix I for discussion.

from the density of seawater using Knudsen's Hydrographical
Tables (1901).

EXPERIMENTAL RESULTS

The partial equivalent volumes of salts in seawater have been determined at various temperatures and salinities and the data are summarized in Table II.

Of the data shown in Table II, only the results from the following salts will be used as the basic data for evaluating the temperature and salinity dependency of \bar{V}_s .

| | |
|---------------------------------|-----------------------------------|
| NaCl | MgSO ₄ |
| KCl | Ca(NO ₃) ₂ |
| Na ₂ SO ₄ | NaNO ₃ |
| K ₂ SO ₄ | KHCO ₃ |

The results of the Mg· acetate and Na· acetate runs were used as additional checks on the experimental method. The partial equivalent volume of MgSO₄ calculated from the Mg· acetate, Na· acetate, and Na₂SO₄ data were found to agree, within experimental error, with the partial equivalent volume actually measured for MgSO₄.

Partial Equivalent Volume Differences

The partial equivalent volume of a particular salt in solution is the summation of the volume contributions from the positive and negative ions. To obtain the partial equivalent volume of single

Table II. Summary of measured values of partial equivalent volumes (ml/eq) of salts in seawater.

| Salt | $S = 30.13^{\circ}/\infty$ | | $S = 34.46^{\circ}/\infty$ | | | $S = 40.07^{\circ}/\infty$ |
|----------------------------|----------------------------|-----------------------------|----------------------------|---------------------------|------------------|-----------------------------|
| | $0^{\text{a/}}$ | $t^{\circ}\text{C}$ 24.5 | 0 | $t^{\circ}\text{C}$ 10 | 24.5 | $t^{\circ}\text{C}$ 24.5 |
| NaCl | 15.89 ± 0.11 | 18.74 ± 0.07 | 15.94 ± 0.08 | 17.55 ± 0.08 | 18.82 ± 0.08 | 19.06 ± 0.09 |
| KCl | 26.52 ± 0.08 | 28.87 ± 0.15 | 26.59 ± 0.20 | 27.83 ± 0.18 | 29.08 ± 0.18 | 29.27 ± 0.20 |
| Na_2SO_4 | 6.55 ± 0.06 | 10.03 ± 0.08 | 6.98 ± 0.08 | 8.77 ± 0.10 | 10.41 ± 0.08 | 10.83 ± 0.07 |
| K_2SO_4 | 17.46 ± 0.12 | 20.50 ± 0.08 | 17.69 ± 0.09 | 19.17 ± 0.09 | 20.77 ± 0.09 | 21.07 ± 0.10 |
| MgSO_4 | -0.86 ± 0.22 | 1.07 ± 0.15 | -0.61 ± 0.17 | 0.27 ± 0.21 | 1.22 ± 0.20 | 1.71 ± 0.17 |
| KHCO_3 | | 36.92 ± 0.20 | 33.41 ± 0.15 | 35.49 ± 0.16 | 37.25 ± 0.21 | 37.56 ± 0.20 |
| NaNO_3 | | 30.13 ± 0.10 | 25.79 ± 0.15 | 27.70 ± 0.15 | 30.40 ± 0.10 | 30.58 ± 0.16 |
| $\text{Ca}(\text{NO}_3)_2$ | | 22.55 ± 0.18 | 18.91 ± 0.23 | 20.73 ± 0.25 | 22.48 ± 0.25 | 22.76 ± 0.20 |
| Mg · acetate | | 32.67 ± 0.24 | | | 32.74 ± 0.20 | 33.04 ± 0.24 |
| Na · acetate | | 41.96 ± 0.33 | | | 41.97 ± 0.30 | 42.33 ± 0.17 |
| KNO_3 | | 40.70 ± 0.24 | | | 40.65 ± 0.17 | 40.92 ± 0.16 |

^{a/} Determinations made at 0.80°C and corrected to 0°C (except for MgSO_4 which was made at 0°C).

ions, various authors have made different assumptions to permit the assignment of partial volumes to individual ions. Table III summarizes these assumptions.

Table III. Assumptions made in estimating the partial equivalent volumes of single ions.

| Author | Assumption |
|--------------------------|---|
| Wirth (1940a) | $\bar{V}_{K^+} = \bar{V}_{F^-}$ |
| Owen and Brinkley (1941) | $\bar{V}_{H^+} = 0$ |
| Zen (1957) | $\left[\bar{V}_{Cs^+} / \bar{V}_{Cl^-} \right]_{\text{infinite dilution}} = \left[V_{Cs^+} / V_{Cl^-} \right]_{\text{crystalline solid}}$ |

The assumptions listed in Table III lead to the removal of redundancy in the data presented by these three authors. The scheme to be described in this paper also removes redundancy in the partial volume data tabulation; however, it does not require any special assumptions. Consider the four salts Aa, Bb, Ab, and BA. If \bar{V}_{Aa} , \bar{V}_{Bb} , \bar{V}_{Ab} , and \bar{V}_{Ba} are experimentally determined, then the system has been overdetermined because of the following requirement:

$$\bar{V}_{Aa} + \bar{V}_{Bb} = \bar{V}_{Ab} + \bar{V}_{Ba}$$

The partial equivalent volume of any one of the above salts can be computed from a knowledge of the partial equivalent volumes of the other three salts, i. e. ,

$$\begin{aligned}\bar{V}_{Ab} &= \bar{V}_{Aa} + \bar{V}_{Bb} - \bar{V}_{Ba} \\ &= \bar{V}_{Aa} + \bar{V}_{(b-a)}\end{aligned}$$

The value of $\bar{V}_{(b-a)}$ is independent of B and is the difference between the partial equivalent volumes of salts of similar anions or cations.

For the data presented in this paper, Aa is taken as NaCl; therefore, for a salt Bc, \bar{V}_{Bc} can be computed from the following relation

$$\bar{V}_{Bc} = \bar{V}_{NaCl} + \bar{V}_{(B - Na^+)} + \bar{V}_{(c - Cl^-)}$$

A tabulation of the partial equivalent volume differences ($\bar{V}_{(B - Na^+)}$ and $\bar{V}_{(c - Cl^-)}$), represented by the symbol \bar{V}_{Δ} , for the following ion differences as a function of salinity and temperature can be found in Table IV.

$$\bar{V}_{(K^+ - Na^+)} \qquad \bar{V}_{(SO_4^{2-} - Cl^-)}$$

$$\bar{V}_{(Mg^{++} - Na^+)} \qquad \bar{V}_{(HCO_3^- - Cl^-)}$$

Table IV. Measured partial equivalent volume differences (ml/eq).

| Partial Volume | Common Ion | S = 30.13 ^o /∞ | | S = 34.46 ^o /∞ | | | S = 40.07 ^o /∞ |
|---|------------------------------|-------------------------------|----------------------|---------------------------|----------------------|----------------------|---------------------------|
| | | t ^o C | | t ^o C | | | t ^o C |
| | | 0 | 24.5 | 0 | 10 | 24.5 | 24.5 |
| \bar{V}_{NaCl} | | 15.89 ± 0.11 | 18.74 ± 0.07 | 15.94 ± 0.08 | 17.55 ± 0.08 | 18.82 ± 0.08 | 19.06 ± 0.09 |
| $\bar{V}_{(\text{K}^+ - \text{Na}^+)}$ | Cl ⁻ | 10.63 ± 0.13 | 10.13 ± 0.17 | 10.65 ± 0.21 | 10.28 ± 0.19 | 10.26 ± 0.19 | 10.21 ± 0.22 |
| $\bar{V}_{(\text{K}^+ - \text{Na}^+)}$ | SO ₄ ⁼ | 10.91 ± 0.13 | 10.47 ± 0.10 | 10.71 ± 0.12 | 10.40 ± 0.13 | 10.36 ± 0.12 | 10.24 ± 0.24 |
| $\bar{V}_{(\text{K}^+ - \text{Na}^+)}$ | ave ^{a/} | <u>10.77 ± 0.13</u> | <u>10.34 ± 0.12</u> | <u>10.69 ± 0.12</u> | <u>10.35 ± 0.12</u> | <u>10.32 ± 0.12</u> | <u>10.23 ± 0.18</u> |
| $\bar{V}_{(\text{Mg}^{++} - \text{Na}^+)}$ | SO ₄ ⁼ | - 7.41 ± 0.23 | - 8.96 ± 0.17 | - 7.59 ± 0.19 | - 8.50 ± 0.23 | - 9.19 ± 0.22 | - 9.12 ± 0.26 |
| $\bar{V}_{(\text{Ca}^{++} - \text{Na}^+)}$ | NO ₃ ⁻ | (- 6.70 ± 0.27) ^{b/} | - 7.58 ± 0.24 | - 6.88 ± 0.27 | - 6.97 ± 0.29 | - 7.92 ± 0.27 | - 7.82 ± 0.26 |
| $\bar{V}_{(\text{SO}_4^{=} - \text{Cl}^-)}$ | Na ⁺ | -9.34 ± 0.12 | - 8.71 ± 0.10 | - 8.96 ± 0.11 | - 8.78 ± 0.12 | - 8.41 ± 0.11 | - 8.23 ± 0.11 |
| $\bar{V}_{(\text{SO}_4^{=} - \text{Cl}^-)}$ | K ⁺ | -9.06 ± 0.15 | - 8.37 ± 0.17 | - 8.90 ± 0.21 | - 8.66 ± 0.20 | - 8.31 ± 0.20 | - 8.20 ± 0.22 |
| $\bar{V}_{(\text{SO}_4^{=} - \text{Cl}^-)}$ | ave ^{a/} | <u>-9.21 ± 0.12</u> | <u>- 8.58 ± 0.12</u> | <u>- 8.94 ± 0.12</u> | <u>- 8.73 ± 0.12</u> | <u>- 8.37 ± 0.12</u> | <u>- 8.22 ± 0.12</u> |
| $\bar{V}_{(\text{HCO}_3^- - \text{Cl}^-)}$ | K ⁺ | (6.70 ± 0.26) ^{b/} | 8.05 ± 0.25 | 6.82 ± 0.25 | 7.66 ± 0.24 | 8.17 ± 0.28 | 8.29 ± 0.28 |
| $\bar{V}_{(\text{NO}_3^- - \text{Cl}^-)}$ | Na ⁺ | (9.80 ± 0.15) ^{b/} | 11.39 ± 0.12 | 9.85 ± 0.17 | 10.15 ± 0.17 | 11.58 ± 0.12 | 11.52 ± 0.18 |
| $\bar{V}_{\text{sea salt}}$ | | 13.70 ± 0.09 | 16.31 ± 0.09 | 13.74 ± 0.09 | 15.20 ± 0.09 | 16.35 ± 0.09 | 16.62 ± 0.09 |

^{a/} Weighted averages.

^{b/} Computed (see Table V).

^{c/} Computed (see Table VII).

$$\bar{V}_{(\text{Ca}^{++} - \text{Na}^+)} \quad \bar{V}_{(\text{NO}_3^- - \text{Cl}^-)}$$

The advantage of presenting the results of this investigation as partial equivalent volume differences are: (1) the scheme is independent of assumptions and (2) combinations of certain partial equivalent volume differences with \bar{V}_{NaCl} enables one to compute the partial equivalent volumes of various salts that were not experimentally determined.

In this investigation, to obtain $\bar{V}_{(\text{K}^+ - \text{Na}^+)}$ and $\bar{V}_{(\text{SO}_4^{=} - \text{Cl}^-)}$, it would only have been necessary to determine \bar{V}_{NaCl} , \bar{V}_{KCl} , and $\bar{V}_{\text{Na}_2\text{SO}_4}$. However, $\bar{V}_{\text{K}_2\text{SO}_4}$ was also determined. Hence, $\bar{V}_{(\text{K}^+ - \text{Na}^+)}$ and $\bar{V}_{(\text{SO}_4^{=} - \text{Cl}^-)}$ have been overdetermined. The difference between $\bar{V}_{(\text{K}^+ - \text{Na}^+)}$ derived from sulfate salts versus that derived from the chlorides was within the experimental error (also true for $\bar{V}_{(\text{SO}_4^{=} - \text{Cl}^-)}$) thus providing a check on the experimental method. The underlined values of $\bar{V}_{(\text{K}^+ - \text{Na}^+)}$ and $\bar{V}_{(\text{SO}_4^{=} - \text{Cl}^-)}$ in Table IV were computed as weighted averages, with respect to the uncertainties in measured values, and represent the most reliable estimates of the partial volumes of $\text{K}^+ - \text{Na}^+$ and $\text{SO}_4^{=} - \text{Cl}^-$.

The results presented in Table IV can be expressed as a power series of the general form:

$$\bar{V}_s(S^{\circ}/\infty, t^{\circ}\text{C}) = \sum_{ij} a_{ij} S^{i,j} t^j$$

where $i = 0 \dots, n$

$j = 0 \dots, m$

To determine the significant terms in the above power series for the experimental results presented in this paper, the partial equivalent volume of sea salt was computed over a salinity range of 30 to 40^o/oo and a temperature range from 0^o to 25^oC using density data in Knudsen's Hydrographical Tables (1901)^{6/}. The values of $\bar{V}_{\text{sea salt}}$, computed from density data, were then fitted to the following form of the above power series:

$$\bar{V}_s (S^{\circ}/\text{oo}, t^{\circ}\text{C}) = a_{00} + a_{01}t + a_{02}t^2 + (a_{10} + a_{11}t)S \quad (2)$$

The maximum difference between calculated (Eq. (2)) and observed values, computed from density data, of $\bar{V}_{\text{sea salt}}$ was ± 0.01 ml/eq which is about the limit of precision for computing partial volumes using density data; hence, it can be concluded that higher order terms in salinity and temperature can be ignored in evaluating the partial equivalent volumes within the above temperature and salinity range.

The results presented in Table IV have been fitted to Eq. (2) and values of the coefficients a_{00} , a_{01} , a_{02} , a_{10} , and a_{11} can be

^{6/} See Appendix III for the computation of $\bar{V}_{\text{sea salt}}$ from density data.

found in Table V. It will be observed from Table II that there are insufficient data to compute the values of a_{11} for $\bar{V}_{(\text{Ca}^{++} - \text{Na}^+)}$, $\bar{V}_{(\text{HCO}_3^- - \text{Cl}^-)}$, and $\bar{V}_{(\text{NO}_3^- - \text{Cl}^-)}$; therefore, calculated values of the partial volumes for these ions using the constants presented in Table V will be in error near $S = 30^{\circ}/\text{oo}$ and $t = 0^{\circ}\text{C}$ due to the slight variation of the salinity coefficient with temperature. The magnitude of this error is about equal to the experimental error.

Calculated (Eq. (2)) and observed values of the partial equivalent volumes of NaCl , KCl , Na_2SO_4 , K_2SO_4 , and MgSO_4 are compared in Table VI. It can be seen that the differences between computed and observed values are less than the experimental error.

The interpretation of $\bar{V}_{(\text{HCO}_3^- - \text{Cl}^-)}$ in this work deserves special discussion. When \bar{V}_{KHCO_3} was determined, the pH of the seawater at the smallest salt addition was about 7.72 (initially the seawater was at pH 8.1). Therefore, \bar{V}_{KHCO_3} , determined in this study, is not the volume change referred solely to KHCO_3 at the initial conditions of the seawater, but contains a small volume contribution due to change in pH of the solution. The magnitude of this volume change cannot be determined from the results of this work.

The Computation of $\bar{V}_{\text{sea salt}}$

The partial equivalent volume of sea salt ($\bar{V}_{\text{sea salt}}$) has been

Table V. The partial equivalent volumes of salts in seawater: Salinity range 30-40^o/oo, temperature range 0^o-25^oC.

$$\bar{V}_{Bc} = \bar{V}_{NaCl} + \bar{V}_{(B - Na^+)} + \bar{V}_{(c - Cl^-)}$$

$$\bar{V}_s(S^o/oo, t^oC) = a_{00} + a_{01}t + a_{02}t^2 + (a_{10} + a_{11}t)S \pm \epsilon \quad \text{ml/eq}$$

| Partial Volume | a_{00} ml/eq | $a_{01} \times 10^2$ ml/(eq deg) | $a_{02} \times 10^2$ ml/(eq deg ²) | $a_{10} \times 10^2$ ml/(eq ^o /oo) | $a_{11} \times 10^2$ ml/(eq ^o /oo deg) | ϵ ml/eq |
|-------------------------------|-------------------|-------------------------------------|---|--|--|---------------------|
| \bar{V}_{NaCl} | 15.54 | 16.0 | -0.289 | 1.16 | 0.086 | ± 0.08 |
| $\bar{V}_{(K^+ - Na^+)}$ | 11.33 | -5.66 | 0.125 | -1.85 | 0.029 | ± 0.12 |
| $\bar{V}_{(Mg^{++} - Na^+)}$ | -6.16 | -14.9 | 0.207 | -4.16 | 0.110 | ± 0.20 |
| $\bar{V}_{(Ca^{++} - Na^+)}$ | -6.03 | 1.41 | -0.231 | -2.21 | 0.0 ^{a/} | ± 0.27 |
| $\bar{V}_{(SO_4^{=} - Cl^-)}$ | -11.09 | 5.78 | 0.0057 | 6.23 | -0.109 | ± 0.12 |
| $\bar{V}_{(HCO_3^- - Cl^-)}$ | 5.98 | 10.4 | -0.199 | 2.40 | 0.0 ^{a/} | ± 0.26 |
| $\bar{V}_{(NO_3^- - Cl^-)}$ | 9.44 | 0.448 | 0.255 | 1.19 | 0.0 ^{a/} | ± 0.15 |
| $\bar{V}_{sea\ salt}$ | 13.42 | 13.9 | -0.254 | 0.924 | 0.093 | ± 0.09 |

^{a/} Insufficient data to compute the value of a_{11} ; the error in the calculated partial volumes of these salts at $S = 30^o/oo$ and $t = 0^oC$ is about the magnitude of the experimental error.

Table VI. Comparison between calculated and observed values of \bar{V} for NaCl, KCl, Na₂SO₄, K₂SO₄, and MgSO₄.

| Salt | t °C | S ‰ | Calculated ml/eq | Observed ml/eq | Calc - Obs |
|---------------------------------|------|-------|---------------------|-------------------|------------|
| NaCl | 0 | 30.13 | 15.89 ± 0.08 | 15.89 ± 0.11 | 0.00 |
| | 0 | 34.46 | 15.94 ± 0.08 | 15.94 ± 0.08 | 0.00 |
| | 10 | 34.46 | 17.55 ± 0.08 | 17.55 ± 0.08 | 0.00 |
| | 24.5 | 30.13 | 18.72 ± 0.08 | 18.74 ± 0.07 | -0.02 |
| | 24.5 | 34.46 | 18.86 ± 0.08 | 18.82 ± 0.08 | +0.04 |
| | 24.5 | 40.07 | 19.04 ± 0.08 | 19.06 ± 0.09 | -0.02 |
| | 24.5 | 40.07 | 19.04 ± 0.08 | 19.06 ± 0.09 | -0.02 |
| KCl | 0 | 30.13 | 26.66 ± 0.14 | 26.52 ± 0.08 | +0.14 |
| | 0 | 34.46 | 26.63 ± 0.14 | 26.59 ± 0.20 | +0.04 |
| | 10 | 34.46 | 27.90 ± 0.14 | 27.83 ± 0.18 | +0.07 |
| | 24.5 | 30.13 | 29.07 ± 0.14 | 28.87 ± 0.15 | +0.20 |
| | 24.5 | 34.46 | 29.16 ± 0.14 | 29.08 ± 0.18 | +0.08 |
| | 24.5 | 40.07 | 29.36 ± 0.14 | 29.27 ± 0.20 | +0.09 |
| | 24.5 | 40.07 | 29.36 ± 0.14 | 29.27 ± 0.20 | +0.09 |
| Na ₂ SO ₄ | 0 | 30.13 | 6.68 ± 0.14 | 6.55 ± 0.06 | +0.13 |
| | 0 | 34.46 | 7.00 ± 0.14 | 6.98 ± 0.08 | +0.02 |
| | 10 | 34.46 | 8.82 ± 0.14 | 8.77 ± 0.10 | +0.05 |
| | 24.5 | 30.13 | 10.16 ± 0.14 | 10.03 ± 0.08 | +0.13 |
| | 24.5 | 34.46 | 10.45 ± 0.14 | 10.41 ± 0.08 | +0.04 |
| | 24.5 | 40.07 | 10.84 ± 0.14 | 10.83 ± 0.07 | +0.01 |
| | 24.5 | 40.07 | 10.84 ± 0.14 | 10.83 ± 0.07 | +0.01 |
| K ₂ SO ₄ | 0 | 30.13 | 17.45 ± 0.19 | 17.46 ± 0.12 | -0.01 |
| | 0 | 34.46 | 17.69 ± 0.19 | 17.69 ± 0.09 | 0.00 |
| | 10 | 34.46 | 19.17 ± 0.19 | 19.17 ± 0.09 | 0.00 |
| | 24.5 | 30.13 | 20.51 ± 0.19 | 20.50 ± 0.08 | +0.01 |
| | 24.5 | 34.46 | 20.75 ± 0.19 | 20.77 ± 0.09 | -0.02 |
| | 24.5 | 40.07 | 21.16 ± 0.19 | 21.07 ± 0.10 | +0.02 |
| | 24.5 | 40.07 | 21.16 ± 0.19 | 21.07 ± 0.10 | +0.02 |
| MgSO ₄ | 0 | 30.13 | -0.73 ± 0.24 | -0.86 ± 0.22 | +0.13 |
| | 0 | 34.46 | -0.59 ± 0.24 | -0.61 ± 0.17 | +0.02 |
| | 10 | 34.46 | 0.32 ± 0.24 | 0.27 ± 0.21 | +0.05 |
| | 24.5 | 30.13 | 1.14 ± 0.24 | 1.07 ± 0.15 | +0.07 |
| | 24.5 | 34.46 | 1.37 ± 0.24 | 1.22 ± 0.20 | +0.15 |
| | 24.5 | 40.07 | 1.67 ± 0.24 | 1.71 ± 0.17 | -0.04 |
| | 24.5 | 40.07 | 1.67 ± 0.24 | 1.71 ± 0.17 | -0.04 |

calculated from the experimental data contained in this paper. Sea salt is defined as an anhydrous mixture of salts whose ions bear the same ratio to chloride as is found in seawater. Using the formula of Lyman and Fleming (1940), seawater of a salinity of 35^o/oo contains 0.60536 equivalents per kg of seawater. $\bar{V}_{\text{sea salt}}$ was computed using the following expression

$$\bar{V}_{\text{sea salt}} = \bar{V}_{\text{NaCl}} + \sum_i x_i \bar{V}_{\Delta_i} \quad (3)$$

where x_i is the ratio of the concentration (n_i), in equivalents per kg of seawater, of an ion to the total equivalents of anion or cation per kg of seawater. Table VII shows a sample calculation of $\bar{V}_{\text{sea salt}}$ at $S = 34.46^{\circ}/\text{oo}$ and $t = 24.5^{\circ}\text{C}$. A tabulation of computed values of $\bar{V}_{\text{sea salt}}$ at various salinities and temperatures can be found in Table IV.

It will be noted from the calculations in Table VII that the volume contributions due to Br^- and F^- were computed as if they were Cl^- , while the Sr^{++} contribution was computed as if it were Mg^{++} . This introduces an uncertainty in the computation of $\bar{V}_{\text{sea salt}}$ which is negligible since the concentrations of these three ions are small. A difference of only 0.03 percent in the partial equivalent volume of sea salt is obtained if Sr^{++} had the same partial equivalent volume as Na^+ instead of Mg^{++} .

Table VII. Sample Calculation of $\bar{V}_{\text{sea salt}}$: $S = 34.46\text{‰}$, $t = 24.5^\circ\text{C}$.

$$\bar{V}_{\text{sea salt}} = \bar{V}_{\text{NaCl}} + \sum_i x_i \bar{V}_{\Delta_i}$$

| Ion | Concentration ^{a/} $\frac{n_i}{\text{eq}/(\text{kg SW})}$ | $x_i = \frac{n_i}{0.59602}$ | \bar{V}_{Δ_i} ml/eq | $x_i \bar{V}_{\Delta_i}$ ml/eq |
|-------------------------------|---|--|---------------------------------|------------------------------------|
| Cl ⁻ | 0.53747 | | | |
| Br ⁻ | 0.00081 | | | |
| SO ₄ ⁼ | 0.05537 | 0.09290 | - 8.37 ± 0.12 | - 0.778 ± 0.011 |
| HCO ₃ ⁻ | 0.00230 | 0.00386 | 8.17 ± 0.28 | 0.032 ± 0.001 |
| F ⁻ | <u>0.00007</u> 0.59602 | | | |
| Ca ⁺⁺ | 0.02004 | 0.03362 | - 7.92 ± 0.27 | - 0.266 ± 0.009 |
| Sr ⁺⁺ | 0.00030 | | | |
| Mg ⁺⁺ | 0.10503 | 0.17672 (Mg ⁺⁺ + Sr ⁺⁺) | - 9.19 ± 0.22 | - 1.624 ± 0.039 |
| K ⁺ | 0.00976 | 0.01638 | 10.32 ± 0.12 | 0.169 ± 0.002 |
| Na ⁺ | <u>0.46089</u> 0.59602 | | | |
| | | | $\sum_i x_i \bar{V}_{\Delta_i}$ | = -2.47 ± 0.04 ml/eq |
| | | | \bar{V}_{NaCl} | = 18.82 ± 0.08 ml/eq |
| | | | $\bar{V}_{\text{sea salt}}$ | = 16.35 ± 0.09 ^{c/} ml/eq |

^{a/} Computed from the formula of Lyman and Fleming (1940). ^{b/} See Table IV.

^{c/} Error computed as the square root of the sum of the squares of the errors.

The values of $\bar{V}_{\text{sea salt}}$ listed in Table IV have been fitted to an empirical equation of the same form as Eq. (2). The values of the constants a_{00} , a_{01} , a_{02} , a_{10} , and a_{11} can be found in Table V.

$\bar{V}_{\text{sea salt}}$ can be computed from density data in Knudsen's Hydrographical Tables (1901) and also from the work of Wirth (1904a). These two methods of obtaining $\bar{V}_{\text{sea salt}}$ will later be compared with values obtained from the summation of the partial volumes of the individual salts.

DISCUSSION

A comparison of the partial equivalent volumes in seawater and in a sodium chloride solution of the same ionic strength^{7/} as seawater is presented in Table VIII. Also shown in Table VIII are partial volumes at infinite dilution. The importance of ionic strength is that it takes into account the valence type of all the ions and is a measure of the gross electrostatic interactions of all the ions in solution.

The partial volumes in sodium chloride solution are estimates proposed by Owen and Brinkley (1941). They have estimated the partial equivalent volumes of salts in a 0.725 molal NaCl solution and they refer to this solution as "salt water" since it has the ionic strength of normal seawater. Their estimates are based on the measurements made by Wirth (1937, 1940b) for HCl, KCl, KBr, K_2SO_4 , and NaCl in sodium chloride solutions. From the behavior of these salts in NaCl solutions, Owen and Brinkley predicted the partial equivalent volumes of the major salts in seawater. As can

^{7/} The ionic strength (μ) of a solution was defined by Lewis and Randall (1923) as:

$$\mu = 1/2 \sum_i c_i z_i^2$$

where c_i and z_i are the molality and valence, respectively, of a particular ion i in solution.

Table VIII. Partial equivalent volumes (ml/eq) of salts in aqueous solutions at 25°C.

| Partial Volume | Infinite Dilution ^{a/} | NaCl Solution ^{b/} $\mu = 0.725$ | Seawater ^{c/} $\mu = 0.725$ | SW - NaCl Solution |
|---|---------------------------------|--|---|--------------------|
| \bar{V}_{NaCl} | 16.6 (0.2) | 19.0 | 18.89 ± 0.08 | -0.1 |
| $\bar{V}_{(\text{K}^+ - \text{Na}^+)}$ | 10.0 (0.6) | 10.3 | 10.29 ± 0.12 | 0.0 |
| $\bar{V}_{(\text{Mg}^{++} - \text{Na}^+)}$ | - 9.1 (0.3) | - 9.9 | $- 9.08 \pm 0.20$ | +0.8 |
| $\bar{V}_{(\text{Ca}^{++} - \text{Na}^+)}$ | - 7.7 (0.7) | - 7.7 | $- 7.90 \pm 0.27$ | -0.2 |
| $\bar{V}_{(\text{SO}_4^{=} - \text{Cl}^-)}$ | -11.0 (0.8) | - 8.6 | $- 8.38 \pm 0.12$ | +0.2 |
| $\bar{V}_{(\text{HCO}_3^- - \text{Cl}^-)}$ | 5.6 (0.5) | 6.4 | 8.18 ± 0.26 | +1.8 |
| $\bar{V}_{(\text{NO}_3^- - \text{Cl}^-)}$ | 11.4 (0.4) | 11.4 | 11.56 ± 0.15 | +0.2 |

^{a/} Data is average of three sources: Wirth (1940a), Owen and Brinkley (1941), and Zen (1957). Values in parenthesis indicate range of disagreement among authors.

^{b/} Data from Owen and Brinkley (1941) for "salt water". The concentration of the NaCl solution is 0.725 molal. \bar{V}_{NaCl} , $\bar{V}_{(\text{K}^+ - \text{Na}^+)}$, and $\bar{V}_{(\text{SO}_4^{=} - \text{Cl}^-)}$ represent results taken from experimental data; all other partial volumes are estimates based on the experimental results of Wirth (1937, 1940b).

^{c/} Partial volumes computed from Eq. (2), $S = 35.10 \text{ }^\circ/\text{oo}$.

be seen from Table VIII, the results of Owen and Brinkley are in good agreement with the work described in this paper; however, only comparisons of \bar{V}_{NaCl} , $\bar{V}_{(\text{K}^+ - \text{Na}^+)}$, and $\bar{V}_{(\text{SO}_4^{=2} - \text{Cl}^-)}$ are justified since these values in 0.725 molal NaCl represent actual experimental data. The inadequacy of Owen and Brinkley's model is shown by the disagreement in $\bar{V}_{(\text{Mg}^{++} - \text{Na}^+)}$ and $\bar{V}_{(\text{HCO}_3^- - \text{Cl}^-)}$ with the values reported in this paper.

The difference between $\bar{V}_{(\text{HCO}_3^- - \text{Cl}^-)}$ in seawater and that obtained from the estimates of Owen and Brinkley (Table VIII) is rather large. This difference may in part be due to the variation in the distribution of the carbonate species in seawater and in a NaCl solution containing a bicarbonate salt. For instance, at pH 7.7 (carbonate alkalinity 2.16 meq/l) the mole percents of the carbonate species in seawater are 1.8% H_2CO_3 , 93% HCO_3^- , and 5.2% $\text{CO}_3^{=2}$, while in a NaCl solution (0.725 molal) the proportions are 1.8% H_2CO_3 , 97% HCO_3^- , and 1.2% $\text{CO}_3^{=2}$. Therefore, seawater contains about five times as much $\text{CO}_3^{=2}$ as would be found in a NaCl solution of the same carbonate alkalinity as seawater; however, the actual $\text{CO}_3^{=2}$ concentration in either solution is small compared to the total carbon dioxide concentration. Hence, this leads one to suspect that the partial volume of carbonate complexes (about 90 percent of the carbonate ion in seawater is in the form of complexes) is large. Additional experimental determinations of $\bar{V}_{(\text{HCO}_3^- - \text{Cl}^-)}$ and

$\bar{V}_{(\text{CO}_3^{2-} - \text{Cl}^-)}$ in NaCl solutions and in seawater are needed to reach a more definite conclusion on the partial volume of carbonate complexes.

An attempt to determine the partial equivalent volume of $\bar{V}_{\text{Na}_2\text{CO}_3}$ was unsuccessful because of the precipitation of CaCO_3 immediately following the addition of the salt to the dilatometer^{8/}. However, it was observed during \bar{V}_{KHCO_3} determinations that nucleation of CaCO_3 occurred about two hours after the KHCO_3 salt additions had been made. It was observed that the volume of the solution increased as a result of the precipitation of CaCO_3 . However, the volume change could not be quantitatively determined because the precipitation of CaCO_3 was followed by the evolution of CO_2 .

Partial Equivalent Volume of Sea Salt

The partial equivalent volume of sea salt has been previously calculated (Eq. (3), Table VII) based on the concentrations of the major ions in seawater and the data contained in this paper. The variation of $\bar{V}_{\text{sea salt}}$ with temperature is shown in Figure 2. The

^{8/} As outlined in Appendix I, salt is introduced into the capillary bulb of the dilatometer and then washed into the bulk of the solution by manipulation of the seawater level. When Na_2CO_3 is added to the wash bulb and then washed into the bulk of the solution with seawater, CaCO_3 immediately precipitates and fouls the surfaces of the capillaries.

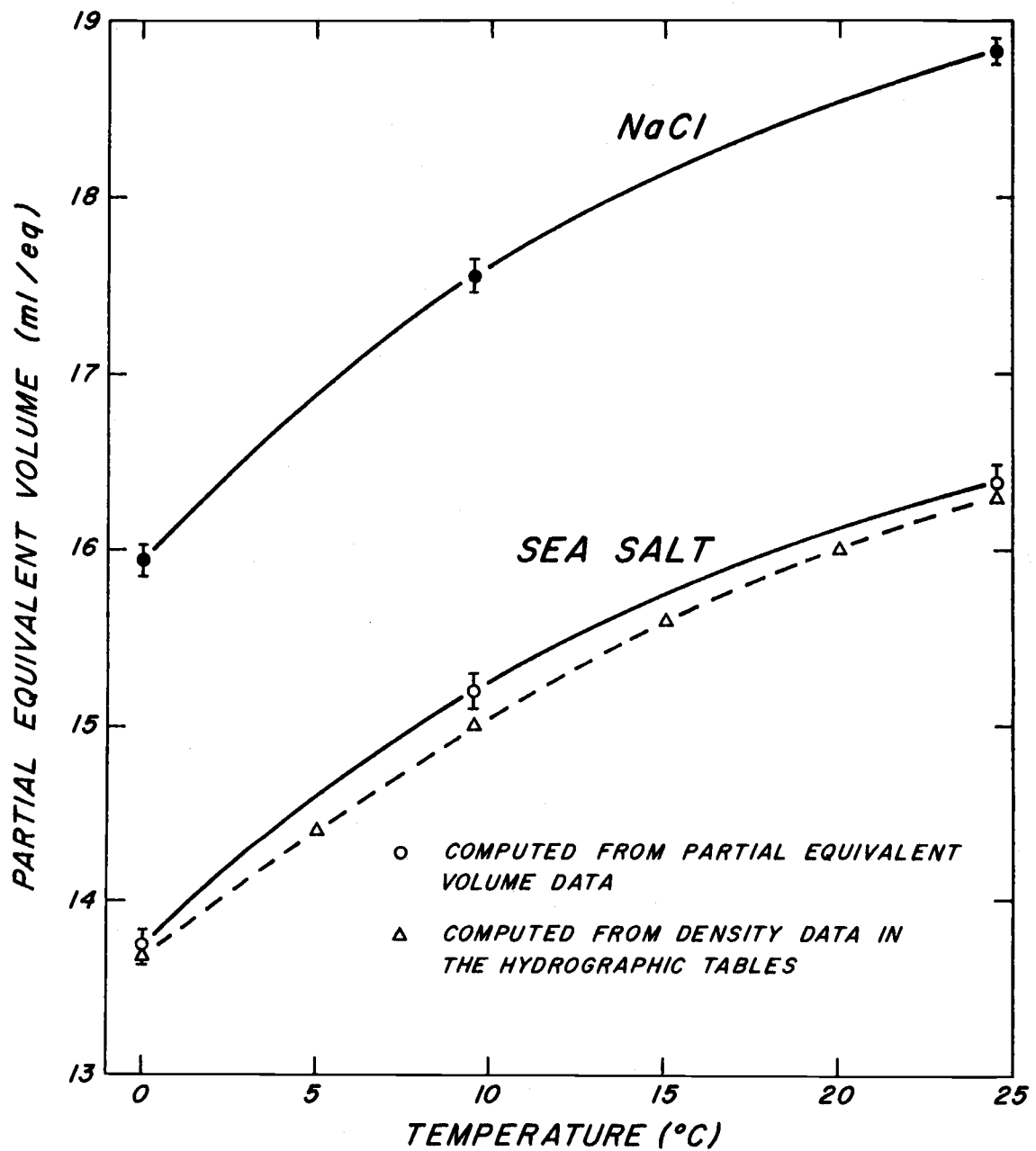


Figure 2. Temperature dependency of the partial equivalent volume of NaCl and sea salt at $S = 34.46^{\circ}/\text{oo}$.

curve indicates a large temperature dependency of $\bar{V}_{\text{sea salt}}$ which probably accounts for the high thermal expansion of seawater versus pure water. Also shown in Figure 2 is the temperature dependency of \bar{V}_{NaCl} . It will be observed that the two curves, NaCl and sea salt, are approximately the same shape and that the sea salt curve is displaced slightly lower than the NaCl curve. The similarity between the two sets of data is due to the fact the Na^+ and Cl^- comprise about 85% of the total mass of sea salt per kg of seawater.

Wirth (1940a) has derived an equation for the partial equivalent volume of sea salt as a function of chlorosity^{9/} based on the data obtained at infinite dilution at 25°C. At $S = 34.46^{\circ}/\text{oo}$, Wirth obtains 16.45 ml/eq as the partial equivalent volume of sea salt while results of this work (Eq. (3)) give 16.43 ± 0.09 ml/eq. The close agreement between these two values is remarkable since they were determined by entirely different methods. The reason for the close agreement is probably due to the fact that NaCl is the major salt in seawater and that the partial equivalent volume of NaCl in a sodium chloride solution of the same ionic strength as seawater has nearly the same value as in seawater (Table VIII).

$\bar{V}_{\text{sea salt}}$ has been computed from data appearing in Knudsen's

^{9/} Chlorosity is defined as chlorinity per liter of seawater at 20°C. Chlorosity is obtained by multiplying the chlorinity of seawater by its density at 20°C.

Hydrographical Tables (Appendix III). This analysis considers seawater as a two-component system comprised of sea salt and water. The values of $\bar{V}_{\text{sea salt}}$ computed from the density tables were found to be in good agreement with the values obtained by summing the partial equivalent volumes of the major salts in seawater (Eq. (3)). Table IX summarizes the various computed values of $\bar{V}_{\text{sea salt}}$ with the values obtained from the work described in this paper.

Table IX. Partial equivalent volume (ml/eq) of sea salt:
 $S = 34.46^{\circ}/\text{oo}$.

| Source | Temperature $^{\circ}\text{C}$ | | |
|--|--------------------------------|------------------|------------------|
| | 0 | 10 | 25 |
| Hydrographic Tables (Appendix III) | 13.7 | 15.0 | 16.3 |
| Wirth (1940a) | --- | --- | 16.45 |
| This work (Tables IV and V) | 13.74 ± 0.09 | 15.20 ± 0.09 | 16.43 ± 0.09 |

SUMMARY AND CONCLUSIONS

The objective of this investigation was to experimentally determine the partial equivalent volumes of the major salts in seawater. The results of this work are summarized:

1. The partial equivalent volumes, presented as differences between salts of similar anion or cation, of the major salts in seawater over a salinity range from 30-40^o/oo and a temperature range from 0^o-25^oC are given by the following empirical equation:

$$\bar{V}_s(S^o/oo, t^oC) = a_{00} + a_{01}t + a_{02}t^2 + (a_{10} + a_{11}t)S$$

Values of the constants a_{00} , a_{01} , a_{02} , a_{10} , and a_{11} can be found in Table V.

2. The partial equivalent volume of sea salt has been computed from the partial equivalent volumes of the salts in seawater.

$\bar{V}_{\text{sea salt}}$ was found to agree with the value computed from density data appearing in the Hydrographic Tables. The variation of

$\bar{V}_{\text{sea salt}}$ with salinity and temperature is given by an empirical equation of the same form as above.

In conclusion, the results presented in this paper can be used to gain a better understanding of the physical chemistry of seawater. The data are especially useful for a quantitative understanding of how the major salts in seawater affect the density of seawater. Probably

the most important application of the results of this work will be in using the partial volume data plus specific conductance data to compute the partial equivalent conductances of the major salts in seawater. This information is needed to gain a better understanding of the density-conductance correlation of seawater.

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APPENDICES

APPENDIX I

Apparatus for Determining the Partial Equivalent
Volumes of Salts in Seawater

Apparatus for Determining the Partial Equivalent Volumes
of Salts in Aqueous Solutions

by

Iver W. Duedall and Peter K. Weyl

Apparatus for Determining the Partial Equivalent Volumes of Salts in Aqueous Solutions

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An apparatus for determining partial equivalent volumes of salts in aqueous solutions is described. Using a cathetometer and a specially designed dilatometer, treated with an organic silicone fluid, the change in volume of a solution due to the addition of a small increment of salt is measured directly. The partial equivalent volume is determined by extrapolating the volume increments to zero salt addition. Results of the determination of the partial equivalent volume of sodium chloride in distilled water at 0.80°C are presented. Also, preliminary results for potassium chloride, sodium chloride, potassium sulfate, and sodium sulfate in sea water are discussed.

INTRODUCTION

THE partial equivalent volume of a solute in solution is given by the equation

$$\bar{U}_{S_1} = (\partial V / \partial n_1)_{T, P, n_2, \dots} \quad (1)$$

where \bar{U}_{S_1} is the increase in volume of an infinitely large volume of solution due to the addition of one equivalent of S_1 .

The most common method for determining the partial equivalent volumes of salts in aqueous solutions is to

measure the density of several solutions as a function of concentration. From a plot of density vs concentration, an empirical equation is derived to fit the data. This equation is typically nonlinear.

The pycnometer is often used to compare densities of aqueous solutions to that of pure water. The pycnometer, filled with a given solution, is placed into a constant temperature bath. After thermal equilibrium has been reached and the volume adjusted to a reference mark, the pycnometer is removed from the bath, dried, and then

weighed. It is obvious that this method is tedious and time consuming, especially if one wishes to determine the partial equivalent volumes of several salts as a function of temperature and salinity. Also, if the partial equivalent volume is to be determined within 1%, densities have to be accurately measured to about 5 parts in 10^5 .

Inconsistencies in the existing data on the partial equivalent volumes of salts in aqueous solution are shown by Zen.¹ He computed the partial equivalent volumes of some common salts from density data found in the *International Critical Tables* and compared his results with values reported by other workers also using density data. For the partial equivalent volume of sodium chloride at 0°C, the range of disagreement between the various workers is from 12.4 to 13.45 cm³/eq.

This paper describes a simple and rapid method for determining partial equivalent volumes of salts in aqueous solutions using a cathetometer and a specially designed dilatometer.

APPARATUS AND METHOD

The dilatometer (Fig. 1) was constructed from 2.54 mm i.d. precision bore tubing² and a 250 ml distillation flask. The length of each tube is approximately 10 cm. Thus, the total capillary volume is about 1 ml or 0.4% of the dilatometer volume. The hose clamp, the rubber hose joining the two T joints, and the screw-driven syringe assist in raising or lowering the position of the water level and equalizing both sides of the dilatometer. A glass enclosed magnetic stirring bar was placed inside the dilatometer.

A nonwetting surface on the inside of the glass was obtained by treating the apparatus with L-45,³ an organic silicone fluid. The dilatometer was flushed with a 1% solution of L-45 in carbon tetrachloride and baked at 300°C for 30 min.

The salt dispenser, also shown in Fig. 1, was constructed from a 15 cm length of 7 mm o.d. Pyrex glass tubing. It is filled with an increment of salt through a small opening near the middle of the dispenser. The glass bead, located at the bottom end of the dispenser, acts as a stopper and is fused on platinum wire that extends through the other end of the dispenser. The bead is under slight tension from a small stainless steel compression spring.

The main steps in the method are the following: (a) the dilatometer is filled with the desired solution and placed into a windowed constant temperature bath; (b) known increments of salt are introduced into the dilatometer by means of a salt dispenser, and the change in position of the menisci is measured with the cathetometer; (c) for each salt addition the cumulative volume change divided by the cumulative equivalents of salt added is

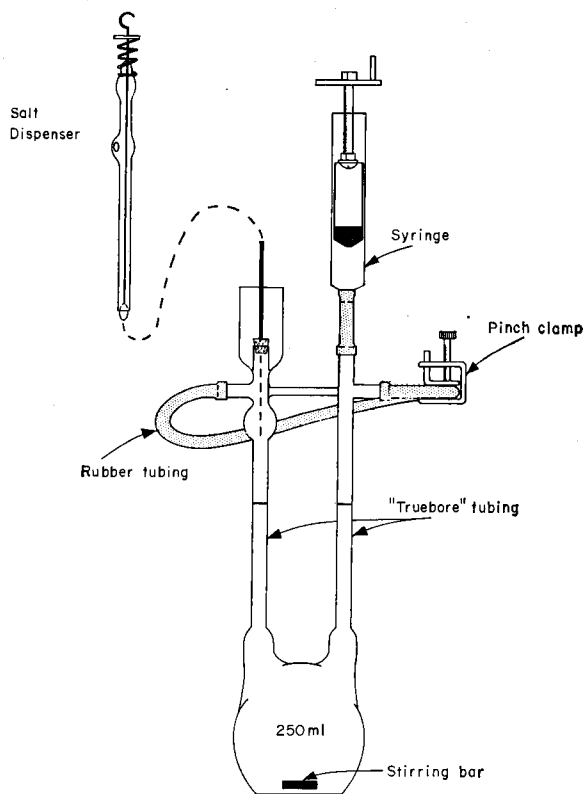


FIG. 1. The dilatometer and salt dispenser.

computed; and (d) the data are extrapolated to zero salt addition to determine the partial equivalent volume of the salt.

In an actual practice, the dilatometer was first filled with the desired solution, visually inspected to insure the absence of air bubbles, and then mounted securely inside a constant temperature bath having a front panel made of Thermopane window glass. The water level of the bath was regulated so that it did not overflow into the stopper chamber of the dilatometer. The temperature of the bath was measured with a Beckmann differential thermometer that had been calibrated with a platinum resistance thermometer. Temperature stability of $\pm 0.02^\circ\text{C}$ was maintained. After the above preliminary steps were made, about 0.3 g of dried, reagent grade salt was placed inside the salt dispenser. The salt dispenser plus its contents was weighed on an analytical balance. The initial level of each meniscus, with respect to a reference mark, was measured with the cathetometer and recorded. The salt dispenser was then slipped into the wash bulb of the dilatometer (Fig. 1). The spring tension on the glass bead holding the salt in the dispenser was momentarily released by depressing the spring located at the top of the dispenser, allowing the salt to fall freely into the wash bulb. The salt dispenser was removed from the dilatometer, dried, and reweighed. By closing the pinch clamp and manipulating the screw-driven syringe, the salt crystals were washed into the bulk of the solution. The siliconed surface insured that

¹ E-an Zen, *Geochim. Cosmochim. Acta* 12, 103 (1957).

² Truebore tubing, made by Ace Glass Inc., Vineland, New Jersey.

³ Union Carbide, Silicones Division, Los Angeles, California.

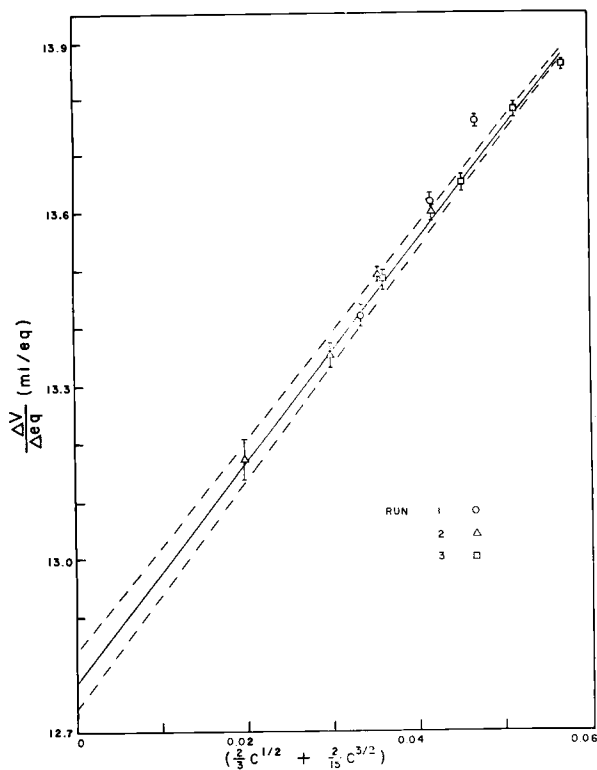


FIG. 2. Data from three experiments to determine the partial equivalent volume of sodium chloride in distilled water at 0.80°C. The partial equivalent volume at infinite dilution is the intercept value. Dashed lines indicate range of uncertainty.

no water was left behind on the walls of the wash bulb and capillaries. The magnetic stirring bar mechanism built into the constant temperature bath mixed the solution. After all the salt had gone into solution, the new menisci levels were measured with respect to the initial reference mark. When recording the initial and final menisci levels, triplicate readings were taken. The above procedure was repeated for each salt addition. The measurement of four additions of salt required only about 5 h of work in the laboratory.

CALIBRATION

The capillary volume of the dilatometer was calibrated with mercury by essentially the same technique used in adding the salt. An increment of mercury was placed inside the salt dispenser and allowed to drop into the dilatometer, thereby displacing an equal volume of water. From the increase in height of the water level in both capillaries, the mass of the mercury increment, and the specific volume of mercury at the bath temperature, a calibration factor was computed. The precision of the capillaries was determined by carrying out eight mercury additions. Random deviations from the average of eight calibration factors showed the tubing was not tapered. The mean of eight calibration factors was 0.05042 ml/cm. The standard deviation of the mean was ± 0.00005 ml/cm.

APPLICATION OF DATA TO THEORY

From Masson's⁴ empirical equation relating the partial molar volume of an electrolyte to the square root of its concentration and the Gibbs-Duhem equation, the partial equivalent volume of an electrolyte at infinite dilution can be found by graphical methods using the dilatometer data.

Masson's empirical equation is

$$\bar{U}_S = A + BC^{\frac{1}{2}}, \quad (2)$$

where A is the partial specific volume (ml/g) of S at infinite dilution, C is the concentration expressed as the mass fraction, B is a constant, and \bar{U}_S is the partial specific volume of S as a function of C . Differentiating Eq. (2) with respect to C gives the following:

$$(\partial \bar{U}_S / \partial C)_{T,P} = B/2C^{-\frac{1}{2}}. \quad (3)$$

The Gibbs-Duhem equation is

$$C(\partial \bar{U}_S / \partial C)_{T,P} + (1-C)(\partial \bar{U}_W / \partial C)_{T,P} = 0, \quad (4)$$

where \bar{U}_W is the partial specific volume of water. Substituting Eq. (3) into Eq. (4) and integrating gives

$$\bar{U}_W = \bar{U}_{W_0} - B/3C^{\frac{3}{2}} - B/5C^{\frac{5}{2}}, \quad (5)$$

where \bar{U}_{W_0} is the specific volume of pure water. The specific volume of a solution is given by the equation

$$V = (1-C)\bar{U}_W + C\bar{U}_S. \quad (6)$$

Therefore, substituting Eqs. (2) and (5) into Eq. (6) and simplifying, it follows that

$$[V - (1-C)\bar{U}_{W_0}] / C = A + B(\frac{2}{3}C^{\frac{1}{2}} + \frac{2}{15}C^{\frac{3}{2}}). \quad (7)$$

From a plot of $[V - (1-C)\bar{U}_{W_0}] / C$ vs $\frac{2}{3}C^{\frac{1}{2}} + \frac{2}{15}C^{\frac{3}{2}}$, the parameters A and B can be evaluated. Hence, the partial equivalent volume as a function of the concentration may be determined. The left side of Eq. (7) is the ratio of volume increment to mass increment for the salt additions. The units of A and B are changed from ml/g to ml/eq. by multiplying Eq. (7) by the equivalent weight of the salt.

RESULTS

Data obtained in three experiments to determine the partial equivalent volume of sodium chloride in distilled water at 0.80°C are shown in Fig. 2. The partial equivalent volume at infinite dilution was found to be 12.78 ml/eq. This number was determined by drawing the best straight line through the data and evaluating the intercept. The uncertainty in the intercept value is about ± 0.06 ml/eq.

The partial equivalent volume of sodium chloride determined by the method of this paper and similar values published by Zen¹ are summarized in Table I. It is readily seen that the partial equivalent volume of sodium chloride determined by the direct method compares favorably

⁴ D. O. Masson, *Phil. Mag.* 8, 218 (1929).

with values reported by workers using density data. Strictly speaking, it is not possible to make a direct comparison since Zen reported volumes at 0°C while our results are at 0.80°C. However, as shown in Zen's paper, the partial equivalent volume of sodium chloride increases only about 1%/degree centigrade.

Also good agreement in the value of the constant B in Eq. (2) was found. Zen reported B at 0°C as 19.08 cm³/eq. while this paper reports the value of B (the slope of line in Fig. 2) as 19.4 ml/eq.

DISCUSSION OF ERROR

The experimental error in the partial equivalent volume of sodium chloride was determined by estimating the range of uncertainty of the extrapolation to zero salt addition. The range of uncertainty comes from two sources: (1) the error in the volumetric calibration factor and (2) the error inherent in manipulation, which decreases as the number of salt additions increases. The error in the weight of salt added is considered negligible since weighings were made to an accuracy of ± 0.00005 g.

The error in the volumetric calibration factor was $\pm 0.1\%$ and was determined by computing the standard deviation of eight calibration factors.

The absolute error inherent in the manipulation was measured by carrying out five blank additions, recording the height of the water level after each blank addition had been made. The blank addition was made by completing all the steps described in the method except for the actual salt addition. If the dilatometer manipulation were ideal, no change in height would have occurred between blank additions. The absolute error in each of the five manipulations was computed from the average height of the water level. When the dilatometer was filled with distilled water, the manipulation changed the water level ± 0.003 cm. Hence if a first and a second salt addition each changed the water level by 3 cm, then a manipulation error of $\pm 0.1\%$ exists for the first addition while the manipulation error for the second addition is only $\pm 0.05\%$ since the data are evaluated for the cumulative change.

The relative error in each cumulative volume increment was determined by adding the relative error in the manipulation to the relative error in the calibration factor and computing the square root of the sum.

TABLE I. The partial equivalent volume (ml/eq.) of sodium chloride determined from density data and by the direct method described in this paper.

| | A | B | $t^\circ\text{C}$ |
|-----------------------------|------------------|----------------|-------------------|
| Direct method | 12.78 \pm 0.06 | 19.4 \pm 0.8 | 0.80 |
| Density method ^a | | | |
| Zen | 13.1 | 19.08 | 0 |
| Akerlöf and Bender | 12.57 | | 0 |
| Batuecus | 13.45 | | 0 |
| Geffcken | 12.4 | | 0 |
| Scott | 12.36 | | 0 |

^a See Ref. 1.

TABLE II. The partial equivalent volumes (ml/eq.) of some major salts in artificial sea water (salinity^a=30.13 ppt) at 0.80°C.

| Ion | Na ⁺ | K ⁺ | $\Delta(\text{K}^+ - \text{Na}^+)$ |
|---|------------------|------------------|------------------------------------|
| $\frac{1}{2}\text{SO}_4^{2-}$ | 6.72 \pm 0.06 | 17.60 \pm 0.12 | 10.88 \pm 0.18 |
| Cl ⁻ | 16.04 \pm 0.11 | 26.63 \pm 0.08 | 10.59 \pm 0.19 |
| $\Delta(\text{Cl}^- - \frac{1}{2}\text{SO}_4^{2-})$ | 9.32 \pm 0.17 | 9.03 \pm 0.20 | |

^a See Ref. 5.

The reproducibility of the data can be seen by examining the overlap of experimental error for the three sets of data shown in Fig. 2. The relative uncertainty in the extrapolated value is shown by the dotted lines.

Caution must be taken when handling the salt dispenser. Any loss of salt after initial weighings have been made would necessarily change the slope and the intercept of the line in Fig. 2. Hence, data are checked by running duplicate determinations.

PRELIMINARY RESULTS ON THE PARTIAL EQUIVALENT VOLUMES OF SALTS IN SEA WATER

The apparatus described in this paper provides a simple and rapid method for determining the partial equivalent volumes of the major salts in sea water as a function of salinity and temperature. The experimental method remains the same except that the dilatometer is filled with artificial sea water instead of distilled water. The partial equivalent volume of a particular salt in sea water is the rate of change in volume of the sea water with equivalents of salt added. This figure is determined from the intercept value (zero salt addition) of a plot of the ratio of cumulative volume changed to cumulative equivalents of salt added vs the mass of salt added.

Preliminary results for NaCl, KCl, Na₂SO₄, and K₂SO₄ in runs using artificial sea water [salinity⁵=30.13 parts per thousand (ppt)] at 0.80°C are listed in Table II. The data are arranged so that the constancy of ionic volumes in sea water can be checked. It is readily seen that the uncertainty in the data approaches the differences in the partial equivalent volumes of any two sets of salts. This suggests that the constancy of ionic volumes in solution is obeyed for sea water.

This work is being continued to determine the temperature and salinity dependency on the partial equivalent volumes of these and other major salts in sea water.

ACKNOWLEDGMENTS

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This paper describes part of Iver W. Duedall's thesis research for the M.S. degree in Chemical Oceanography at Oregon State University.

⁵ Term used by oceanographers expressing the concentration of sea water as the weight in grams of dry salt contained in 1000 g of the sea water.

APPENDIX II

Instructions for the Preparation of Artificial Seawater

(20 kg of S = 34.34^o/oo)

Lyman and Fleming (1940) Formula

| <u>Salt</u> | gm |
|---------------------------------|-----------|
| NaCl | 469.54 |
| MgCl ₂ | 99.62 |
| Na ₂ SO ₄ | 78.34 |
| CaCl ₂ | 22.04 |
| KCl | 13.28 |
| NaHCO ₃ | 3.84 |
| KBr | 1.92 |
| H ₃ BO ₃ | 0.52 |
| SrCl ₂ | 0.48 |
| NaF | 0.06 |
| H ₂ O to | 20,000.00 |

Step 1. Use the following reagent grade salts:

| | |
|---------------------------------------|---------------------------------------|
| NaCl | NaHCO ₃ |
| MgCl ₂ · 6H ₂ O | KBr |
| Na ₂ SO ₄ | H ₃ BO ₃ |
| CaCl ₂ · 2H ₂ O | SrCl ₂ · 6H ₂ O |
| KCl | NaF |

Step 2. Of the above list, oven dry only the following salts at 150^oC:

| | |
|---------------------------------|-----|
| NaCl | KBr |
| Na ₂ SO ₄ | NaF |
| KCl | |

APPENDIX II (Continued)

- Step 3. Prepare stock solutions of MgCl_2 , CaCl_2 , and SrCl_2 :
- MgCl_2 soln: add the contents of a one pound jar of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to a 2 liter volumetric flask and dilute to the mark.
 - CaCl_2 soln: add about 130 gm of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to a 1000 ml volumetric flask and dilute to the mark.
 - SrCl_2 soln: Add about 18 gm of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ to a 100 ml volumetric flask and dilute to the mark.
 - Estimate the molar concentration of chloride ion in each of the above stock solutions.
- Step 4. Prepare standard AgNO_3 solution:
- Prepare NaCl solution as a primary standard: 2.9225 gm dilute to 250 ml (0.2000 M)
 - Add about 17 gm of AgNO_3 to a 1 liter volumetric flask.
 - Carry out a Mohr determination of chloride (Blaedel and Meloche, 1957): to a 15 ml aliquot of standard NaCl soln, containing 3 drops of 0.002 M sodium chromate as the indicator, titrate with AgNO_3 . The end-point of the titration is a color change from yellow to pale orange. The pale orange color must persist for at least 1 minute. Carry out two additional titrations. The range between the three end-points should be about 2 ppt.
 - Compute the molar concentration of the AgNO_3 solution.
- Step 5. Carry out titrations of MgCl_2 , CaCl_2 , and SrCl_2 stock solutions:
- Take suitable aliquots of the stock solutions and carry out a titration of chloride using the Mohr method.
 - Compute molar concentration of Mg^{++} , Ca^{++} , and Sr^{++} from the chloride determination.

APPENDIX II (Continued)

- c. Determine the density of the MgCl_2 solution (use 50 ml volumetric flask and accurate balance). This information will be used later when it becomes necessary to know the mass of solution added.

Step 6. Mixing the salts:

- a. Obtain two carboys and a 2 liter volumetric flask.
- b. Label one carboy $\text{SO}_4^{=}$ and HCO_3^- . To this carboy add two liters of distilled water from the volumetric flask and the correct amount of Na_2SO_4 and NaHCO_3 as given by the Lyman and Fleming formula. Shake well to dissolve the salts. Volumetrically add another 4 liters of distilled water.
- c. To the other carboy add 4 liters of distilled water and the remaining salts. The order of the salt addition is not important. The salts that are prepared as stock solutions will be transferred volumetrically. Therefore, the number of moles of each salt per 20 kg of seawater divided by the respective molar concentration is the volume (in liters) added. The mass of each stock solution added is recorded. From the density of the MgCl_2 solution, the mass can be computed. Since only small amounts of CaCl_2 and SrCl_2 stock solutions were added their densities are assumed unity.
- d. At this point all the salts have been added to a given mass of water. Subtract the total mass of the solutions from 20 kg and the difference is the amount of water yet to be added (the mass of distilled water added is computed from density tables). Divide this difference equally between the two solutions in each carboy and shake well. Now transfer the contents of either carboy into the other and shake well.

- Step 7. Aeration of the solution: With one hole of a two-hole rubber stopper fitted with a glass-frit (submerged into the seawater) and the other connected to a vacuum source, introduce air into the solution. Aeration of the solution should be continued until the pH reaches about 8.15.

APPENDIX II (Continued)

- Step 8. Filtration of the solution: Since the salts used contain some insoluble compounds, the final solution should be filtered. A 0.45 micron Millipore filter is used.
- Step 9. Determine the salinity using a salinometer: The measured salinity should agree closely with the computed salinity.

APPENDIX III

Calculation of $\bar{V}_{\text{sea salt}}$ and $\bar{V}_{\text{H}_2\text{O}}$ from Density Data

Seawater can be considered a two-component system comprised of sea salt and water. The following derivations and computations illustrate the calculation of $\bar{V}_{\text{sea salt}}$ and $\bar{V}_{\text{H}_2\text{O}}$ from density data appearing in Knudsen's Hydrographical Tables (1901).

The specific volume of seawater is the sum of the partial volume of the water in seawater and the partial volume of sea salt:

$$V = (1 - C)\bar{V}_w + C\bar{V}_{\text{sea salt}} \quad (4)$$

where V = specific volume of seawater (ml/gm)

\bar{V}_w = partial specific volume (ml/gm) of water in seawater

$\bar{V}_{\text{sea salt}}$ = partial specific volume (ml/gm) of sea salt

C = salinity of seawater expressed as the mass fraction.

The Gibbs-Duhem equation is

$$(1 - C)\frac{\partial \bar{V}_w}{\partial C} + C\frac{\partial \bar{V}_{\text{sea salt}}}{\partial C} = 0. \quad (5)$$

Over the limited salinity range of 30 to 40^o/∞, $\bar{V}_{\text{sea salt}}$ is given by the linear equation

$$\bar{V}_{\text{sea salt}} = b_1 + b_2 C \quad (6)$$

where b_1 and b_2 are empirical constants to be determined.

APPENDIX III (Continued)

Differentiating Eq. (6) with respect to C gives the following:

$$\frac{\partial \bar{V}_{\text{sea salt}}}{\partial C} = b_2 \quad (7)$$

Substituting Eq. (7) into Eq. (5) and integrating gives

$$\bar{V}_w = b_0 - b_2 (C^2/2 + C^3/3) \quad (8)$$

where b_0 is an empirical constant valid over a given salinity range.

Therefore, substituting Eqs. (6) and (8) into Eq. (4) and simplifying, it follows that

$$V = b_0 + (b_1 - b_0)C + b_2 C^2/2 \quad (9)$$

Eq. (9) is second order in C and an evaluation of the constants b_0 , b_1 , and b_2 can be carried out in the following manner; consider the following three equations:

$$\begin{aligned} Y(x_1) &= c_0 + c_1 x_1 + c_2 x_1^2 \\ Y(x_1 + \xi) &= c_0 + c_1 (x_1 + \xi) + c_2 (x_1 + \xi)^2 \\ Y(x_1 - \xi) &= c_0 + c_1 (x_1 - \xi) + c_2 (x_1 - \xi)^2 \end{aligned} \quad (10)$$

APPENDIX III (Continued)

From Eqs. (9) and (10), it follows that

$$b_0 = c$$

$$(b_1 - b_0) = c_1$$

$$b_2/2 = c_2$$

It can be shown that the values of c_2 , c_1 , and c_0 can be computed using the following relationships:

$$c_2 = \frac{a - \beta}{2\xi^2} \quad (11)$$

$$c_1 = \frac{a + \beta - 2x_1 \left(\frac{a - \beta}{\xi} \right)}{2\xi} \quad (12)$$

$$c_0 = Y(x_1) - c_1 x_1 - c_2 x_2 \quad (13)$$

where

$$a = Y(x_1 + \xi) - Y(x_1)$$

$$\beta = Y(x_1) - Y(x_1 - \xi)$$

For $x_1 = 0.035$ and $\xi = 0.005$, values for c_0 , c_1 , and c_2 have been calculated at 0° , 5° , 10° , 15° , 20° , and 25°C and from these computations, b_0 , b_1 , and b_2 were determined. Table X summarizes

APPENDIX III (Continued)

these computations. Table XI presents values of \bar{V}_w at various salinities and temperatures.

Table X. Tabulation of empirical constants for Eqs. (6), (8), and (9).

| Temperature | b_0 | b_1 | b_2 |
|--------------------|----------|-------|-------|
| $^{\circ}\text{C}$ | ml/gm | ml/gm | ml/gm |
| 0 | 0.999780 | 0.211 | 0.76 |
| 5 | 0.999677 | 0.227 | 0.68 |
| 10 | 1.00001 | 0.237 | 0.68 |
| 15 | 1.00063 | 0.248 | 0.64 |
| 20 | 1.00155 | 0.256 | 0.60 |
| 25 | 1.00271 | 0.264 | 0.52 |

Table XI. Partial molar volume (ml/mole) of water in seawater: Computed from Eq. (8).

| Temperature | Salinity $^{\circ}/\text{oo}$ | | |
|-------------|-------------------------------|--------|--------|
| | $^{\circ}\text{C}$ | 30.13 | 34.46 |
| 0 | 18.006 | 18.004 | 18.001 |
| 10 | 18.010 | 18.009 | 18.007 |
| 24.5 | 18.058 | 18.057 | 18.055 |

APPENDIX III (Continued)

The results presented in Table X have been used to compute $\bar{V}_{\text{sea salt}}$ (Eq. (6)) over the salinity range of 30-40^o/oo and a temperature range of 0^o-25^oC. The values of $\bar{V}_{\text{sea salt}}$ were fitted to a power series of the following form:

$$\bar{V}_s (S^{\circ}/\text{oo}, t^{\circ}\text{C}) = a_{00} + a_{01}t + a_{02}t^2 + (a_{10} + a_{11}t)S \pm \epsilon$$

where $a_{00} = 12.17 \text{ ml/eq}$

$$a_{01} = 0.175 \text{ ml/(eq deg)}$$

$$a_{02} = -0.00207 \text{ ml/(eq deg}^2\text{)}$$

$$a_{10} = 0.0442 \text{ ml/(eq }^{\circ}\text{/oo)}$$

$$a_{11} = 0.000563 \text{ ml/(eq }^{\circ}\text{/oo deg)}$$

$$\epsilon = \pm 0.01 \text{ ml/eq.}$$