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# THE PROBLEM OF THE DENSITY OF SEA WATER

By

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## INTRODUCTION

### *The Density of Aqueous Solutions*

The density of a solution can be determined easily and is of interest not only for its own sake but also in the calculation of other physical quantities. Many investigators have therefore determined the density and concentration of aqueous solutions. Of the older works, those of Kohlrausch, Kohlrausch and Hallwachs, Baxter and Wallace, and Lamb and Lee are outstanding for their precision.

Many attempts have been made to interpret the observed variations in the volumes of solutions calculated from the densities. If it is assumed that the volume of the solvent is not changed in forming a solution then the increase in volume resulting from the addition of a solute represents the volume of that solute. The volume change referred to one mole is called the apparent molal volume and may be calculated using the relation:

$$\text{Apparent Molal Volume} = \Phi = \frac{V_{\text{solution}} - V_{\text{solvent}}}{C}$$

If the concentration ( $C$ ) is expressed as moles per liter of solution then  $V_{\text{solution}} = 1000$ ,  $V_{\text{solvent}} = \frac{1000 d_1 - CM}{d_0}$  where  $d_0$  is the density of the pure solvent,  $d_1$  is the density of the solution at the temperature in question and  $M$  is the molecular weight of the solute. Therefore:

$$\Phi = \frac{M}{d_0} - \frac{1000 (d_1 - d_0)}{C d_0} \quad \text{Eq. 1}$$

For non-electrolytes such as sugar the apparent molal volumes vary slightly with concentration and are of approximately the same magnitude as the volume of a mole of pure solute.

The apparent molal volumes of electrolytes change rapidly with concentration and in dilute solution are usually much less than the molal volume of the pure solute. In not a few instances negative values of  $\Phi$  are found (magnesium sulfate, sodium hydroxide). This

of course shows that the original assumption of constancy of volume of the solvent is incorrect. Attempts have been made to explain the changes in volume on solution in terms of the compression of the solvent by the charged ions (electrostriction). Baxter (1.) in reviewing the work up to 1911 sums up as follows: "The existing data show beyond question that the phenomena which take place are complex. Since these phenomena include both contraction and expansion at least two important influences must be at work . . . at any rate the following two changes take place during solution and dissociation: (a) The salt is freed in large part from compression due to chemical affinity and to molecular cohesion. (b) When the ions and probably the molecules are combined with water both the hydrated substance and the water undergo compression. The latter effect varies regularly with the compressibilities of the substances involved as well as their affinities for each other. . . ."

At least one very interesting property of the apparent molal volumes at infinite dilution ( $\Phi^\circ$ , obtained by extrapolation to zero concentration of the curve of  $\Phi$  vs. some function of the concentration) was discovered very early: the volumes are additive for the ions. While it is not possible to determine experimentally the volume of any ion,<sup>1</sup> the apparent molal volume at infinite dilution of any salt can be calculated from the values of three other properly chosen salts. For example,  $\Phi^\circ_{\text{K}_2\text{SO}_4} = 2\Phi^\circ_{\text{KCl}} + \Phi^\circ_{\text{Na}_2\text{SO}_4} - 2\Phi^\circ_{\text{NaCl}}$ . If an arbitrary value is assigned to the volume of any one ion the volumes of all other ions are determined.

The usefulness of the above concept was limited by lack of knowledge of the relationship between  $\Phi$  and  $C$ . It was not until 1929 that Masson (11.) discovered empirically that over very large concentration ranges the apparent molal volume is a linear function of the square root of the concentration:

$$\Phi = \Phi^\circ + mC^{1/2}.$$

It is very surprising that this relationship was not discovered much earlier. Kohlrausch and Hallwachs (8.) were looking for a relationship for apparent molal volumes and chose the cube root of the concentration as the variable, although Kohlrausch discovered the square root law for equivalent conductivity.

The Masson relationship was independently discovered by Geffcken (3.) and has been thoroughly checked by Scott (15.) and others.

<sup>1</sup>The equivalent conductivity of an electrolyte at infinite dilution is also an additive property of the conductivities of the ions. In this case knowledge of the transference numbers makes possible the assignment of definite values to the equivalent conductivity of each ion. No such method is available for  $\Phi$ .

Further advance was made when Redlich and Rosenfeld (13.) derived from the Debye-Hückel theory the relationship between the *partial* molal volume and the square root of the volume concentration. The Redlich-Rosenfeld equation not only gave the same concentration variable ( $C^{1/2}$ ) but also predicted the magnitude of the slope, the way in which valence type of the solute would affect the slope and the effect of change of solvent. The derived equation was:

$$\bar{V}_2 = V_2^0 + q\omega^{3/2}C_v^{1/2}$$

where  $q$  is a complex factor determined by the temperature and the properties of the solvent, and  $\omega$  is one-half the summation of the number of ions times the square of the valence of the ion. The equation may be rewritten:

$$\bar{V}_2 = V_2^0 + q\omega\mu_v^{1/2} \quad \text{Eq. 2}$$

where  $\omega C_v = \mu_v$ , the volume ionic strength of the solution. While applying strictly only to extremely dilute solutions the relationship has been of great value in interpreting results at moderate concentrations.

The partial molal volume referred to above is defined as the rate of change of the volume of the solution with respect to moles of a constituent ( $\bar{V}_n = \partial V / \partial n_n$ ). It is also the increase in volume of an infinite volume of solution due to the addition of one mole of the constituent being considered. At infinite dilution ( $C_v = 0$ ) the apparent and partial molal volumes become identical. At other concentrations the partial molal volumes can be calculated from the apparent molal volumes or the density data using methods developed by Gucker (5.) or Gibson (4.). For dilute solutions Geffcken (3.) has shown that  $q\omega^{3/2} = 3/2$  m. (Eq. 3). The partial molal volume of the solvent can be calculated from the partial molal volumes of the solutes.

As an important deduction from the relationship discovered by Masson, Root (14.) proposed the following equation for expressing the densities of solutions in terms of concentration:

$$d_1 = d_0 + a'C + b'C^{3/2} \quad \text{Eq. 4}$$

where  $a'$  and  $b'$  are constants. Over very wide concentration ranges it is sometimes necessary to include an additional term in  $C^2$  but ordinarily density data can be very accurately expressed by the simple Root formula. For purposes of plotting to establish the constants the equation can be rearranged to give

$$\frac{1000(d_1 - d_0)}{C} = a + bC^{1/2}. \quad \text{Eq. 5}$$

The densities of solutions containing more than one solute have been studied by but a few investigators. Two series of investigations however refer directly to the present discussion.

Bremner, Thompson and Utterback (2.) determined the densities of two mixtures (NaCl-KCl and NaCl-MgSO<sub>4</sub>) in which the ratios of the two salts were kept constant and at the value found in sea water. Their results were expressed by means of the Root equation where the variable was the total equivalent concentration.

Wirth (18.) has shown that the *partial* molal volumes of potassium chloride, potassium bromide and potassium sulfate in sodium chloride solutions depend on the total volume ionic strength of the solution as predicted by the Redlich-Rosenfeld equation. The apparent molal volumes are greater in the mixed solutions than in pure solutions of the same total concentration. The increase is roughly proportional to the concentration of the sodium chloride in the mixture. These results show the value of the partial molal volume over the apparent molal volume which has no real physical significance. In solutions containing two or more solutes the apparent molal volume of a given solute becomes more and more difficult to define and measure, whereas the partial molal volume is a definite determinable quantity no matter how many components are present.

### APPLICATION TO SEA WATER

The basic data of Knudsen and coworkers (7.) used in the preparation of the Hydrographic Tables were determined with extraordinary precision. The choice of samples, however, does not seem to be so fortunate as the density of dilute sea water is based entirely on samples from the Baltic Sea. Work by Thompson and Wirth (17.) showed that experimentally determined densities were higher by 0.02  $\sigma_0$  units than those calculated from the Knudsen equation. Use of 1930 atomic weights largely compensated for the difference. As samples of rather high chlorinity (18-22) were used, no check was made on the applicability of Knudsen's values to dilute sea water.

If the assumption of constant ion ratios in sea water is made then the total equivalent salt concentration present in any sample of sea water is given by the relation:  $C_v = k Cl_v$ .<sup>2</sup> Substituting in the Root equation, the density of sea water should be given by an equation of the type:

<sup>2</sup>It has been found that density relationships can be expressed more simply if volume concentrations are used. The chlorinity per liter ( $Cl_v$ ) will therefore be employed throughout the present discussion.

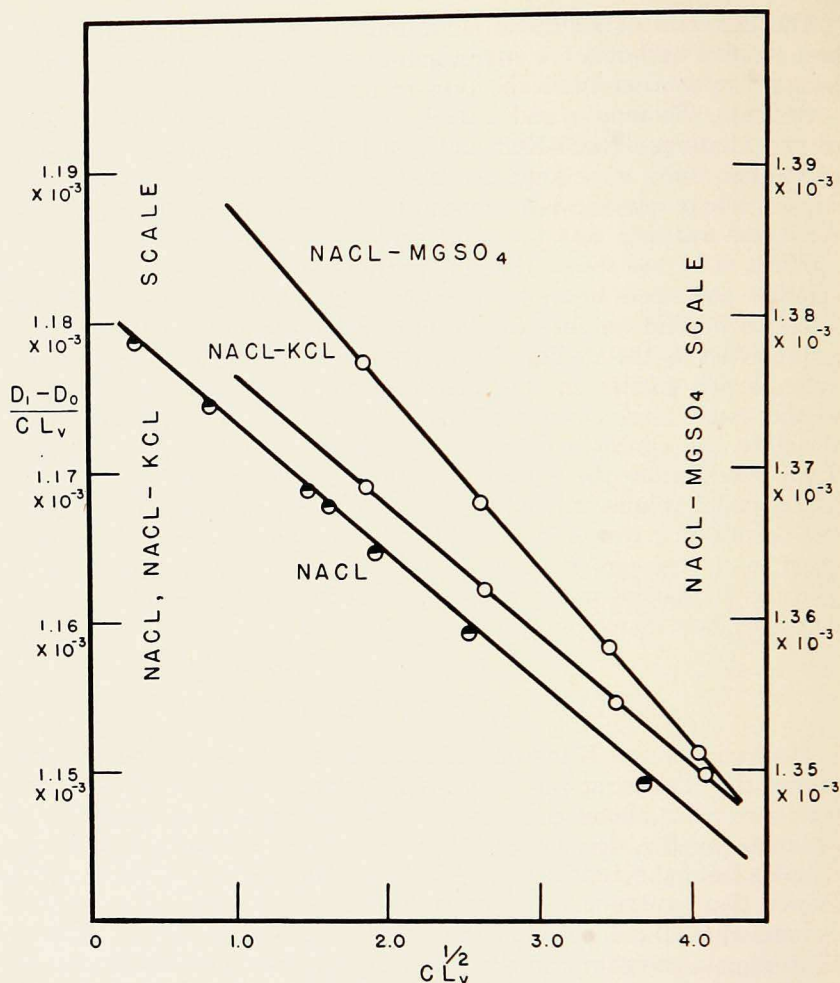


Figure 57. Results of Bremner, Thompson and Utterback for mixtures of NaCl and  $MgSO_4$ , and NaCl and KCl and for NaCl alone compared with the results of Kruis for NaCl. ( $25^\circ C.$ )

$$\frac{1000 (d_1 - d_0)}{C l_v} = A + B C l_v^{1/2} \quad \text{Eq. 6}$$

Figure 57 shows that the data of Bremner, Thompson and Utterback (2.) for mixtures of NaCl-KCl and NaCl- $MgSO_4$  (where the mole ratios were kept constant and only the total concentration varied) can be represented by such an equation with  $C l_v^{1/2}$  as the

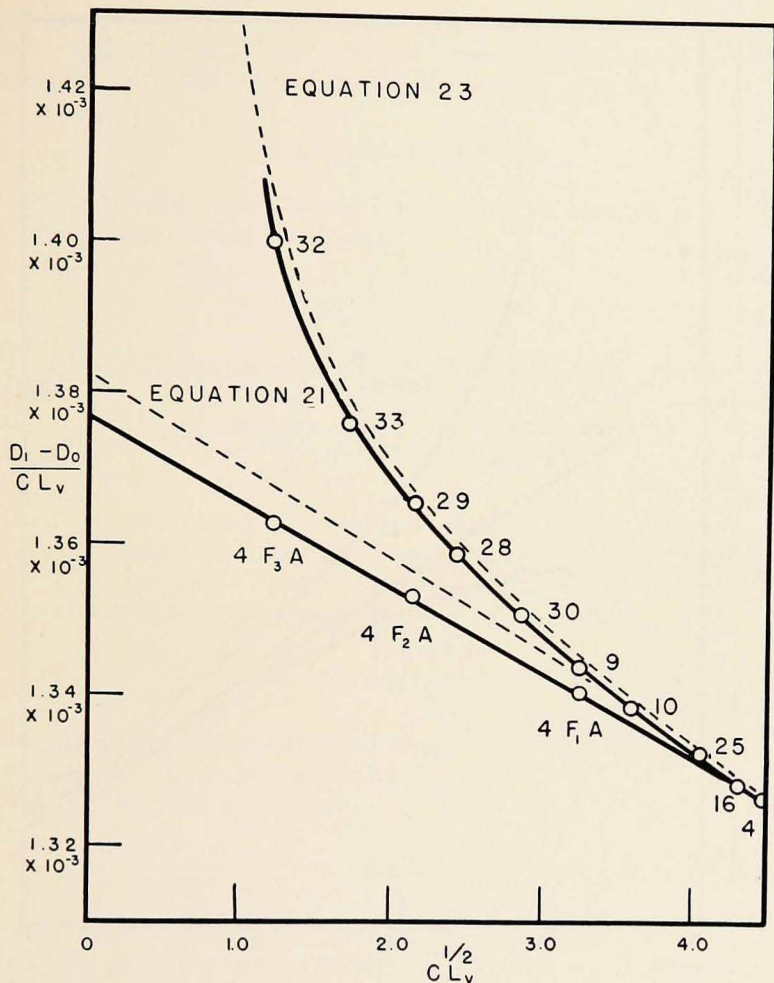


Figure 58. Experimental data of Knudsen for the density of sea water. (25° C.) Numbers are Knudsen's sample numbers. The 4F series was prepared by diluting Sample 4 with distilled water. The derived equations are represented by the dashed curves.

variable. On plotting the original data of Knudsen a curve is obtained which apparently will not intersect the Y-axis (Fig. 58).

Knudsen also determined the densities of a series of samples prepared by diluting a North Sea sample with distilled water. These values, also shown in Figure 58, deviate widely from the natural sea water from the Baltic Sea and can be represented by an equation of the correct theoretical form.

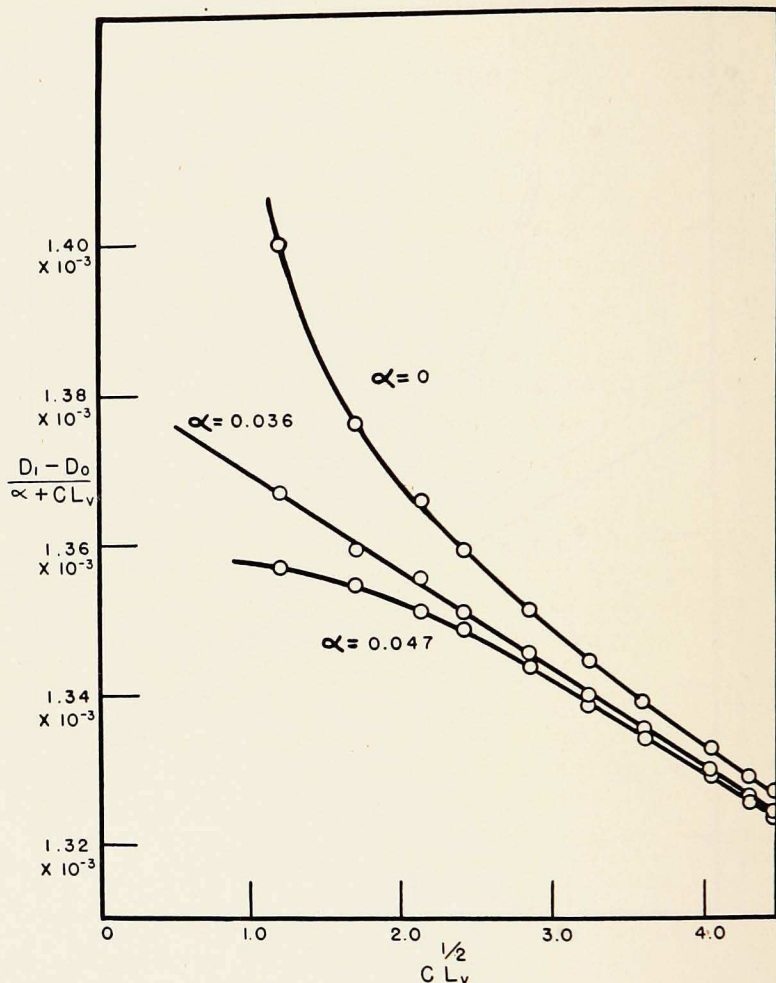


Figure 59. Experimental data of Knudsen plotted to establish the value of  $\alpha$ . (25° C.)

The wide spread between the curve for sea water diluted with distilled water and the natural sea water can be attributed to natural dilution with water containing relatively more dissolved salts in proportion to its chloride content than is found in sea water. This is of course the actual condition where sea water is diluted with river water which normally contains  $\text{CO}_3^{=}$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  and relatively little  $\text{Cl}^-$ . The effect of this dilution has been thoroughly discussed by Lyman and Fleming (10.) for the water of the Baltic and



they have developed equations giving the concentrations of the  $\text{SO}_4^-$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$  and  $\text{HCO}_3^-$  ions in terms of the chlorinity. These equations have the same form as the salinity equation of Knudsen and Sorensen (7.):

$$S = 0.030 + 1.8050 \text{ Cl}$$

If a concentration variable of this type is substituted in the Root equation, the following is obtained:

$$\frac{1000 (d_1 - d_0)}{\alpha + \text{Cl}_v} = A + B (\alpha + \text{Cl}_v)^{1/2}. \quad \text{Eq. 7}$$

If  $\alpha$  is small compared to  $\text{Cl}_v$  and  $B$  is also small compared with  $A$ , then

$$\frac{1000 (d_1 - d_0)}{\alpha + \text{Cl}_v} = A + B \text{Cl}_v^{1/2}. \quad \text{Eq. 8}$$

$\alpha$  can be determined by plotting various values of  $(d_1 - d_0)/(\alpha + \text{Cl}_v)$  against  $\text{Cl}_v^{1/2}$  and choosing the value of  $\alpha$  which most nearly gives a straight line. Figure 59 shows a series of such plots. At  $25^\circ \text{C}$ . the equation that will best fit the data of Knudsen is

$$\frac{1000 (d_1 - d_0)}{0.0360 + \text{Cl}_v} = 1.38271 - 0.013121 \text{Cl}_v^{1/2}. \quad \text{Eq. 9}$$

This represents the experimental data with an average deviation of five parts per million in the density.

At  $0^\circ \text{C}$ . the best equation is:

$$\frac{1000 (d_1 - d_0)}{0.0307 + \text{Cl}_v} = 1.49828 - 0.018289 \text{Cl}_v^{1/2}. \quad \text{Eq. 10}$$

This equation represents the experimental data with an average deviation of 3.7 parts per million in the density, whereas Knudsen's equation:

$$\sigma_0 = -0.069 + 1.4708 \text{ Cl} - 0.001570 \text{ Cl}^2 + 0.0000398 \text{ Cl}^3 \quad \text{Eq. 11}$$

represents the experimental data with an average deviation of 4.5 parts per million. Equation 10 has one less constant to be determined than Equation 11 and the constants can be obtained very accurately from large scale plots, whereas the method of least squares must be used in obtaining the constants in the Knudsen equation.

The value of  $\alpha$  obtained is very dependent on the most dilute sample. Slight errors in the density determination also have pro-

portionately greater effect on  $(d_1 - d_0)/(\alpha + Cl_v)$  at these low concentrations. It is not surprising that the values of  $\alpha$  are different at different temperatures.

The difference between the density of a diluted sea water found on the assumption (a) that the diluting water is distilled water and (b) that the diluting water is of the same kind as that diluting the Baltic amounts to about fifty parts per million when the chlorinity is less than ten. This is at least ten times the experimental error in the determination of density. Knudsen's equations should not be expected to give highly precise values where the character of the diluting water is unknown. It is to be emphasized that no criticism of the Knudsen relationships at relatively high chlorinities or for samples taken in the open sea is intended here. It is only where the sea water is greatly diluted that the applicability of constants found for the Finnish Gulf to any and all other diluting water is questioned.

#### DERIVATION OF THEORETICAL DENSITY EQUATION

Another approach to the problem is to attempt a calculation of the density of sea water from known densities of the constituents assuming (a) that the constituents are in constant ratio to the chlorinity or (b) that the concentrations of the constituents are given by the equations of Lyman and Fleming (10.).

The total volume of a sample of sea water is given by the relation

$$V = n_0 \bar{V}_0 + n_1 \bar{V}_1 + n_2 \bar{V}_2 + n_3 \bar{V}_3 + \dots \quad \text{Eq. 12}$$

where  $n_0$  is the number of moles of water,  $n_1, n_2, \dots$  are the number of moles of each salt present and  $\bar{V}_0, \bar{V}_1, \bar{V}_2, \dots$  are the corresponding values of the partial molal volumes. For the purposes of this discussion it is more convenient to consider  $n_1, n_2, \dots$  as the number of equivalents of each ion present while  $\bar{V}_1, \bar{V}_2, \dots$  would be the corresponding partial "equivalent" volumes of the ions. If we consider sea water to be a solution of a single salt, then the concentration of this salt is  $n (= \frac{1}{2}(n_1 + n_2 + n_3 + \dots)) = \frac{1}{2}\Sigma n_n$  and has a partial equivalent volume  $\bar{V}$ , so that

$$V = n_0 \bar{V}_0 + n \bar{V}. \quad \text{Eq. 13}$$

From equations 12 and 13:

$$\bar{V} = \frac{1}{\frac{1}{2}\Sigma n_n} (n_1 \bar{V}_1 + n_2 \bar{V}_2 + n_3 \bar{V}_3 + \dots). \quad \text{Eq. 14}$$

By analogy to Equation 2 each partial equivalent volume can be represented by an equation of the type:

$$\bar{V}_n = \bar{V}_n^0 + q_n \omega_n' \mu_v^{1/2} \quad \text{Eq. 15}$$

where  $\bar{V}_n^0$  is the partial (or apparent) equivalent volume of the ion at infinite dilution,  $\omega_n'$  is one-half the square of the valence of the ion divided by the valence,<sup>3</sup> and  $\mu_v$  is the volume ionic strength of the solution.

Equation 15 can be expected to hold with accuracy for the alkali salts in sea water and probably also for the alkaline earth salts. It is known to be incorrect for solutions of hydrochloric acid in sodium chloride, and it is to be expected that deviations will be found whenever the slope of the partial molal volume-square root of concentration curve for the single solute differs largely from that predicted by the Redlich-Rosenfeld equation. Wirth (19.).

Introducing equations 15 into Equation 14

$$\bar{V} = \frac{n_1}{\frac{1}{2}\sum n_n} (\bar{V}_1^0 + q_1 \omega_1' \mu_v^{1/2}) + \frac{n_2}{\frac{1}{2}\sum n_n} (\bar{V}_2^0 + q_2 \omega_2' \mu_v^{1/2}) + \dots \quad \text{Eq. 16}$$

which can be rearranged to give

$$\bar{V} = \frac{1}{\frac{1}{2}\sum n_n} (n_1 \bar{V}_1^0 + n_2 \bar{V}_2^0 + \dots) + \frac{\mu_v^{1/2}}{\frac{1}{2}\sum n_n} (n_1 q_1 \omega_1' + n_2 q_2 \omega_2' + \dots) \quad \text{Eq. 17}$$

The first term in Equation 17 is by analogy to Equation 14 equal to  $\bar{V}^0$ , the partial equivalent volume at infinite dilution of the theoretical salt present in sea water.

To evaluate the terms in Equation 17 either of two assumptions can be made. The first is that the ion ratios for the major ions present in sea water are constant. This should express the results found in the open ocean or for sea water diluted with distilled water. The second assumption is that the concentrations of the magnesium, calcium, sulfate and bicarbonate ions are given by equations of the form: Ion concentration =  $E + F \text{ Cl}_v$ . If the equations of Lyman and Fleming (10.) are used it should be possible to estimate the density of water from the Baltic Sea.<sup>4</sup>

<sup>3</sup>This takes into account the use of equivalent concentration as the variable.

<sup>4</sup>These equations are:

$$\text{SO}_4 \% = 0.0061 + 0.1391 \text{ Cl}\%$$

$$\text{Ca} \% = 0.0154 + 0.02025 \text{ Cl}\%$$

$$\text{Mg} \% = 0.0020 + 0.06684 \text{ Cl}\%$$

$$\text{HCO}_3 \% = 0.0493 + 0.004755 \text{ Cl}\%$$

Returning to the first assumption, in Table I are given the equivalent concentrations ( $n$ ) of each of the major ions in sea water of chlorinity 19.00 as taken from Table III of Lyman and Fleming. The concentration at any other chlorinity is assumed to be  $n \text{ Cl}_v/19.00$ . The total equivalent concentration ( $1/2 \sum n_n$ ) is 0.59360. The volume ionic strength ( $1/2 \sum \omega_n' n_n$ ) at  $\text{Cl}_v = 19.00$  is 0.68360 and at any other chlorinity is given by  $0.68360 \text{ Cl}_v/19.00$ .

In Table II are given the apparent (and partial) equivalent volumes at infinite dilution ( $\bar{V}_n^0$ ) of certain salts as calculated from density values appearing in the literature. On the assumption that the volume of the potassium ion equals the volume of the fluoride ion the individual partial equivalent volumes of the ions were calculated. The partial equivalent volume of the theoretical salt present in sea water ( $\bar{V}^0 = \sum n_n \bar{V}_n^0 / 1/2 \sum n_n$ ) was found to be 13.854. This value is quite independent of the assumption as to the volume of the potassium ion.

The experimentally determined slopes ( $\partial \Phi_n / \partial \mu_v^{1/2}$ ) for the single salts are also given in Table II. The slope for sodium chloride which has the greatest influence on the result was evaluated from the results of Kruis (9.) and of Wirth (19.) and represents the best value in the range 0.1–1.0 N, ignoring the change in slope at concentrations below 0.1 N. The value 16.56 for  $\bar{V}_{\text{NaCl}}^0$  is consistent with this slope. The slopes characteristic of the ions were then calculated using the assumption that  $\partial \Phi / \partial \mu_v^{1/2}$  for potassium ion equals  $\partial \Phi / \partial \mu_v^{1/2}$  for fluoride ion.  $\sum n_n (\partial \Phi / \partial \mu_v^{1/2}) / 1/2 \sum n_n$  was found to be 2.063. Applying Equation 3,  $\sum n_n q_n \omega_n' / 1/2 \sum n_n = 3/2 (2.063)$ .

Introducing these experimental values into Equation 17:

$$\begin{aligned} \bar{V} &= 13.854 + 3/2 (2.063) (0.68360/19.00)^{1/2} \text{Cl}_v^{1/2} \\ &= 13.854 + 3/2 (0.3913) \text{Cl}_v^{1/2} \end{aligned} \quad \text{Eq. 18}$$

The apparent equivalent volume of the theoretical salt in sea water will be given by:

$$\Phi = 13.854 + 0.3913 \text{Cl}_v^{1/2} \quad \text{Eq. 19}$$

Substituting in the defining equation for  $\Phi$  (Equation 1) where  $M$  is given by  $\sum n_n M_n / 1/2 \sum n_n = 58.044$  (Table I):

$$\begin{aligned} \frac{1000 (d_1 - d_0)}{\text{Cl}_v} &= \left[ \frac{58.044}{0.99707} - 13.854 - 0.3913 \text{Cl}_v^{1/2} \right] \frac{(0.99707)(0.5936)}{19.00} \\ &= 1.3819 - 0.01219 \text{Cl}_v^{1/2} \end{aligned} \quad \text{Eq. 20}$$

TABLE I

## COMPOSITION OF SEA WATER

(Based on Tables and Equations of Lyman and Fleming)

Ion	$n_n$	$n_n$ (Equiv./Liter)	$\omega_n n_n$	$\omega_n n_n$	$\frac{n_n M_n}{\frac{1}{2} \sum n_n}$	$n_n M_n$
	$Cl_v = 19$	As Function of $Cl_v$	$Cl_v = 19$	As Function of $Cl_v$		As Function of $Cl_v$
$Cl^-$	0.53529	0.028174 $Cl_v$	0.53529	0.028174 $Cl_v$	31.974	0.9989 $Cl_v$
$Br^-$	0.00081	0.000042 $Cl_v$	0.00081	0.000042 $Cl_v$	0.109	0.0034 $Cl_v$
$SO_4^{=}$	0.05514	0.000127 + 0.002896 $Cl_v$	0.11028	0.000254 + 0.005792 $Cl_v$	4.462	0.0061 + 0.1391 $Cl_v$
$HCO_3^-$	0.00229	0.000808 + 0.000078 $Cl_v$	0.00229	0.000808 + 0.000078 $Cl_v$	0.236	0.0493 + 0.0048 $Cl_v$
$F^-$	0.00007	0.000004 $Cl_v$	0.00007	0.000004 $Cl_v$	0.002	0.0001 $Cl_v$
$Ca^{++}$	0.01996	0.000769 + 0.001010 $Cl_v$	0.03992	0.001538 + 0.002020 $Cl_v$	0.673	0.0154 + 0.0203 $Cl_v$
$Mg^{++}$	0.10460	0.000165 + 0.005496 $Cl_v$	0.20920	0.000330 + 0.010992 $Cl_v$	2.143	0.0020 + 0.0668 $Cl_v$
$K^+$	0.00972	0.000512 $Cl_v$	0.00972	0.000512 $Cl_v$	0.640	0.0200 $Cl_v$
$Sr^{++}$	0.00030	0.000016 $Cl_v$	0.00060	0.000032 $Cl_v$	0.022	0.0007 $Cl_v$
$Na^+$	0.45902	0.024160 $Cl_v$	0.45902	0.024160 $Cl_v$	17.783	0.5556 $Cl_v$
$\Sigma =$	1.18720	0.00187 + 0.062386 $Cl_v$	1.36720	0.00293 + 0.071804 $Cl_v$	58.044	0.073 + 1.8096 $Cl_v$

TABLE II

EQUIVALENT VOLUMES OF SALTS IN SEA WATER (25°)

Salt	$\bar{V}_{salt}^0$	$\frac{\partial\Phi}{\partial\mu_v^{\frac{1}{2}}}$	Ion	$\bar{V}_{ion}^0$	$\frac{\partial\Phi}{\partial\mu_v^{\frac{1}{2}}}$	$\frac{n_n \bar{V}_n^0}{\frac{1}{2}\Sigma n_n}$	$n_n \bar{V}_n^0$ As Function of $Cl_v$	$\frac{n_n(\partial\Phi/\partial\mu_v^{\frac{1}{2}})}{\frac{1}{2}\Sigma n_n}$	$n_n(\partial\Phi/\partial\mu_v^{\frac{1}{2}})$ As Function of $Cl_v$	
<i>KCl</i>	26.74a	2.08	Cl <sup>-</sup>	23.44 <sub>0</sub>	0.41	21.138	0.66039 Cl <sub>v</sub>	0.370	0.01155 Cl <sub>v</sub>	
<i>NaCl</i>	16.56bc	1.945	Na <sup>+</sup>	- 6.88 <sub>0</sub>	1.535	-5.320	-0.16622 Cl <sub>v</sub>	1.187	0.03708 Cl <sub>v</sub>	
<i>KBr</i>	33.97a	1.85	Br <sup>-</sup>	30.67	0.18	0.042	0.00131 Cl <sub>v</sub>	0.000	0.00001 Cl <sub>v</sub>	
$\frac{1}{2}K_2SO_4$	16.14a	3.47	$\frac{1}{2}SO_4^{=}$	12.84	1.80	1.193	0.0016+0.03719 Cl <sub>v</sub>	0.167	0.00023+0.00522 Cl <sub>v</sub>	
<i>NaHCO<sub>3</sub></i>	22. d	3.	HCO <sub>3</sub> <sup>-</sup>	28.9	1.5	0.112	0.0233+0.00225 Cl <sub>v</sub>	0.006	0.00121+0.00012 Cl <sub>v</sub>	
<i>KF</i>	6.60e	3.35	F <sup>-</sup>	3.30	1.67	0.000	0.00001 Cl <sub>v</sub>	0.000	0.00001 Cl <sub>v</sub>	
$\frac{1}{2}CaCl_2$	8.43f	1.99	$\frac{1}{2}Ca^{++}$	-15.01	1.58	-0.505	-0.0116-0.01517 Cl <sub>v</sub>	0.053	0.00122+0.00160 Cl <sub>v</sub>	
$\frac{1}{2}MgCl_2$	7.25gh	1.84	$\frac{1}{2}Mg^{++}$	-16.19	1.43	-2.853	-0.0027-0.08900 Cl <sub>v</sub>	0.252	0.00024+0.00786 Cl <sub>v</sub>	
			K <sup>+</sup>	3.30	1.67	0.054	0.00169 Cl <sub>v</sub>	0.027	0.00085 Cl <sub>v</sub>	
$\frac{1}{2}SrCl_2$	9.35g	1.73	$\frac{1}{2}Sr^{++}$	-14.09	1.32	-0.007	-0.00022 Cl <sub>v</sub>	0.001	0.00002 Cl <sub>v</sub>	
						$\Sigma =$	13.854	0.0106+0.43223 Cl <sub>v</sub>	2.063	0.0029 +0.06432 Cl <sub>v</sub>

(a) Wirth (18), (b) Kruis (9), (c) Wirth (19), (d) International Critical Tables, (e) Geffcken (3), (f) Pesce (12), (g) Shedlovsky and Brown (16), (h) Herz (6).

In order to take into account the boric acid of which 0.004 moles are present in sea water of  $Cl_v = 19.00$ , it is assumed that its apparent molal volume does not depend on concentration and is equal to the molal volume of the solid (density of solid = 1.44). Then

$$\frac{1000 (d_1 - d_0)}{C} = M - \Phi d_0 = 61.8 - \frac{61.8}{1.44} = 18.7$$

$$\frac{1000 (d_1 - d_0)}{Cl_v} = \frac{(18.7)(0.0004)}{19.00} = 0.0004$$

Adding this to Equation 20,

$$\frac{1000 (d_1 - d_0)}{Cl_v} = 1.3823 - 0.01219 Cl_v^{1/2} \quad \text{Eq. 21}$$

Equation 21 is plotted in Figure 58 and compared with the values found by Knudsen for North Sea water diluted with distilled water. The intercept for  $Cl_v^{1/2} = 0$  is greater than the experimental value (1.3823 as compared with 1.3770). The calculated slope (0.01219) is greater than the experimental value (0.0112) by about 9%. Values of the density calculated using Equation 21 are compared with the experimental results of Knudsen in Table III. The maximum variation is 28 parts per million in the density.

The above calculation can be repeated on the assumption that the ion ratios for  $Ca^{++}$ ,  $Mg^{++}$ ,  $SO_4^-$  and  $HCO_3^-$  are not constant. In Table I the concentration in equivalents per liter (Column 3), the volume ionic strength (Column 5) and the equivalent weight of the salt present in sea water (Column 7) are given as functions of the chlorinity. In Table II the equivalent volume at infinite dilution and the slope of the apparent equivalent volume-square root of volume ionic strength curve are also represented as functions of the chlorinity.

Introducing these functions into Equation 17:

$$\bar{V} = \frac{0.0106 + 0.43223 Cl_v}{0.000935 + 0.031193 Cl_v} + \frac{3/2(0.00147 + 0.035902 Cl_v)^{1/2} (0.0029 + 0.06432 Cl_v)}{0.000935 + 0.031193 Cl_v} \quad \text{Eq. 22}$$

Substituting the corresponding equation for  $\Phi$  in Equation 1 and proceeding as before (Equations 19-20) the expression for the difference in density reduces to:

$$\frac{1000(d_1 - d_0)}{0.045 + Cl_v} = 1.3786 - 0.01215(0.041 + Cl_v)^{1/2}$$

Correcting for the boric acid in the same manner as before, the final equation becomes:

$$\frac{1000(d_1 - d_0)}{0.045 + Cl_v} = 1.3790 - 0.01215(0.041 + Cl_v)^{1/2} \quad \text{Eq. 23}$$

TABLE III

Knudsen's Sample No.	Cl <sup>o</sup> /∞	CALCULATED DENSITY OF SEA WATER				Difference
		Cl <sub>v</sub>	1000(d <sub>1</sub> -d <sub>0</sub> ) Eq. 21	1000(d <sub>1</sub> -d <sub>0</sub> ) Eq. 23	1000(d <sub>1</sub> -d <sub>0</sub> ) Observed Knudsen	
Sea Water Diluted With Distilled Water						
4	19.584	20.049	26.620		26.592	0.028
4F <sub>1a</sub>	10.441	10.559	14.177		14.158	0.019
4F <sub>2a</sub>	4.548	4.563	6.189		6.176	0.013
4F <sub>3a</sub>	1.508	1.507	2.061		2.053	0.008
Natural Sea Water						
23	22.237	22.846		30.237	30.212	0.025
21	20.415	20.923		27.450	27.731	0.019
4	19.584	20.049		26.615	26.592	0.023
16	18.142	18.537		24.649	24.626	0.023
25	16.020	16.323		21.766	21.752	0.014
10	12.842	13.030		17.455	17.443	0.012
9	10.410	10.528		14.163	14.150	0.013
30	8.089	8.155		11.022	11.017	0.005
28	5.837	5.867		7.978	7.973	0.005
29	4.608	4.624		6.316	6.314	0.002
33	2.927	2.931		4.041	4.033	0.008
32	1.474	1.473		2.070	2.062	0.008

In Table III the density differences calculated from this derived equation are compared with the experimental values of Knudsen (7.). Throughout the whole range of chlorinities the maximum difference found between the calculated and observed values is only 25 parts per million in the density. Equation 23 is also plotted in Figure 58.

It is very interesting that the calculated densities are uniformly higher than those found by Knudsen. This agrees almost exactly with the variation found experimentally by Thompson and Wirth (17.) at 0° C.

The excellent agreement obtained indicates that the Lyman and Fleming equations correctly represent the concentration relationships



in the Baltic Sea. It also shows the correctness of the method developed for obtaining the density of complex mixtures when the concentration can be expressed as a function of a single variable.

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### SUMMARY

The original data of Knudsen on which the Hydrographic Tables are based have been examined on the basis of the modern theory of the density of aqueous solutions. The data can be made to fit a curve of the correct theoretical form only if it is assumed that the diluting water has a relatively greater salt content than indicated by the chlorinity.

The constant characteristic of the diluting water is believed to be applicable only to the dilute sea water from the Baltic Sea.

Equations have been derived using known physical constants of the constituents of sea water on the assumptions that (a) the ion ratios are constant and that (b) the ion concentrations are given by the equations of Lyman and Fleming. The first assumption leads to an equation which represents the density of sea water diluted with distilled water, while the second assumption leads to an equation representing the density of sea water found in the Baltic.

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