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THE THERMODYNAMICS OF SEAWATER AT ONE ATMOSPHERE*

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ABSTRACT. The solution thermodynamic properties of seawater at 1 atm have been examined over the range of 0° to 40°C and 0 to 40‰ salinity. By combining the osmotic coefficients [$\phi = -(55.51/2m) \ln a_1$, where m is the molality and a_1 is the activity of water] determined from the freezing point measurements of Doherty and Kester (1974), with the heat capacity data of Millero, Perron, and Desnoyers (1973), and the enthalpy data of Millero, Hansen, and Hoff (1973), we have determined the osmotic coefficients over the range of 0° to 40°C at 1 atm using the extended Debye-Hückel equation

$$1 - \phi = 2.303\, S_\gamma I^{1/2}(\sigma/3) + B_\gamma I + C_\gamma I^{3/2} + D_\gamma I^2$$

where S_γ, B_γ, C_γ, and D_γ are temperature dependent parameters. The results at 25°C were found to be in excellent agreement with the results of Robinson (1954). From the osmotic coefficient data, the vapor pressure and osmotic pressure have been determined. The osmotic coefficient data at 0°C has been used to calculate the mean activity coefficient ($\gamma\pm$) and activity (a_2) of "sea salt". By using the thermodynamic equation $\partial \ln a_2/\partial T = -\bar{L}_2/RT$, activities have been determined at other temperatures (0° to 40°C). The relative free energies of seawater, $G - G^\circ = 55.51\ RT \ln a_1 + m\ RT \ln a_2$, have been calculated from the osmotic and activity data. The relative entropy of seawater ($S - S^\circ$) was determined from the relative free energies by using the thermodynamic relationship, $S - S^\circ = [(G - G^\circ) - (H - H^\circ)]/T$, where $H - H^\circ$ is the relative enthalpy. All the specific thermochemical properties (P) of seawater have been fitted to equations of the form

$$P = P^0 + A\, S(‰) + B\, S(‰)^{3/2}$$

where S(‰) is the salinity in parts per thousand, P^0 is the thermochemical property of water, and A and B are temperature dependent parameters.

INTRODUCTION

In recent years, a number of reliable measurements have been made on the thermochemical properties of seawater at 1 atm from 0° to 40°C. For example, reliable enthalpy (Bromley, 1968a; Bromley and others, 1970; Connors, 1970; Millero, Hansen, and Hoff, 1973; Singh and Bromley, 1973), heat capacity (Bromley, 1968b; Bromley and others, 1967; Cox and Smith, 1959; Millero, Perron, and Desnoyers, 1973), and freezing point data (Doherty and Kester, 1974; Kester, 1974; Fujino, Lewis, and Perkins, 1974) are available for seawater from 0° to 40°C and 0 to 40‰ salinity. From this thermochemical data, it is possible to characterize completely the thermodynamic properties of seawater. The purpose of this paper is to analyze completely this data and tabulate the most reliable thermodynamic data for seawater at 1 atm.

Thermodynamics of Seawater Solutions

When treating the thermodynamic properties of electrolyte solutions, it is convenient to use the concept of partial molal quantities (Lewis and Randall, 1961). Partial molal properties are useful when examining how

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the changes in composition affect a given extensive thermodynamic property. If (Y) is any extensive property (such as H, the enthalpy) which is the function of temperature (T), pressure (P), and the amounts of several components, the total differential is given by

$$dY = (\partial Y/\partial T)_{P,n_i}\, dT + (\partial Y/\partial P)_{T,n_i}\, dP + \sum_i (\partial Y/\partial n_i)_{T,P,n_{j\neq i}}\, dn_i \quad (1)$$

where n_i is the moles of component *i*. At a given temperature and pressure, we have

$$dY = (\partial Y/\partial n_1)\, dn_1 + (\partial Y/\partial n_2)\, dn_2 + \ldots \quad (2)$$

The derivatives of Y are given by

$$(\partial Y/\partial n_i)_{T,P,n_{j\neq i}} = \overline{Y}_i \quad (3)$$

where $\overline{Y}_i$ is the partial molal property. Substituting equation (3) for each constituent into equation (2), we have the general equation

$$dY = \overline{Y}_1\, dn_1 + \overline{Y}_2\, dn_2 + \ldots \quad (4)$$

where $\overline{Y}_1$, $\overline{Y}_2$, et cetera are intensive properties. By using the Euler equation, we have

$$Y = n_1\, \overline{Y}_1 + n_2\, \overline{Y}_2 + \ldots \quad (5)$$

This equation can be used to define the composition of any thermodynamic property Y in terms of the components 1, 2, et cetera. If we differentiate equation (5) and combine it with equation (4), we obtain

$$n_1\, d\overline{Y}_1 + n_2\, d\overline{Y}_2 + \ldots = 0 \quad (6)$$

If we regard the moles of one constituent, say n_2, as the main composition variable, we have upon differentiation of equation (6)

$$n_1\, (\partial \overline{Y}_1/\partial n_2) + n_2\, (\partial \overline{Y}_2/\partial n_2) + \ldots = 0 \quad (7)$$

which is called the Gibbs-Duhem equation. For a two component solution, this relationship is particularly useful, since upon rearranging we have

$$(\partial \overline{Y}_1/\partial n_2) \,/\, (\partial \overline{Y}_2/\partial n_2) = -\, n_2/n_1 \quad (8)$$

Thus, if $\overline{Y}_1$ and $\overline{Y}_2$ are plotted against n_2, the two differentials or slopes are interdependent. At $n_2 = n_1$, the slopes of the two curves must be equal and opposite in sign. It should be pointed out that for 1 mole of solution, n_1 and n_2 can be replaced by N_1 and N_2, the mole fractions of components 1 and 2.

The partial molal properties of solutions can be determined by a number of methods (Lewis and Randall, 1961). The use of the apparent molal property, Φ, is normally more convenient in determining partial

molal properties (Millero, 1971, 1972). The apparent molal property for a two component solution is defined by

$$\Phi = (Y - Y_{H_2O}) / n_2 \tag{9}$$

where Y_{H_2O} is the thermodynamic property of pure water. The quantity $(Y - Y_{H_2O})$ is the change one would measure in a given property when n_2 moles of solute are added to n_1 moles of water. By rearranging equation (9) and noting that $Y_{H_2O} = n_1 \overline{Y}_1^0$ (where $\overline{Y}_1^0$ is the partial molal property of pure water), we have

$$Y = n_1 \overline{Y}_1^0 + n_2 \Phi \tag{10}$$

By differentiating this equation with respect to n_2, we have

$$\overline{Y}_2 = \Phi + n_2 (\partial\Phi/\partial n_2)_{T,P,n_1} \tag{11}$$

From equation (5), we have for $\overline{Y}_1$

$$\overline{Y}_1 = (Y - n_2\overline{Y}_2) / n_1 = (1/n_1) [n_1 \overline{Y}_1^0 - n_2^2 (\partial\Phi/\partial n_2)] \tag{12}$$

Thus, if Φ is known as a function of n_2, both $\overline{Y}_1$ and $\overline{Y}_2$ can easily be determined. From equation (11) it is clear that at $n_2 = 0$, $\Phi^0 = \overline{Y}_2^0$ (the infinite dilution apparent molal property is equal to the infinite dilution partial molal property).

The ionic strength ($I = 1/2 \sum \nu_i m_i Z_i$, where Z_i is the charge, ν_i is the number, and m_i is the molality of ionic species i) dependence of the Φ for electrolyte solutions are frequently (Lewis and Randall, 1961; Robinson and Stokes, 1959; Harned and Owen, 1958) fitted to an extended Debye-Hückel equation (in order to determine partial molal properties and obtain reliable extrapolations to infinite dilution)

$$\Phi = \Phi^0 + SI^{1/2} [1/(1 + A\text{å } I^{1/2}) - \sigma/3] + BI + CI^{3/2} + \ldots \tag{13}$$

where S is the limiting law slope,

$$\sigma = (3/I^{3/2}) [(1 + I^{1/2}) - 1/(1 + I^{1/2}) - 2 \ln (1 + I^{1/2})] \tag{14}$$

and B and C are temperature dependent empirical parameters. The constants S and A are related to the dielectric constant of water, and å is called the ion size parameter (related to the distance of closest approach of ions). Since the ion size parameter cannot be measured or accurately estimated, the (Aå) term is usually fixed (some workers have treated å as an adjustable parameter — Whitfield, 1973). Values selected for (Aå) range from 1.0 to 1.5 (Robinson and Stokes, 1959; Harned and Owen, 1958). The values obtained for Φ^0 (as well as $\overline{Y}_1$ and $\overline{Y}_2$) are not greatly effected by the value selected for (Aå). For a molal solution, $n_1 = 1000/18.015 = 55.51$ and $n_2 = m$ (the molality); while the ionic strength $I = w\ m$, where w is the valence factor ($w = 1/2 \sum \nu_i Z_i^2$). Using these relations, it can be shown that the differentials of Φ with respect to

molality and ionic strength are given by $m\ \partial\Phi/\partial m = I\ \partial\Phi/\partial I$. Thus, the partial molal properties can be determined from equation (13) and its differential by substituting into equation (11) and (12)

$$\overline{Y}_2 = \Phi^0 + SI^{1/2}/(1 + I^{1/2}) + 2BI + 2.5CI^{3/2} + \ldots \quad (15)$$

$$\overline{Y}_1 = \overline{Y}_1^0 - (m/55.51)\ (\Phi - \overline{Y}_2) \quad (16)$$

Stoichiometry of Seawater

In all the thermodynamic calculations to be made in this paper we will be concerned with seawater of the fixed composition (Millero, 1976) given in table 1. We, thus, will consider the mean apparent and partial molal properties of "sea salt". The apparent and partial molal properties of sea salt are defined by

$$n_T\Phi = n_2\phi_2 + n_3\phi_3 + \ldots \quad (17)$$

$$n_T\overline{Y} = n_2\overline{Y}_2 + n_3\overline{Y}_3 + \ldots \quad (18)$$

where n_2, n_3, et cetera are the moles of the components of sea salts. Since the nonelectrolyte boric acid is one of the major components of seawater and the sea salts should balance in terms of equivalents, in our past work we have used another modification

$$e_T\Phi' = 1/2\ (\underset{\text{cations}}{\Sigma}\ e_i\phi'_i + \underset{\text{anions}}{\Sigma}\ e_i\phi'_j) + n_B\ \Phi'_B \quad (19)$$

where $e_T = 1/2\ (\Sigma\ e_i + \Sigma\ e_j) + n_B$, e_i is the equivalents of cation i, e_j is the equivalents of anion j, n_B is the number of moles of boric acid, and ϕ_B is the apparent molal volume of boric acid. Using similar reasoning for the molal properties, we have

$$n_T = 1/2\ (\Sigma n_i + \Sigma n_j) + n_B \quad (20)$$

TABLE 1

The composition of one kilogram of natural seawater at 25°C and pH = 8.1

Solute	g_i/Cl(‰)*	g_i, g/kg SW (Cl(‰) = 19.374)	m_i, mol/kg H_2O
Na^+	0.55653	10.7822	0.48609
Mg^{2+}	0.06626	1.2837	0.05474
Ca^{2+}	0.02127	0.4121	0.01066
K^+	0.02060	0.3991	0.01058
Sr^{2+}	0.00041	0.0079	0.00009
Cl^-	0.99891	19.3529	0.54577
SO_4^{2-}	0.14000	2.7124	0.02927
HCO_3^-	0.00586	0.1135	0.00193
Br^-	0.00347	0.0672	0.00087
CO_3^{2-}	0.00060	0.0116	0.00020
$B(OH)_4^-$	0.00034	0.0066	0.00009
F^-	0.00006_7	0.0013	0.00007
$B(OH)_3$	0.00105	0.0203	0.00034
	1.81536_7	35.1708	

* Taken from the compilation of Millero (1976).

When dealing with the prediction of the thermodynamic properties of seawater as well as other multicomponent electrolyte solutions containing different charge types, it is convenient to use apparent equivalent properties. The excess properties ($Y - Y^0$) are independent of the concentration units, that is

$$n_T\Phi = e_T\Phi' \tag{21}$$

The apparent and partial molal properties differ from the apparent and partial equivalent properties by a constant e_T/n_T (= 1.082 for seawater, Millero, 1976).

The molality and ionic strength of seawater are related to the salinity [S(‰) = 1.80655 Cl(‰); UNESCO, 1966], by

$$m = 16.0030\ S(‰) \ / \ [1000 - 1.004880\ S(‰)] \tag{22}$$

$$I = 19.9201\ S(‰) \ / \ [1000 - 1.004880\ S(‰)] \tag{23}$$

From the ratio of I/m the valence factor w is given by 1.245 (Millero, 1976). The molecular weight of sea salt ($M = \Sigma\ N_i\ M_i$, where N_i is the mole fraction and M_i is the molecular weight of constituent i) is equal to 62.793 (Millero, 1976). The total grams of sea salt per kilogram of seawater are related to the salinity by $g_T = 1.004880\ S(‰)$ (Millero, 1976).

In all the subsequent discussions of the thermodynamics of seawater, we shall consider the solution to be composed of two components: water (component 1) and sea salt (component 2). (that is, e_T and n_T will be replaced by e_2 and n_2).

The Enthalpy of Seawater

The enthalpy and its temperature dependence, the heat capacity, are quite useful thermodynamic functions since (as will be seen later) they can be used to estimate the effect of temperature on the activity of water (a_1) and the activity of sea salt (a_2) in seawater.

$$(\partial \ln a_1/\partial T) = -\bar{L}_1/RT^2 \tag{24}$$

$$(\partial \ln a_2/\partial T) = -\bar{L}_2/RT^2 \tag{25}$$

(where $\bar{L}_1$ and $\bar{L}_2$ are the relative partial molal enthalpies of water and sea salt). Much of the interest in the thermochemical properties of seawater solutions in recent years has been an attempt to understand the thermodynamics of multicomponent electrolyte solutions (Millero, 1974a, b). For very dilute solutions, the enthalpies of dilution follow the Debye-Hückel theory; however, at moderate concentrations the deviations from theory can be quite large. Many workers have examined these deviations and attempted to use various models to estimate or predict the thermochemical properties of seawater (Robinson and Wood, 1972; Millero, 1971, 1974a, b; Whitfield, 1973, 1974; Leyendekkers, 1973; Rush and Johnson, 1966; Millero, Perron, and Desnoyers, 1973). As discussed earlier, the thermochemical properties of seawater can be examined by treating

the solution as being a mixture of sea salt and water. The enthalpy of seawater (H) at a constant temperature and pressure is given by

$$H = n_1 \bar{H}_1 + n_2 \bar{H}_2 \tag{26}$$

where n_1 and n_2 are the moles of water and sea salt, and $\bar{H}_1$ and $\bar{H}_2$ are the partial molal enthalpy of water and sea salt given by

$$\bar{H}_1 = (\partial H/\partial n_1)_{T,P,n_2} \tag{27}$$

$$\bar{H}_2 = (\partial H/\partial n_2)_{T,P,n_1} \tag{28}$$

As with other partial molal quantities, it is more convenient to use the apparent molal enthalpy, Φ_H, defined by

$$\Phi_H = (H - n_1 \bar{H}_1^0) / n_2 \tag{29}$$

where $\bar{H}_1^0$ is the infinite dilution partial molal enthalpy of pure water. The apparent and partial molal enthalpies for sea salt are related by

$$\bar{H}_2 = \Phi_H + n_2 (\partial \Phi_H/\partial n_2)_{T,P,n_1} \tag{30}$$

Thus the infinite dilution partial molal enthalpy is equal to the apparent molal enthalpy, $\bar{H}_2^0 = \Phi_H^0$. Since absolute values of the enthalpy cannot be measured experimentally, it is necessary to use the corresponding relative enthalpies (relative to infinite dilution)

$$H - H^0 = n_1 (\bar{H}_1 - \bar{H}_1^0) + n_2 (\bar{H}_2 - \bar{H}_2^0) = n_2 (\Phi_H - \Phi_H^0) \tag{31}$$

The relative enthalpies can be redefined by $L = H - H^0$, $\bar{L}_1 = \bar{H}_1 - \bar{H}_1^0$, $\bar{L}_2 = \bar{H}_2 - \bar{H}_2^0$, and $\Phi_L = \Phi_H - \Phi_H^0$ which give

$$L = n_1 \bar{L}_1 + n_2 \bar{L}_2 = n_2 \Phi_L \tag{32}$$

The relative apparent molal enthalpy (Φ_L) is equal and opposite in sign to the heat of dilution (ΔH_{dil}) of one mole of sea salt with an infinite amount of water. That is

$$n_2 \Delta H_{dil} = - n_1 \bar{L}_1 - n_2 \bar{L}_2 = - n_2 \Phi_L \tag{33}$$

According to this definition, ΔH_{dil} is positive when the dilution process is accompanied by the absorption of heat.

By differentiating equation (32) with respect to n_2 (at constant T, P, and n_1), we obtain

$$\bar{L}_2 = (\partial L/\partial n_2)_{T,P,n_1} = \Phi_L + n_2 (\partial \Phi_L/\partial n_2) \tag{34}$$

Thus, $\bar{L}_2$ can be determined from the concentration dependence of Φ_L. The relative partial molal enthalpy of water ($\bar{L}_1$) in seawater can be obtained by combining equations (32) and (34).

$$\bar{L}_1 = (\partial \bar{L}/\partial n_1)_{P,T,n_2} = (-n_2^2/n_1) (\partial \Phi_L/\partial n_2) \tag{35}$$

To obtain reliable values for $\bar{L}_1$ and $\bar{L}_2$ it is necessary to have reliable Φ_L data in order to extrapolate the data to infinite dilution.

In recent years a number of workers have made measurements on the enthalpy of dilution of seawater. Connors (1970) derived an empirical equation for the relative specific enthalpy (h) as a function of temperature (0° to 30°C) and salinity (10 to 40‰). He used the heat capacity data of Cox and Smith (1959) together with his measured enthalpies of mixing (from 2° to 25°C) to generate the equation (in j g^{-1})

$$h = 4.2044t - 0.00057t^2 - S(‰)10^{-3}\,[6.99t - 0.0343t^2] - [S(‰)10^{-3}]^2\,[464 - 19.6t + 0.3t^2] \quad (36)$$

Since these enthalpies were not related to an infinite dilution reference state, they can only be used to examine differences in the enthalpy of seawater of different concentrations.

Bromley (1968a) measured the enthalpies of dilution of seawater over the salinity range of 0 to 120(‰) at 25°C. He fitted his results to an extended Debye-Hückel equation and determined the partial specific enthalpy of water and sea salt. More recently, Singh and Bromley (1973) measured the enthalpy of seawater at 3, 50, and 73°C from 0 to 120‰ salinity. They showed that their results were consistent with the heat capacity data of Bromley (1968b), Bromley and others (1967), and Bromley and others (1970) and the measurements of Connors. Millero, Hansen, and Hoff (1973) made extensive measurements on the enthalpy of dilution of seawater from 0 to 30°C and from 0 to 40(‰) salinity. They fitted their relative enthalpies of dilution to the extended Debye-Hückel equation

$$\Phi_L = S_H I^{1/2}\,[1/(1 + I^{1/2}) - \sigma/3] + B_H I + C_H I^{3/2} \quad (37)$$

where S_H is the Debye-Hückel limiting law slope (Lewis and Randall, 1961), I is the molal ionic strength, and σ is given by equation (14). The relative apparent molal enthalpy (Φ_L) for seawater solutions at 25°C obtained by Bromley (1967 and 1970) and Millero, Hansen, and Hoff is in agreement to within ± 20 j mol^{-1} (Millero, Hansen, and Hoff, 1973) over the concentration range of 0 to 40‰ salinity. This agreement is within the combined experimental errors of the measurements.

By differentiating equation (37) with respect to ionic strength, we obtain from equation (34) the relative partial molal enthalpy of sea salt

$$\bar{L}_2 = S_H\, I^{1/2}/(1 + I^{1/2}) + 2\, B_H\, I + 2.5\, C_H\, I^{3/2} \quad (38)$$

Values of $\bar{L}_2$ calculated from this equation using the S_H, B_H, and C_H constants given by Millero, Hansen, and Hoff (1973) agree with the results of Bromley and others (1967 and 1970) at 25°C to within ± 25 j mol^{-1}. The relative values of $\bar{L}_2$ between 40‰ and 30‰ salinity determined from equation (37) are also in reasonable agreement (within ± 37 j mol^{-1}) with the values determined from Connor's work (from eq 35).

The relative partial molal enthalpy of water in seawater ($\bar{L}_1$) can be calculated from the Φ_L and $\bar{L}_2$ values by combining equations (32), (34), and (35),

$$\bar{L}_1 = (n_2/n_1)\ (\Phi_L - \bar{L}_2) = (m/55.51)\ (\Phi_L - \bar{L}_2) \tag{39}$$

Values of $\bar{L}_1 \times 55.51$ (j kg^{-1} H_2O) determined by Millero, Hansen, and Hoff (1973) at 25°C agree with the results of Bromley and others (1967 and 1970) to within ± 21 j kg^{-1} H_2O.

The temperature dependencies of enthalpy of seawater are related to the relative heat capacities by the equations

$$\partial(\Phi_H - \Phi_H{}^0) / \partial T = (\partial\Phi_L/\partial T) = \Phi_{cp} - \Phi_{cp}{}^0 = \Phi_J \tag{40}$$

$$\partial(\bar{H}_2 - \bar{H}_2{}^0) / \partial T = (\partial\bar{L}_2/\partial T) = \bar{C}p_2 - \bar{C}p_2{}^0 = \bar{J}_2 \tag{41}$$

$$\partial(\bar{H}_1 - \bar{H}_1{}^0) / \partial T = (\partial\bar{L}_1/\partial T) = \bar{C}p_1 - \bar{C}p_1{}^0 = \bar{J}_1 \tag{42}$$

where Φ_{cp} is the apparent molal heat capacity of sea salt (described in the next section), Φ_J is the relative apparent molal heat capacity of sea salt, $\bar{C}p_2$ is the partial molal heat capacity of sea salt, $\bar{J}_2$ is the relative partial molal heat capacity of sea salt, $\bar{C}p_1$ is the partial molal heat capacity of water, and $\bar{J}_1$ is the relative partial molal heat capacity of water (the superscript zero refers to the reference state, infinite dilution). As is clear from these equations, the quantities Φ_J, $\bar{J}_2$, and $\bar{J}_1$ can be determined in two ways: (1) from the temperature dependence of enthalpy data, and (2) from heat capacity data. By comparing the values determined by the two methods, one can examine the reliability of the thermochemical data. The most reliable values of Φ_J, $\bar{J}_2$, and $\bar{J}_1$ can be determined from heat capacity data providing the extrapolations to infinite dilution are properly made. By differentiating equations (37) and (38) with respect to temperature, we have

$$\Phi_J = (\partial S_H/\partial T)\ I^{1/2}\ [1/(1 + I^{1/2}) - \sigma/3] + (\partial B_H/\partial T)\ I + (\partial C_H/\partial T)\ I^{3/2} \tag{43}$$

$$\bar{J}_2 = (\partial S_H/\partial T)\ [I^{1/2}/(1 + I^{1/2})] + 2(\partial B_H/\partial T)\ I + 2.5(\partial C_H/\partial T)\ I^{3/2} \tag{44}$$

Millero, Hansen, and Hoff (1973) have determined the Φ_J and $\bar{J}_2$ from these equations and showed that they are in good agreement (within ± 8 j $mol^{-1}deg^{-1}$) with the values determined from the heat capacity data of Bromley and others (1967 and 1970). In the next section the values determined from the temperature dependence of enthalpy data and from heat capacity data will be examined.

The effect of pressure on the relative molal enthalpy of seawater can be determined by differentiating the definition of enthalpy (dH = TdS − PdV) with respect to pressure

$$(\partial H/\partial P)_T = T\ (\partial S/\partial P)_T + V \tag{45}$$

since $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$, we have upon substitution

$$(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P \tag{46}$$

By integrating this equation, we have

$$H(P) - H(O) = \int_O^P [V - T(\partial V/\partial T)_P]\, dP \tag{47}$$

Thus, the values of V and $\partial V/\partial T$ determined from the equation of state of seawater (Millero, Gonzalez, and Ward, 1976; Chen and Millero, 1976) can be used to estimate the effect of pressure on the relative enthalpy. It should be pointed out that similar equations can be derived for the relative specific enthalpy (h in j g^{-1}), the apparent enthalpy, and the relative enthalpy

$$(\partial h/\partial P)_T = v - T(\partial v/\partial T)_P \tag{48}$$

$$\partial(\Phi_H - \Phi_H^0) / \partial P = \partial\Phi_L/\partial P = (\Phi_V - \Phi_V^0) - T[\partial(\Phi_V - \Phi_V^0) / \partial T] \tag{49}$$

$$\partial(\bar{H}_2 - \bar{H}_2^0) / \partial P = \partial\bar{L}_2/\partial P = (\bar{V}_2 - \bar{V}_2^0) - T[\partial(\bar{V}_2 - \bar{V}_2^0) / \partial T] \tag{50}$$

$$\partial(\bar{H}_1 - \bar{H}_1^0) / \partial P = \partial\bar{L}_1/\partial P = (\bar{V}_1 - \bar{V}_1^0) - T[\partial(\bar{V}_1 - \bar{V}_1^0) / \partial T] \tag{51}$$

where Φ_V and $\bar{V}$ are the apparent and partial molal volumes, and v is the specific volume. Values for the effect of pressure on the specific enthalpy of water and seawater at various temperatures and pressures are given elsewhere (Millero, 1976). The effect of pressure on the specific enthalpy of seawater is not strongly affected by pressure, temperature, and salinity ($\partial h/\partial P = 0.09 \pm 0.01$ j $g^{-1}bar^{-1}$ from 0° to 25°C, 0 to 35‰, and 0 to 1000 bars, Millero, 1976).

The Heat Capacity of Seawater

The earliest measurements on the specific heat (cp) of seawater were made by Thoulet and Chevallier (1889). In recent years a number of workers (Cox and Smith, 1959; Bromley and others, 1967; Bromley, 1968a and b; and Bromley and others, 1970; Millero, Perron, and Desnoyers, 1973) have determined the heat capacity of seawater solutions at 1 atm as a function of temperature and salinity. Cox and Smith (1959) measured the specific heat of seawater solutions from 0 to 120‰ salinity and −2° to 30°C to a quoted probable error of ± 0.0015 j g^{-1} deg^{-1} and a maximum error of ± 0.003 j g^{-1} deg^{-1}. Bromley and others (1967) measured the specific heat of seawater solutions from 0 to 120‰ salinity and 2° to 80°C to a quoted probable error of ± 0.004 j g^{-1} deg^{-1}. Bromley (1968a and b) determined the apparent specific heat capacity from these specific heats. He fitted these apparent specific heat capacities

to an extended Debye-Hückel equation. From the concentration dependence of the apparent specific heat capacity, Bromley determined the partial specific properties. Bromley and others (1970) measured the specific heat of seawater solutions from 0 to 120‰ salinity from 80° to 200°C. They also determined the apparent and partial specific properties of seawater solutions.

More recently, Millero, Perron, and Desnoyers (1973) have measured the specific heats of seawater solutions from 0.4 to 40‰ salinity and 5° to 35°C relative to pure water. These measurements were made using a new precision heat capacity calorimeter (Picker and others, 1971) which measures the specific heat relative to pure water to a precision of 0.0001 j g^{-1} deg^{-1}. They fitted the specific heats to the equation (std deviation 0.0003 j g^{-1} deg^{-1})

$$cp = cp_o + A_{cp}\, S(‰) + B_{cp}\, S(‰)^{3/2} \tag{52}$$

where cp_o is the specific heat of water (Stimson, 1955) given by

$$cp_o = 4.2174 - 3.720283 \times 10^{-3} + 1.412855 \times 10^{-4}t^2 - 2.654387 \times 10^{-6}t^3 + 2.093236 \times 10^{-8}t^4$$

and A_{cp} and B_{cp} are given by

$$-10^3\, A_{cp} = 7.644 - 0.10727t + 0.00138t^2$$
$$10^3\, B_{cp} = 0.177 - 0.00408t + 0.0000535t^2$$

The specific heats as a function of salinity and temperature taken from Millero, Perron, and Desnoyers (1973) are given in table 2. Over most of the oceanographic range of salinity and temperature, the results of Millero are in good agreement (± 0.002 j g^{-1} deg^{-1}) with the results of Cox and Smith and Bromley and others (1967). At 0° and low salinities the results of Cox and Smith are high by as much as 0.006 j g^{-1} deg^{-1} compared to the results of Bromley and others (1967) and Millero, Perron, and Desnoyers (1973). These differences are due to the fact that the low salinities samples used by Cox and Smith were diluted with Baltic Sea water.

The specific heats of seawater solutions can be used to determine the apparent molal heat capacity

$$\Phi_{cp} = 1000(cp - cp_o) / m + Mcp \tag{53}$$

where m is the molality and M is the mean molecular weight of sea salt. The values of Φ_{cp} determined from the specific heats given in table 2 using equation (53) are given in table 3. Millero, Perron and Desnoyers (1973) fitted the apparent equivalent heat capacity of sea salt to the equation (std deviation ± 0.7 j eq^{-1} deg^{-1})

$$\Phi_{cp} = \Phi_{cp}^0 + S_{cp}\, I^{1/2} + b_{cp}\, I \tag{54}$$

where Φ_{cp}^0 is the infinite dilution apparent equivalent heat capacity, S_{cp} is Debye-Hückel limiting law slope (1.15 × the limiting law slope for a

1 — 1 electrolyte), and b_{cp} is an empirical parameter. The relative apparent equivalent heat capacities $\Phi_J = \Phi_{cp} - \Phi_{cp}^0$ determined from the heat capacity data of Millero and others, have been shown to be in good agreement (± 10 j eq^{-1} deg^{-1}) with the values determined from enthalpy data (Millero, Hansen, and Hoff, 1973) from 5° to 25°C. Millero, Perron, and Desnoyers (1973) have estimated the Φ_{cp} of sea salt from Young's rule (Young and Smith, 1954). The estimated Φ_{cp}'s and the resultant cp's were found to be in excellent agreement with the measured values (within ± 1.5 j eq^{-1} deg^{-1} in Φ_{cp} and ± 0.0004 j g^{-1} deg^{-1} in cp).

To make the Φ_{cp}'s consistent with the enthalpy data, we have fitted the values given in table 3 to an extended Debye-Hückel equation (std deviation, 0.6 j mol^{-1} deg^{-1})

$$\Phi_{cp} = \Phi_{cp}^0 + S_J\, I^{1/2}\,[1/(1 + 1^{1/2}) - \sigma/3] + B_J\, I + C_J\, I^{3/2} \tag{55}$$

where Φ_{cp}^0, S_J, B_J, and C_J are given by (T in °K)

$$\begin{aligned}
\Phi_{cp}^0 &= -\ 7580.13 + 48.15824T - 0.07736T^2 \\
S_J &= -\ 142.13 + 0.6614_6T \\
B_J &= \quad 2621.67 - 16.3967T + 2.58926 \times 10^{-3}T^2 \\
C_J &= -\ 1166.71 + 7.3883T - 1.17970 \times 10^{-2}T^2
\end{aligned}$$

The partial molal heat capacities of sea salt calculated from

$$\bar{C}p_2 = \Phi_{cp}^0 + S_J\, I^{1/2}/(1 + I^{1/2}) + 2B_J I + 2.5\, C_J\, I^{3/2} \tag{56}$$

are given in table 4. The partial molal heat capacity of water in seawater can be calculated from the equation

$$\bar{C}p_1 = \bar{C}p_1^0 - (m\ I/55.51)\ (\partial\Phi_{cp}/\partial I) \tag{57}$$

where $\bar{C}p_1^0 = cp_o \times 18.015$ is partial molal heat capacity of pure water. Values of $\bar{C}p_1$ determined from equation (57) are given in table 5.

The relative apparent molal ($\Phi_J = \Phi_{cp} - \Phi_{cp}^0$) and relative partial molal ($\bar{J}_2 = \bar{C}p_2 - \bar{C}p_2$) heat capacity of sea salt calculated from equa-

TABLE 2

The specific heat of seawater solutions*

cp(j g^{-1} deg^{-1})

	Salinity								
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	4.2174	4.1812	4.1466	4.1130	4.0804	4.0484	4.0172	3.9865	3.9564
5	4.2019	4.1679	4.1354	4.1038	4.0730	4.0428	4.0132	3.9842	3.9556
10	4.1919	4.1599	4.1292	4.0994	4.0702	4.0417	4.0136	3.9861	3.9590
15	4.1855	4.1553	4.1263	4.0982	4.0706	4.0437	4.0172	3.9912	3.9655
20	4.1816	4.1526	4.1247	4.0975	4.0709	4.0448	4.0190	3.9937	3.9688
25	4.1793	4.1513	4.1242	4.0977	4.0717	4.0462	4.0210	3.9962	3.9718
30	4.1782	4.1510	4.1248	4.0992	4.0740	4.0494	4.0251	4.0011	3.9775
35	4.1779	4.1511	4.1252	4.0999	4.0751	4.0508	4.0268	4.0031	3.9797
40	4.1783	4.1516	4.1257	4.1005	4.0758	4.0514	4.0275	4.0039	3.9806

* Millero, Perron, and Desnoyers (1973).

TABLE 3

The apparent molal heat capacity of seawater solutions
$-\Phi_{cp}$ (j mol^{-1} deg^{-1})

	Salinity								
Temp	0(‰)*	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	197.2	187.6	177.6	170.1	163.2	157.6	152.2	147.4	142.9
5	170.7	161.1	151.7	144.8	138.9	133.8	129.2	124.8	120.9
10	146.9	136.7	128.6	122.1	117.0	112.2	108.2	104.2	100.6
15	125.4	114.6	107.1	100.9	96.2	91.6	87.7	84.1	80.9
20	110.9	99.9	93.0	87.8	83.3	79.4	76.1	72.9	69.9
25	99.3	87.5	81.9	77.5	73.8	70.3	67.3	64.5	61.7
30	89.7	77.6	71.3	66.7	63.2	59.6	56.5	53.8	51.2
35	85.6	72.6	67.0	62.6	58.8	55.3	52.4	49.7	47.3
40	85.9	71.3	66.3	61.7	57.9	59.8	51.7	49.0	46.5

* Determined at each temperature using equation (55).

TABLE 4

The partial molal heat capacity of "sea salt"
$-\bar{C}p_2$ (j mol^{-1} deg^{-1})

	Salinity								
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	197.6	175.7	162.1	150.6	140.5	131.4	123.3	116.0	109.5
5	170.1	149.1	136.8	126.5	117.4	109.3	102.1	95.5	89.7
10	146.4	126.2	114.9	105.6	97.4	90.2	83.7	77.8	72.5
15	126.6	109.9	96.6	88.1	80.8	74.3	68.4	63.1	58.3
20	110.6	91.3	81.7	74.0	67.3	61.4	56.1	51.3	46.9
25	98.5	79.3	70.3	63.1	57.0	51.6	46.7	42.4	38.4
30	90.3	71.0	62.4	55.6	49.9	44.8	40.3	36.3	32.6
35	86.0	66.4	58.0	51.5	46.1	41.3	37.1	33.3	29.9
40	85.5	65.4	57.1	50.7	45.3	40.7	36.6	33.0	29.7

TABLE 5

The partial molal heat capacity of water in seawater
$\bar{C}p_1$ (j mol^{-1} deg^{-1})

	Salinity								
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	75.9765	75.9639	75.9351	75.8918	75.8414	75.7801	75.7153	75.6432	75.5712
5	75.6972	75.6846	75.6594	75.6215	75.5747	75.5207	75.4630	75.4000	75.3333
10	75.5171	75.5063	75.4811	75.4468	75.4054	75.3586	75.3063	75.2487	75.1892
15	75.4018	75.3910	75.3694	75.3387	75.3009	75.2577	75.2108	75.1586	75.1046
20	75.3315	75.3207	75.3009	75.2739	75.2378	75.2000	75.1568	75.1099	75.0613
25	75.2901	75.2811	75.2613	75.2343	75.2036	75.1676	75.1280	75.0865	75.0415
30	75.2703	75.2613	75.2415	75.2181	75.1892	75.1550	75.1172	75.0793	75.0379
35	75.2649	75.2559	75.2379	75.2127	75.1856	75.1532	75.1208	75.0829	75.0451
40	75.2721	75.2631	75.2451	75.2217	75.1946	75.1640	75.1298	75.0956	75.0577

TABLE 6

The relative apparent molal heat capacity of "sea salt"
Φ_J (j mol^{-1} deg^{-1})

	Salinity							
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	13.2	21.1	27.9	34.1	39.7	45.0	49.8	54.4
5	0	12.8	20.1	26.4	31.9	37.0	41.7	46.1	50.1
10	0	12.6	19.4	25.0	30.1	34.7	39.0	42.9	46.6
15	0	12.4	18.8	24.0	28.6	32.8	36.7	40.2	43.6
20	0	12.4	18.4	23.3	27.5	31.4	34.9	38.1	41.2
25	0	12.5	18.2	22.8	26.8	30.4	33.6	36.6	39.4
30	0	12.7	18.3	22.7	26.5	29.9	32.9	35.7	38.3
35	0	13.0	18.5	22.8	26.5	29.7	32.7	35.3	37.8
40	0	13.4	19.0	23.3	26.9	30.1	33.0	35.6	38.0

TABLE 7

The relative partial molal heat capacity of "sea salt"
$\bar{J}_2$ (j mol^{-1} deg^{-1})

	Salinity							
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	21.9	35.5	47.0	57.1	66.2	74.3	81.6	88.1
5	0	21.0	33.3	43.6	52.7	60.8	68.0	74.6	80.4
10	0	20.2	31.5	40.8	49.0	56.2	62.7	68.6	73.9
15	0	19.7	30.0	38.5	45.8	52.3	58.2	63.5	68.3
20	0	19.3	28.9	36.6	43.3	49.2	54.5	59.3	63.7
25	0	19.2	28.2	35.4	41.5	46.9	51.8	56.1	60.1
30	0	19.3	27.9	34.7	40.4	45.5	50.0	54.0	57.7
35	0	19.6	28.0	34.5	39.9	44.7	48.9	52.7	56.1
40	0	20.1	28.4	34.8	40.2	44.8	48.9	52.5	55.8

TABLE 8

The relative partial molal heat capacity of water in seawater solutions
$\bar{J}_1 \times 55.51$ (j kg^{-1} deg^{-1})

	Salinity							
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	—0.7	—2.3	—4.7	—7.5	—10.9	—14.5	—18.5	—22.5
5	0	—0.7	—2.1	—4.2	—6.8	— 9.8	—13.0	—16.5	—20.2
10	0	—0.6	—2.0	—3.9	—6.2	— 8.8	—11.7	—14.9	—18.2
15	0	—0.6	—1.8	—3.5	—5.6	— 8.0	—10.6	—13.5	—16.5
20	0	—0.6	—1.7	—3.2	—5.2	— 7.3	— 9.7	—12.3	—15.0
25	0	—0.5	—1.6	—3.1	—4.8	— 6.8	— 9.0	—11.3	—13.8
30	0	—0.5	—1.6	—2.9	—4.5	— 6.4	— 8.5	—10.6	—12.9
35	0	—0.5	—1.5	—2.9	—4.4	— 6.2	— 8.0	—10.1	—12.2
40	0	—0.5	—1.5	—2.8	—4.3	— 6.0	— 7.9	— 9.8	—11.9

tions (55) and (56) are given in tables 6 and 7. The relative partial molal heat capacities of water ($\bar{J}_1$) calculated from

$$\bar{J}_1 = (m/55.51)\ (\Phi_J - \bar{J}_2) \tag{58}$$

are given in table 8.

A comparison of the Φ_J's obtained by various workers are given elsewhere (Millero, 1976). Over most of the temperature and salinity range the Φ_J's determined from heat capacity data are in good agreement with those determined from enthalpy data. The Φ_J's determined from equation (55) agree to within ± 10 j deg^{-1} mol^{-1} with those determined from enthalpy data and ± 5 j deg^{-1} mol^{-1} with those determined from equation (54).

Since the most reliable values of Φ_J and $\bar{J}$ are those determined from heat capacity data, it is possible to derive a consistent set of enthalpies by integrating the equations

$$\Phi_L = \Phi_L\ (273.15) + \int_{273.15}^{T} \Phi_J\ dT \tag{59}$$

$$\bar{L} = \bar{L}\ (273.15) + \int_{273.15}^{T} \bar{J}\ dT \tag{60}$$

The parameters S_H, B_H, and C_H of equations (37) and (38) can be obtained from the equations

$$S_H = S_H\ (273.15) + \int_{273.15}^{T} S_J\ dT \tag{61}$$

$$B_H = B_H\ (273.15) + \int_{273.15}^{T} B_J\ dT \tag{62}$$

$$C_H = C_H\ (273.15) + \int_{273.15}^{T} C_J\ dT \tag{63}$$

By using the 25°C Φ_L data of Millero, Hansen, and Hoff (1973), we have integrated these equations and obtain

$$S_H = 16563.70 - 142.1326T + 0.3307_4T^2 \tag{64}$$

$$B_H = -283072.28 + 2621.67T - 8.1983T^2 + 8.63086 \times 10^{-3}T^3 \tag{65}$$

$$C_H = 124171.12 - 1166.708T + 3.6941_5T^2 - 3.93233 \times 10^{-3}T^3 \quad (66)$$

Values for Φ_L and $\bar{L}_2$ calculated from equations (37) and (38) using the smooth values of S_H, B_H, and C_H (from eqs 64-66) are given in tables 9 and 10.

Comparisons of the relative apparent molal enthalpy of seawater determined from equation (37) and the directly measured values of Millero, Hansen, and Hoff (1973) agree on the average to ± 5 j mol^{-1} deg^{-1} with a maximum deviation of 13 j mol^{-1} deg^{-1} (Millero, 1976). The relative partial molal enthalpy of water ($\bar{L}_1$) in seawater determined from equation (39) is given in table 11.

Since the total relative enthalpy of seawater (L, j mol^{-1}) is equal to $n_2\Phi_L$, the relative specific enthalpy (h, j g^{-1}) for seawater can be obtained by multiplying the values of Φ_L by n_2 in moles per gram of seawater (1.6003×10^{-5} S(‰) × Φ_L). In table 12 values for the specific enthalpy of seawater are given as a function of temperature and salinity.

TABLE 9

The relative apparent molal enthalpy of "sea salt"
Φ_L (j mol^{-1})

	Salinity							
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	168.5	77.4	—40.4	—166.5	—294.6	—421.7	—546.2	—667.3
5	0	233.4	180.4	95.2	— 1.6	—102.9	—205.2	—306.7	—406.2
10	0	296.8	279.0	223.6	153.2	76.2	— 3.8	— 84.5	—164.6
15	0	359.2	374.2	346.0	299.8	244.7	184.9	122.9	60.3
20	0	421.3	467.1	464.2	440.2	405.1	363.8	318.9	272.2
25	0	483.5	558.6	579.2	575.7	559.1	534.6	505.3	473.0
30	0	546.4	649.7	692.8	708.8	709.4	700.7	685.9	667.1
35	0	610.5	741.6	806.5	841.0	858.1	864.3	863.2	857.1
40	0	676.5	835.3	921.7	974.4	1007.6	1028.3	1040.4	1046.4

TABLE 10

The relative partial molal enthalpy of "sea salt"
$\bar{L}_2$ (j mol^{-1})

	Salinity							
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	107.1	—139.6	—405.4	—667.3	—918.1	—1154.9	—1376.6	—1582.3
5	0	214.4	32.3	—179.0	—392.9	—600.9	— 799.4	— 986.5	—1161.3
10	0	317.3	194.1	31.9	—139.0	—308.7	— 472.7	— 628.8	— 775.7
15	0	416.9	347.4	229.7	97.4	— 37.9	— 170.0	— 299.3	— 421.0
20	0	514.4	494.6	417.4	320.2	216.1	110.9	8.0	— 90.9
25	0	610.5	636.9	596.8	531.6	455.7	375.8	295.6	217.3
30	0	706.5	776.9	771.7	736.1	686.3	629.7	570.5	511.1
35	0	803.6	916.3	944.2	936.7	911.3	876.5	836.7	795.0
40	0	902.6	1057.1	1117.2	1137.6	1134.8	1120.7	1099.5	1074.3

These specific enthalpies have been fitted to the equation (std deviation, 0.003 j g^{-1})

$$h = A\ S(‰) + B\ S(‰)^{3/2} + C\ S(‰)^2 \tag{67}$$

where

$$A = 3.4086 \times 10^{-3} - 6.3798 \times 10^{-5}t + 1.3877 \times 10^{-6}t^2 - 1.0512 \times 10^{-8}t^3$$

$$B = 7.9350 \times 10^{-4} + 1.0760 \times 10^{-4}t - 6.3923 \times 10^{-7}t^2 + 8.60 \times 10^{-9}t^3$$

$$C = -4.7989 \times 10^{-4} + 6.3787 \times 10^{-6}t - 1.1647 \times 10^{-7}t^2 + 5.717 \times 10^{-10}t^3$$

In figure 1 the relative specific enthalpies of seawater solutions are shown at various temperatures and salinities.

TABLE 11

The relative partial molal enthalpy of water in seawater solutions
$55.51 \times \bar{L}_1$ (j kg^{-1})

	Salinity							
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	4.9	35.1	89.0	163.6	255.9	362.9	482.1	610.2
5	0	1.5	23.9	66.8	127.8	204.4	294.1	394.6	503.6
10	0	— 1.6	13.7	46.7	95.4	158.0	232.1	316.0	407.6
15	0	— 4.6	4.3	28.3	66.1	116.0	175.7	245.1	321.0
20	0	— 7.5	— 4.4	11.4	39.2	77.6	125.2	180.5	242.2
25	0	—10.2	—12.7	— 4.3	14.4	42.4	78.6	121.7	170.5
30	0	—12.9	—20.6	—19.2	— 8.9	9.5	35.1	67.0	104.0
35	0	—15.5	—28.2	—33.6	—31.3	—21.8	— 6.0	15.4	41.4
40	0	—18.2	—35.9	—47.6	—53.3	—52.2	—45.7	—34.3	—18.6

TABLE 12

The relative specific enthalpy of seawater
$10^2 \times h$ (j g^{-1})

	Salinity							
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	1.35	1.24	— 0.97	— 5.33	—11.79	—20.22	—30.59	—42.72
5	0	1.87	2.89	2.29	— 0.05	— 4.12	— 9.85	—17.18	—26.00
10	0	2.38	4.47	5.37	4.90	3.05	— 0.18	— 4.73	—10.54
15	0	2.87	5.99	8.31	9.60	9.79	8.88	6.88	3.86
20	0	3.37	7.47	11.14	14.09	16.21	17.47	17.86	17.42
25	0	3.87	8.94	13.90	18.43	22.37	25.67	28.30	30.28
30	0	4.37	10.39	16.63	22.69	28.38	33.64	38.42	42.70
35	0	4.88	11.86	19.36	26.92	34.33	41.49	48.35	54.86
40	0	5.41	13.36	22.12	31.19	40.31	49.37	58.27	66.98

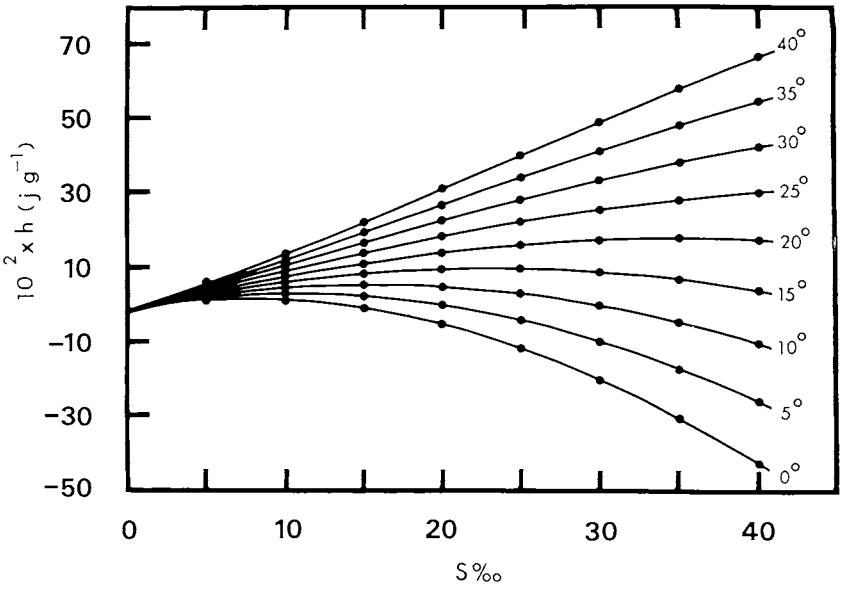

Fig. 1. The relative specific enthalpies of seawater solutions at various salinities and temperatures.

The effect of pressure on the apparent molal heat capacity, the partial molal heat capacity, and the specific heat of seawater solutions can be determined from equations

$$(\partial\Phi_{cp}/\partial P) = -T\ (\partial^2\Phi_V/\partial T^2) = -T\ (\partial\Phi_E/\partial T) \tag{68}$$

$$(\partial\bar{C}p/\partial P) = -T\ (\partial^2\bar{V}/\partial T^2) = -T\ (\partial\bar{E}/\partial T) \tag{69}$$

$$(\partial cp/\partial P) = -T\ (\partial^2 v/\partial T^2) \tag{70}$$

where Φ_E and $\bar{E}$ are the apparent and partial molal expansibilities. Values of $(\partial cp/\partial P)$ calculated from equation (70) with values of $\partial^2 v/\partial T^2$ determined from the equation of state of water (Fine and Millero, 1973) and seawater (Wang and Millero, 1973; Millero, Gonzalez, and Ward, 1976; Chen and Millero, 1976) at various salinities are given elsewhere (Millero, 1976). At 1000 bars applied pressure $(\partial cp/\partial P) = 1.49$ j g^{-1} bar^{-1} at 0°C and 35‰ salinity. Although direct measurements of $\partial cp/\partial P$ have not been made on seawater, the calculated results for water are in good agreement with the direct measurements of Sirota and Shrago (1968).

The specific heat of seawater at constant volume (as well as the related apparent and partial equivalent properties) can be determined from the equation of state of seawater (Millero, 1976) using the relationship

$$c_V = cp - T\ \alpha^2 v/\beta \tag{71}$$

where the expansibility $\alpha = 1/v(\partial v/\partial T)_P$ and the compressibility $\beta = -1(\partial v/\partial P)$. The specific heats at constant volume determined from equa-

tion (71) at 1 atm are given elsewhere (Millero and Kubinski, 1975). The values of c_V have been fitted (Millero and Kubinski, 1975) to an equation of the form (std deviation, ± 0.0002 j g^{-1} deg^{-1})

$$c_V = c_V^0 + A_V\ S(‰) + B_V\ S(‰)^{3/2} \tag{72}$$

where c_V^0 the heat capacity of pure water is given by

$$c_V^0 = 4.214945455 - 2.464624908 \times 10^{-3}t - 2.997402041 \times 10^{-5}t^2 + 5.85857688 \times 10^{-8}t^3$$

and the coefficients A_V and B_V are given by

$$A_V = (-7.26069 \times 10^{-3}) + (1.24863 \times 10^{-5})t + (1.89738 \times 10^{-6})t^2 - (3.14117 \times 10^{-8})t^3$$

$$B_V = (1.16061 \times 10^{-4}) + (2.33820 \times 10^{-6})t - (1.57201 \times 10^{-7})t^2 + (1.40111 \times 10^{-9})t^3$$

Free Energy of Seawater

The absolute free energy of seawater cannot be experimentally determined. It is thus necessary to examine the relative free energy (relative to an infinite dilution reference state). The total differential for the change in the free energy of a solution is given by

$$dG = (\partial G/\partial T)_P\ dT + (\partial G/\partial P)_T\ dP + \Sigma\ (\partial G/\partial n_i) \times dn_i \tag{73}$$

At a constant T and P, dG is given by

$$dG = \overline{G}_1\ dn_1 + \overline{G}_2\ dn_2 \tag{74}$$

where

$$\overline{G}_i = \mu_i = (\partial G/\partial n_i)_{T,P,j=i} \tag{75}$$

is the partial molal free energy or the chemical potential (μ_i) of species i. The chemical potential of each constituent *i* relative to an infinite dilution standard state is related to the activity by

$$\overline{G}_i - \overline{G}_i^0 = \mu_i - \mu_i^0 = RT\ \ln\ a_i \tag{76}$$

Since G is an extensive property, by using equation (5), we have

$$G = n_1\ \overline{G}_1 + n_2\ \overline{G}_2 \tag{77}$$

By substituting the definition of the chemical potential into equation (77), we obtain

$$G = n_1\ (\overline{G}_1^0 + RT\ \ln\ a_1) + n_2\ (\overline{G}_2^0 + RT\ \ln\ a_2) \tag{78}$$

where a_1 is the activity of water and a_2 is the activity of sea salt. Collecting terms in $\overline{G}_i^0$ and defining the reference state $G^0 = \Sigma n_i G_i^0$, the relative molal free energy is given by

$$G - G^0 = n_1\ RT\ \ln\ a_1 + n_2\ RT\ \ln\ a_2 \tag{79}$$

For a solution containing 55.51 moles of water this equation becomes

$$G - G^0 = 55.51\ RT\ \ln a_1 + m\ RT\ \ln a_2 \tag{80}$$

Activity of water.—The activity of water in seawater can be determined from the colligative properties of seawater (vapor pressures, freezing points, et cetera). The activity of sea salt can be determined from the activity of water by using the Gibbs-Duhem equation. It is usually more convenient to express the activity of water in a solution in terms of the practical osmotic coefficient (Lewis and Randall, 1961) given by

$$\phi = -(55.51/2m)\ \ln a_1 \tag{81}$$

where $2m = \Sigma\ m_i$, the sum of the molalities of the ionic components of the solution. The osmotic coefficients of electrolyte solutions are normally determined from vapor pressure measurements or freezing point measurements.

When an aqueous solution is in equilibrium with its vapor, we have

$$d\ \ln a_1 = d\ \ln a_{vap} \tag{82}$$

where a_{vap} is the activity of water in the vapor. The activity of water vapor can be determined from the molal volume of water vapor

$$V_{vap} = RT\ (\partial \ln a_{vap}/\partial P) \tag{83}$$

At low pressures the molal volume of water vapor can be expressed by

$$V_{vap} = RT/P - B \tag{84}$$

where B is the second virial coefficient (Robinson and Stokes, 1959). Substituting equations (83) and (84) into equation (82), we have upon integration between p and p_o the vapor pressures of the solution and pure water

$$\ln a_1 = \ln (p/p_o) - \int_{p_o}^{p} (B/RT)\ dP \tag{85}$$

which becomes, after substitution of equation (81)

$$\phi = -(55.51/2m)\ \ln (p/p_o) + (55.51/2m\ RT) \int_{p_o}^{p} BdP \tag{86}$$

In actual practice, the BdP term is neglected since it is smaller than the experimental errors involved in vapor pressure measurements. One also disregards the fact that the values of a_1 and ϕ calculated from direct manometric measurements are derived under a pressure (P) which varies

with the composition of the solution (Robinson and Stokes, 1959). The activity of water is, thus, given by

$$a_1 = p/p_o \tag{87}$$

Once the vapor pressure of water has been accurately made in one solution, one can use the isopiestic method (Robinson and Stokes, 1959) to obtain the vapor pressure or a_1 and ϕ of an unknown solution. In the isopiestic method two solutions (a standard and an unknown) are equilibrated until their water vapor pressures are equal. From the molalities of the two solutions at (equilibrium), one can determine the isopiestic ratio

$$\mathbf{R} = \nu_R m_R / \nu_S m_S \tag{88}$$

where ν_R and ν_S are the numbers of ions produced by a reference solute (usually NaCl) of molality m_R and the sample of molality m_S. By knowing the osmotic coefficient of the reference (ϕ_R), the osmotic coefficient of the unknown solute can be determined from

$$\phi = \mathbf{R}\ \phi_R \tag{89}$$

Robinson (1954) made isopiestic measurements on seawater using NaCl solutions as a standard. The results of Robinson over the salinity range

TABLE 13

The osmotic coefficient of seawater solutions at 25°C from isopiestic measurements (Robinson, 1954)

Cl(‰)	I†	ϕ†† Experimental	ϕ††† Calculated	Δ††††
14.79*	0.54735	0.8997	0.8975	0.0022
18.62*	0.69405	0.9021	0.9016	0.0005
19.90*	0.74355	0.9036	0.9036	0.0000
21.01*	0.78667	0.9043	0.9056	—0.0013
9.44**	0.34590	0.8969	0.8969	0.0000
13.08**	0.48253	0.8967	0.8966	0.0001
14.60**	0.54013	0.8956	0.8973	—0.0017
15.04**	0.55686	0.8954	0.8976	—0.0022
16.35**	0.60685	0.8950	0.8988	—0.0038
18.72**	0.69791	0.9034	0.9017	0.0017
20.02**	0.74820	0.9045	0.9038	0.0007
20.96**	0.78472	0.9045	0.9055	—0.0010
15.87***	0.58850	0.9016	0.8983	0.0033
19.52***	0.72883	0.9068	0.9029	0.0039
				mean ± 0.0016

* Standard seawater, P17, 31 Oct. 1948, Cl(‰) = 19.386.

** Artificial seawater, 28.85 g kg^{-1} NaCl, 0.811 g kg^{-1}, KCl, 2.633 g kg^{-1}, $MgCl_2$, 1.244 g kg^{-1}, $CaCl_2$, and 3.649 g kg^{-1} $MgSO_4$.

*** Seawater from the Straits of Singapore.

† Determined from equation (23) by converting Cl(‰) to S(‰), S(‰) = 1.80655 Cl(‰).

†† The experimental ϕ was determined from equation (89) using the $R = m_{NaCl}/m_{SW}$ determined from Robinson (1954) and $\phi_{NaCl} = 0.94204 - 0.11953m + 0.194983\ m^2 - 0.08215\ m^3$ (Millero, 1974a).

††† The calculated ϕ was determined from equation (91).

†††† ϕ(experimental) — ϕ(calculated).

of 16 to 40‰ (I = 0.3 to 0.8) are shown in table 13. In our earlier work we (Millero, 1974a) fitted these results to the equation

$$\phi = 0.90799 - 0.07221\ I + 0.11904\ I^2 - 0.03830\ I^3 - 0.00092\ I^4 \quad (90)$$

To obtain reliable thermodynamic data from osmotic coefficient data, it is necessary to extrapolate the results to infinite dilution. The equation we have selected for this extrapolation is the extended Debye-Hückel equation (Lewis and Randall, 1961)

$$1 - \phi = 2.303\ S_\gamma\ I^{1/2}\ (\sigma/3) + B_\gamma I + C_\gamma I^{3/2} + D_\gamma I^2 \quad (91)$$

where S_γ is the Debye-Hückel theoretical slope limiting law ($S_\gamma = 0.63693$ at 25°C), B_γ, C_γ, and D_γ are temperature dependent parameters. By rearranging equation (91), we have the quadratic equation

$$[j - 2.303\ S_\gamma\ I^{1/2}\ (\sigma/3)]\ /\ I = B_\gamma + C_\gamma I^{1/2} + D_\gamma I \quad (92)$$

where $j = 1 - \phi$. A plot of the left hand side of equation (92) versus $I^{1/2}$ determined from Robinson's ϕ data (given in table 13) is shown in figure 2. A least squares fit of the data gives $B_\gamma = -0.25973$, $C_\gamma = 0.36681$, and $D_\gamma = -0.19325$ with a standard deviation of 0.002 in ϕ. The smoothed values of ϕ determined from equation (91) are given in table 14.

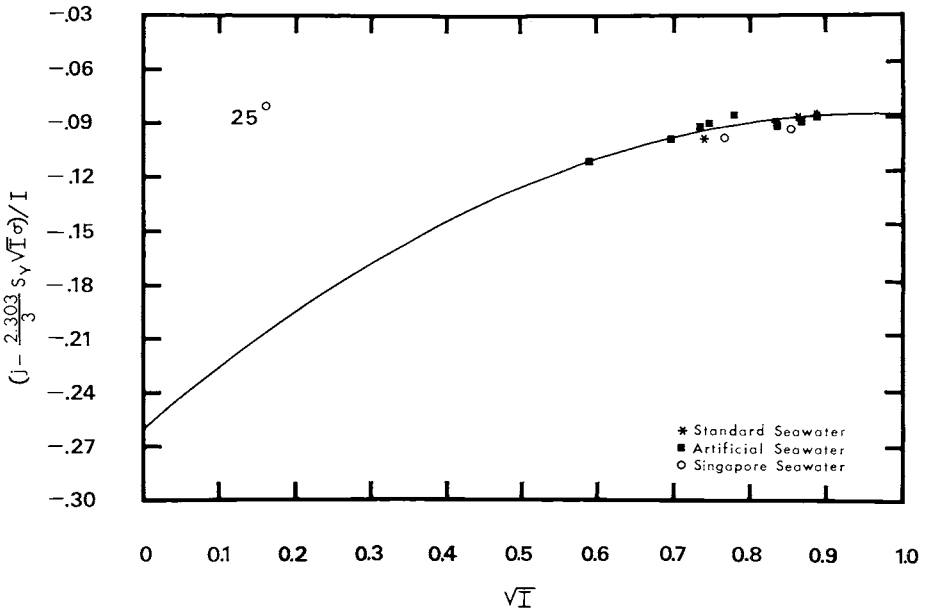

Fig. 2. A plot of the left hand side of equation (92) versus the square root of the ionic strength of seawater at 25°C (using the results from Robinson, 1954).

In recent years a number of workers have determined the osmotic coefficient of artificial seawater solutions (Rush and Johnson, 1966; Gibbard and Scatchard, 1972) as well as made estimates of ϕ using multicomponent electrolyte solution theories (Robinson and Wood, 1972; Whitfield, 1973). The predicted values of ϕ agree with the measured values to $\pm$ 0.003 over the range of salinities of 15 to 40‰.

The most reliable method of determining the osmotic coefficient of solutions is the use of freezing point measurements (Lewis and Randall, 1961). At the freezing point of a seawater solution $T = T_f - \theta$, where θ is the freezing point depression, and T_f is the freezing point of water. Since the freezing points at various concentrations vary over a range of temperatures, one must convert the data to a single temperature. The freezing point of the pure solvent is normally selected as the reference temperature (273.15°K). To calculate the free energy for the equilibrium between ice and solution at T_f, one must make some corrections for the effect of temperature and composition on the heat of fusion of water (Lewis and Randall, 1961). This correction is made by considering the effect of temperature on the free energy for the freezing process given by

$$\partial(\Delta G/T)\ /\partial\theta = \Delta\bar{H}/T^2 = \Delta\bar{H}/(T_f - \theta)^2 \qquad (93)$$

where $\Delta G = \bar{G}_1(\text{soln}) - \bar{G}_1(\text{solid})$, and $\Delta\bar{H} = \bar{H}_1(\text{soln}) - \bar{H}_1(\text{solid}) = \Delta H_f$, the heat of fusion of water. By assuming $\Delta\bar{H}$ is a second degree function of temperature ($\partial\Delta\bar{H}/\partial T = \Delta\bar{C}p = \Delta a + \Delta bT$), we obtain by integrating equation (93) (Lewis and Randall, 1961)

$$\Delta G/T_f = R \ln a_1 = -[\Delta H_f^0 + \bar{L}_1/T_f^2]\theta - [\Delta H_f^0 + \bar{L}_1/T_f^3 - (\Delta C_f^0 + \bar{J}_1)\ /\ 2T_f^2]\ \theta^2 - [\Delta H_f^0 + \bar{L}_1/T_f^4 - 2(\Delta C_f^0 + \bar{J}_1)/3T_f^3 + \Delta b/6T_f^2]\ \theta^3 + \ldots \qquad (94)$$

TABLE 14

A comparison of the osmotic coefficients of seawater solutions at 25°C obtained from vapor pressure and freezing point measurements

S(‰)	ϕ Vapor Pressure*	ϕ Freezing Point**	Δ
0	1.0000	1.0000	0
5	0.9145	0.9142	0.0003
10	0.9025	0.9024	0.0001
15	0.8978	0.8981	0.0003
20	0.8964	0.8967	0.0003
25	0.8969	0.8971	0.0002
30	0.8990	0.8989	0.0001
35	0.9027	0.9017	0.0010
40	0.9080	0.9057	0.0023
			mean 0.0006

* From equation (107) using $S_\gamma = 0.63693$, $B_\gamma = -0.25973$, $C_\gamma = 0.36681$, and $D_\gamma = -0.19325$.

** From equation (107) using $S_\gamma = 0.63595$, $B_\gamma = -0.24330$, $C_\gamma = 0.31368$, and $D_\gamma = -0.15113$.

where $\Delta H_f^0 = 6800\text{j mol}^{-1}$ is the heat of fusion of pure water (at infinite dilution), $\bar{L}_1$ is the relative partial molal enthalpy of water in seawater at 0°C, $\Delta C_f^0 = 38.1\text{j mol}^{-1}\text{ deg}^{-1}$ is the change in the heat capacity for the fusion process (at infinite dilution), and $\bar{J}_1$ is the relative partial molal heat capacity of water at 0°C. When θ is small the last term can be omitted, and upon substituting the definition of ϕ, we have

$$2m\lambda\phi = (1 + \bar{L}_1/\Delta H_f^0)\theta + [1/T_f - \Delta C_f^0/2\Delta H_f^0 + \bar{L}_1/T_f\Delta H_f^0 - \bar{J}_1/2\ H_f^0]\theta^2 \quad (95)$$

where the molal freezing point lowering constant (λ) is given by

$$\lambda = RT_f^2/55.51\ \Delta H_f^0 = 1.860 \quad (96)$$

For θ's below 3°C, equation (95) becomes

$$m\ \phi = (0.2888 + 4.807 \times 10^{-5}\ \bar{L}_1)\ \theta + 1.32 \times 10^{-4}\theta^2 \quad (97)$$

Recently, three independent studies have been made on the freezing point of seawater solutions (Murray and Murray as quoted by Riley and Chester, 1971; Doherty and Kester, 1974; Fujino, Lewis, and Perkins, 1974). These three studies are in good agreement with each other and clear up the differences that existed in the earlier studies of Hansen (1904) and Miyake (1939). These earlier studies yielded freezing points for 35‰ salinity seawater that differed by as much as 0.08°C. Hansen (1904) fitted his freezing point depression to the equation

$$\theta = 0.0086 + 0.064633\sigma_0 + 1.055 \times 10^{-4}\sigma_0^2 \quad (98)$$

where σ_0 are from the density work of Knudsen, Forch, and Sörensen (1902). Miyake (1939) fitted his results to the equation

$$\theta = 0.102710\ \text{Cl}(‰) \quad (99)$$

A comparison of these two studies is shown in table 15.

TABLE 15

Comparisons of the freezing point depression of seawater obtained by various workers

θ(°C)

S(‰)	A	B	C	D	E
5	0.268	0.284	0.268	0.288	0.275
10	0.535	0.569	0.535	0.546	0.541
15	0.803	0.853	0.801	0.810	0.810
20	1.075	1.137	1.068	1.079	1.082
25	1.350	1.421	1.341	1.354	1.359
30	1.628	1.706	1.621	1.634	1.638
35	1.910	1.990	1.906	1.920	1.922
40	2.196	2.274	2.196	2.211	2.209

A. Hansen (1904).
B. Miyake (1939).
C. Murray and Murray as quoted by Riley and Chester (1971).
D. Fujino, Lewis, and Perkin (1974).
E. Doherty and Kester (1974).

More recently, L. A. Murray (formerly Mayneord) and C. N. Murray (as quoted by Riley and Chester, p. 35, 1971) have made some measurements on the freezing point of seawater using the equilibrium method. These measurements (shown in table 15) are in excellent agreement with the early work of Hansen (1904). Fujino, Lewis, and Perkin (1974) measured the freezing point of seawater from 18 to 35‰ salinity. They fitted their results (std deviation ± 0.0025°C) to the equation

$$\theta = 0.036 + 0.0499\ S(‰) + 1.12 \times 10^{-4} S(‰)^2 \qquad (100)$$

Their results from 5 to 40‰ salinity are given in table 15. Doherty and Kester (1974) have made the most comprehensive and what appear to be the most accurate measurements on the freezing point of seawater from 4 to 40‰ salinity. They fitted their results to the equation (std deviation ± 0.002°C)

$$\theta = 0.0137 + 0.051990\ S(‰) + 7.225 \times 10^{-5}\ S(‰)^2 \qquad (101)$$

Both these recent studies (shown in table 15) are in agreement with the earlier data of Hansen (1904) to 0.01°C between 20 to 35‰ salinity and agree with each other to ± 0.005. Although both studies were made by diluting seawater with pure water, the equations they developed to fit their data have a zero salinity intercept. These intercepts have no affect on calculations of θ; however, they can yield unreliable osmotic coefficients in dilute solutions (necessary to obtain the free energy of seawater solutions on a infinite dilution standard state). We have thus used the direct experimental freezing point data to derive osmotic coefficients for seawater. The freezing point measurements of Doherty and Kester were used to determine ϕ because their measurements were made over a wide concentration range. Their results obtained by two separate freezing point techniques (the flow and equilibrium methods) are in agreement to ± 0.002 °C, and they have demonstrated that their experimental methods yield reliable freezing points for electrolyte solutions to ± 0.001 °C.

The experimental values of ϕ at 0°C determined from the directly measured freezing point data of Doherty and Kester by using equation (98) and the values of $\bar{L}_1$ determined from equation (39) are given in table 16. A plot of the left hand side of equation (92) determined from these values of ϕ and $S_\gamma = 0.61229$ is shown plotted vs $I^{1/2}$ in figure 3. The experimental values of ϕ have been fitted using a least squares method to equation (92), and the constants were found to be $B_\gamma = -0.20576$, $C_\gamma = 0.29435$, and $D_\gamma = -0.15112_5$. The values of ϕ determined from equation (91) are compared to the measured values in table 16. The standard deviation of the fitted values of ϕ was 0.001, which is two times better than the fit of ϕ at 25°C determined from vapor pressure measurements. Also given in table 16 are the calculated values of θ determined from the smoothed values of ϕ. The calculated values for the freezing point lowerings agree with the measured values to ± 0.003°C with a mean of ± 0.001_3°C. Since the values of θ determined from the

TABLE 16

Comparison of the calculated and measured freezing point depression (θ) and osmotic coefficients (ϕ) for seawater solutions at 0°C (Doherty and Kester, 1974)

Experimental	Salinity	θ* (meas)	θ** (calc)	$\Delta\theta$	ϕ† (meas)	ϕ†† (calc)	$\Delta\phi$
Flow method	36.52	2.010	2.009	—0.001	0.8935	0.8931	—0.0004
	35.49	1.950	1.950	0	0.8927	0.8926	—0.0001
	34.50	1.894	1.893	—0.001	0.8928	0.8922	—0.0006
	33.00	1.808	1.807	—0.001	0.8922	0.8917	—0.0005
	30.00	1.637	1.637	0	0.8910	0.8909	—0.0001
	27.01	1.471	1.469	—0.002	0.8916	0.8906	—0.0010
	22.01	1.195	1.193	—0.002	0.8930	0.8912	—0.0018
	16.99	0.920	0.919	—0.001	0.8948	0.8935	—0.0013
	11.97	0.649	0.648	—0.001	0.9003	0.8983	—0.0020
	6.97	0.381	0.381	0	0.9120	0.9115	—0.0005
Equilibration method	40.20	2.220	2.224	0.004	0.8936	0.8954	0.0018
	39.75	2.197	2.196	—0.001	0.8947	0.8950	—0.0003
	36.96	2.032	2.035	0.003	0.8921	0.8934	0.0013
	36.18	1.990	1.990	0	0.8931	0.8930	—0.0001
	35.06	1.925	1.925	0	0.8925	0.8925	—0.0000
	34.90	1.916	1.916	0	0.8925	0.8924	—0.0001
	34.42	1.888	1.888	0	0.8921	0.8922	0.0001
	32.14	1.758	1.758	0	0.8914	0.8914	0
	31.65	1.731	1.730	—0.001	0.8917	0.8913	—0.0004
	30.22	1.652	1.649	—0.003	0.8924	0.8909	—0.0015
	28.15	1.535	1.533	—0.002	0.8918	0.8907	—0.0011
	24.59	1.333	1.335	0.002	0.8895	0.8907	0.0012
	24.53	1.330	1.331	0.001	0.8897	0.8907	0.0010
	20.04	1.086	1.085	—0.001	0.8929	0.8919	0.0010
	19.81	1.072	1.072	0	0.8918	0.8920	0.0002
	16.81	0.906	0.909	0.003	0.8908	0.8936	0.0028
	16.44	0.886	0.889	0.003	0.8910	0.8939	0.0029
	12.33	0.665	0.667	0.002	0.8952	0.8978	0.0026
	11.95	0.648	0.646	—0.001	0.9004	0.8983	—0.0021
	8.38	0.457	0.456	—0.001	0.9088	0.9068	0.0020
	3.78	0.208	0.208	0	0.9209	0.9209	0

* The measured values of the freezing point lowering of water in seawater are taken from the work of B. T. Doherty and D. R. Kester (1974).

** θ(calc) determined from equation (97) using the calculated values of ϕ given in column six.

† ϕ(meas) using equation (97).

†† ϕ(calc) calculated from the extended Debye-Hückel equation (92) with $S_\gamma = 0.61229$, $B_\gamma = -0.20576$, $C_\gamma = 0.29435$, and $D_\gamma = -0.15112_5$.

smoothed values of ϕ are consistent with the limiting law, we have derived an equation to represent the calculated values of θ as a function of salinity

$$\theta = 0.057_5\, S(‰) - 1.710523 \times 10^{-3}\, S(‰)^{3/2} + 2.154996 \times 10^{-4}\, (S‰)^2 \tag{102}$$

The equation fits the smooth values of θ on the average to ± 0.0003°C. It should be pointed out that equation (102) fits the smooth values of θ three times better than a quadratic function of S(‰) (with an intercept) used by other workers. The values of T_f obtained from equation (102) are compared to other workers in table 17.

Recently Watson, Wood, and Millero (1975) determined the freezing point of seawater at 35‰ salinity from values of ϕ at 25°C estimated by the methods of Robinson and Wood (1972) and using the enthalpy data of Millero, Hansen, and Hoff (1973). The estimated freezing point depression (1.927°C) agrees very well with the measured values (1.922°C) of both Doherty and Kester (1974) and Fujino, Lewis, and Perkin (1974).

As discussed by Doherty and Kester and Fujino, Lewis, and Perkin the effect of pressure on the freezing point of seawater is of particular interest in studying the formation of super cooled waters and ice formations on the bottom of ice shelves. Fujino, Lewis, and Perkin, made measurements on the effect of pressure (to 100 bars) on the freezing point of seawater from 27 to 35‰. They found that the freezing point decreased by 7.59×10^{-3}deg bar^{-1} independent of salinity. The effect of pressure on the freezing point of seawater has also been estimated by Doherty and Kester using the Clausius-Clapeyon equation

$$(\partial T_f/\partial P) = T(\Delta \bar{V}_f/\Delta \bar{H}_f) \tag{103}$$

where $\Delta \bar{V}_f = \bar{V}_{ice} - \bar{V}_1$ is the change in the molal volume of water upon the formation of ice ($\bar{V}_{ice} = 18.015/\rho_{ice}$ and $\bar{V}_1$ is the molal volume of water in seawater), and $\Delta \bar{H}_f$ is the heat of fusion. Doherty and Kester found that at 1 atm $(\partial T_f/\partial P) = -7.43 \times 10^{-3}$deg bar^{-1} for water and -7.45×10^{-3}deg bar^{-1} for 35‰ salinity seawater. At 40 bars they found $(\partial T_f/\partial P) = -7.51 \times 10^{-3}$deg bar^{-1} for 35‰ salinity seawater. They selected a value of -7.48×10^{-3}deg bar^{-1} as being representative over

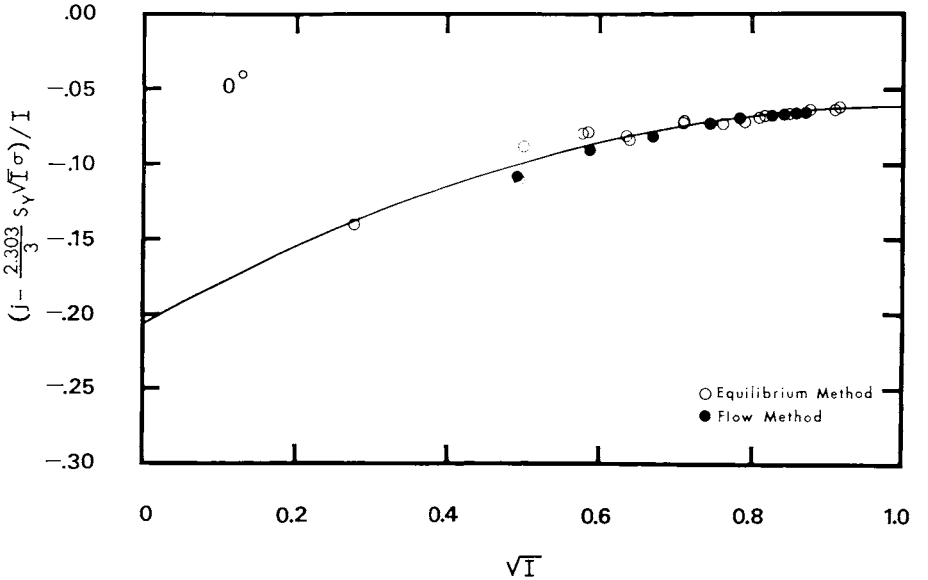

Fig. 3. A plot of the left hand side of equation (92) versus the square root of the ionic strength of seawater at 0°C (using the results from Doherty and Kester, 1974).

the range of 0 to 500 m (50 bars) which is in reasonable agreement with the directly measured value of Fujino, Lewis, and Perkin. It is interesting to note that the differences between $(\partial T_f/\partial P)$ in pure water and seawater is slight. This is due to the fact that $\Delta\bar{V}_f \cong \Delta\bar{V}_f{}^0$ (that is $\bar{V}_1 \cong \bar{V}_1{}^0$) and $\Delta H_f \cong \Delta H_f{}^0$ (that is $\bar{L}_1$ is small). More reliable calculations are possible for values of $(\partial T_f/\partial P)$ by making a correction to $\Delta\bar{H}_f$ for $\bar{L}_1$. For example, we obtain $(\partial T_f/\partial P) = -7.48 \times 10^{-3}$deg bar^{-1} at 0 bar and -7.58×10^{-3}deg bar^{-1} at 100 bars (applied pressure) which are slightly closer to the values measured by Fujino, Lewis, and Perkin. Over a 50 bar range the differences between the measured (-7.59×10^{-3}) and average calculated (-7.53×10^{-3}) value of 0.06×10^{-4} in $(\partial T_f/\partial P)$ will result in only a difference of 0.0003°C, which is well within the present capabilities of in situ temperature measurements.

The osmotic coefficient of seawater solutions calculated from freezing point measurements can be determined by using equation (24). By substituting equation (81) into equation (24) and rearranging, we have

$$(\partial\phi/\partial T) = -(\bar{L}_1/RT^2)\ (55.51/2m) \tag{104}$$

Upon integration, this equation becomes

$$1 - \phi\ (T°K) = 1 - \phi\ (273.15) - (55.51/2mR) \int_{273.15}^{T} (\bar{L}_1/T^2)dT \tag{105}$$

By substituting the definitions of ϕ_L and $\bar{L}_2$ into equation (39) the $\bar{L}_1$ needed to solve equation (105) is given by

$$\bar{L}_1 = (-m/55.51)\ [S_H I^{1/2}\ (\sigma/3) + B_H I + 1.5\ C_H I^{3/2}] \tag{106}$$

TABLE 17

Comparisons of the freezing point depression of seawater determined from smoothed ϕ data and by other workers

		θ(ours) — θ(others)				
S‰	θ (ours)	A	B	C	D	E
5	0.274	0.006	—0.010	0.006	—0.014	—0.001
10	0.542	0.007	—0.027	0.007	—0.004	0.001
15	0.811	0.008	—0.042	0.010	0.001	0.001
20	1.083	0.008	—0.054	0.015	0.004	0.001
25	1.358	0.008	—0.063	0.017	0.004	—0.001
30	1.637	0.009	—0.069	0.016	0.003	—0.001
35	1.922	0.012	—0.068	0.016	0.002	0.000
40	2.211	0.015	—0.063	0.015	0.000	0.002

A. θ(ours) — θ(Hansen, 1904).
B. θ(ours) — θ(Miyake, 1939).
C. θ(ours) — θ(Murray and Murray).
D. θ(ours) — θ(Fujino, Lewis, and Perkin, 1974).
E. θ(ours) — θ(Doherty and Kester, 1974).

where S_H, B_H, and C_H are given by equations (64), (65), and (66). Substituting equation (106) into equation (104) and integrating, we obtain

$$1 - \phi = 2.303\ S_\gamma' I^{1/2}\ (\sigma/3) + B_\gamma' I + C_\gamma' I^{3/2} + D_\gamma' I^2 \qquad (107)$$

where $S_\gamma' = S_\gamma(273.15°K) + (4.606R)^{-1} \int_{273.15}^{T} (S_H/T^2)dT$, $B_\gamma' = B_\gamma(273.15°K) + (2R)^{-1} \int_{273.15}^{T} (B_H/T^2)\ dT$, $C_\gamma' = C_\gamma(273.15°K) + (1.5/2R) \int_{273.15}^{T} (C_H/T^2)\ dT$, and $D_\gamma' = D_\gamma(273.15°K)$. Upon integration of equations (64), (65), and (66), we obtain

$$S_\gamma' = 20.660673 - 432.578663/T - 3.711944 \ln T + 8.637627 \times 10^{-3}T$$

$$B_\gamma' = -831.658611 + 17022.3989/T + 157.65271 \ln T - 0.493000T + 2.595060 \times 10^{-4}T^2$$

$$C_\gamma' = 553.905988 - 11200.445/T - 105.239035 \ln T + 0.333219T - 1.773514 \times 10^{-4}T^2$$

$$D_\gamma' = -0.15112_5$$

The osmotic coefficients calculated from equation (107) at various temperatures and salinities are given in table 18. The ϕ at 25°C determined from equation (107) are compared to those obtained earlier from vapor pressure measurements in table 14. The values of ϕ agree on the average to 0.0006 with a maximum deviation of 0.0023 at 40‰ salinity seawater (which is within the experimental error of the values of ϕ determined from vapor pressure measurements – 0.002).

The activities of water in seawater determined from these osmotic coefficients are given in table 19, and the vapor pressures (in mm Hg) of seawater determined from equation (87) are given in table 20. The values of p_o were taken from the recent work of Ambrose and Lawrenson (1972). The vapor pressures of seawater have been fitted to the equation (std deviation 0.001 mm Hg)

$$p = p_o + A\ S(‰) + B\ S(‰)^{3/2} \qquad (108)$$

where

$$A = -2.3311 \times 10^{-3} - 1.4799 \times 10^{-4}t - 7.520 \times 10^{-6}t^2 - 5.5185 \times 10^{-8}t^3$$

$$B = -1.1320 \times 10^{-5} - 8.7086 \times 10^{-6}t + 7.4936 \times 10^{-7}t^2 - 2.6327 \times 10^{-8}t^3$$

The osmotic pressure (π) can be determined from the activity of water in seawater or the osmotic coefficient by using the equation

$$\pi = (-RT/\bar{V}_1) \ln a_1 = (2m\ RT/55.51\ \bar{V}_1)\phi \qquad (109)$$

TABLE 18

The osmotic coefficient of seawater

ϕ

Temp	Salinity 0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	1.0000	0.9149	0.0913	0.8950	0.8919	0.8907	0.8909	0.8925	0.8952
5	1.0000	0.9151	0.9020	0.8963	0.8937	0.8929	0.8936	0.8954	0.8986
10	1.0000	0.9151	0.9024	0.8972	0.8950	0.8946	0.8956	0.8978	0.9011
15	1.0000	0.9149	0.9026	0.8977	0.8959	0.8958	0.8971	0.8996	0.9032
20	1.0000	0.9146	0.9026	0.8980	0.8965	0.8967	0.8982	0.9009	0.9047
25	1.0000	0.9143	0.9025	0.8981	0.8967	0.8972	0.8989	0.9017	0.9057
30	1.0000	0.9138	0.9021	0.8979	0.8968	0.8974	0.8993	0.9023	0.9064
35	1.0000	0.9132	0.9016	0.8976	0.8966	0.8973	0.8994	0.9025	0.9068
40	1.000	0.9126	0.9010	0.8971	0.8962	0.8970	0.8992	0.9025	0.9068

TABLE 19

Activity of water in seawater

a_1

Temp	Salinity 0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	1.0000	0.9973_5	0.9947_6	0.9921_7	0.9895_6	0.9869_2	0.9842_1	0.9815_1	0.9787_2
5	1.0000	0.9973_5	0.9947_6	0.9921_6	0.9895_4	0.9868_8	0.9841_6	0.9814_5	0.9786_4
10	1.0000	0.9973_5	0.9947_6	0.9921_5	0.9895_2	0.9868_6	0.9841_5	0.9814_0	0.9785_8
15	1.0000	0.9973_5	0.9947_6	0.9921_5	0.9895_1	0.9868_4	0.9841_3	0.9813_6	0.9785_3
20	1.0000	0.9973_5	0.9947_6	0.9921_4	0.9895_1	0.9868_3	0.9841_1	0.9813_3	0.9785_0
25	1.0000	0.9973_5	0.9947_5	0.9921_4	0.9895_0	0.9868_2	0.9840_9	0.9813_2	0.9784_7
30	1.0000	0.9973_6	0.9947_6	0.9921_4	0.9895_0	0.9868_2	0.9840_9	0.9813_0	0.9784_6
35	1.0000	0.9973_6	0.9947_6	0.9921_5	0.9895_0	0.9868_2	0.9840_9	0.9813_0	0.9784_5
40	1.0000	0.9973_6	0.9947_7	0.9921_5	0.9895_1	0.9868_2	0.9840_9	0.9813_0	0.9784_5

TABLE 20

The vapor pressure of seawater

p(mm Hg)

Temp	Salinity 0(‰)*	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	4.5806	4.5685	4.5566	4.5447	4.5328	4.5207	4.5084	4.4959	4.4831
5	6.5409	6.5236	6.5066	6.4896	6.4725	6.4551	6.4375	6.4196	6.4012
10	9.2078	9.1834	9.1596	9.1355	9.1113	9.0868	9.0619	9.0365	9.0106
15	12.7892	12.7553	12.7222	12.6888	12.6550	12.6209	12.5862	12.5508	12.5146
20	17.5393	17.4928	17.4474	17.4014	17.3553	17.3083	17.2606	17.2118	17.1622
25	23.7665	23.7035	23.6419	23.5797	23.5169	23.4532	23.3884	23.3225	23.2548
30	31.8407	31.7566	31.6739	31.5907	31.5064	31.4210	31.3341	31.2453	31.1549
35	42.2012	42.0898	41.9801	41.8699	41.7581	41.6450	41.5298	41.4120	41.2918
40	55.3639	55.2177	55.0743	54.9293	54.7831	54.6342	54.4831	54.3286	54.1708

* The vapor pressure of pure water, p_o, are taken from Ambrose and Lawrenson (1972).

where $\bar{V}_1$ is the partial molal volume of water in seawater (Millero, 1975). Values of π (bar) determined from equation (109), using the values of ϕ given in table 16 and the values of $\bar{V}_1$ given elsewhere (Millero, 1975), are given in table 21. These values of π have been fitted to the equation (std deviation 0.003 bar)

$$\pi = A\ S(‰) + B\ S(‰)^{3/2} + C\ S(‰)^2 \qquad (110)$$

where

$$A = 0.70249 + 2.3938 \times 10^{-3}t - 3.7170 \times 10^{-6}t^2$$

$$B = -2.1601 \times 10^{-2} + 4.8460 \times 10^{-6}t - 1.0492 \times 10^{-6}t^2$$

$$C = 2.7984 \times 10^{-3} + 1.5520 \times 10^{-5}t - 2.7048 \times 10^{-8}t^2$$

A comparison of the vapor pressure and osmotic pressures given in tables 20 and 21 with the results obtained by other workers Miyake (1952), Robinson (1954), and Wilson and Arons (1955) is given in table 22.

TABLE 21

The osmotic pressure of seawater

π (bar)

	Salinity							
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	3.341	6.616	9.905	13.231	16.602	20.033	23.537	27.124
5	0	3.403	6.743	10.103	13.500	16.949	20.460	24.046	27.828
10	0	3.464	6.866	10.292	13.761	17.283	20.875	24.544	28.306
15	0	3.522	6.985	10.473	14.010	17.603	21.267	25.017	28.859
20	0	3.579	7.100	10.649	14.249	17.911	21.643	25.462	29.879
25	0	3.634	7.212	10.820	14.480	18.208	22.007	25.896	29.887
30	0	3.688	7.319	10.983	14.702	18.492	22.354	26.309	30.371
35	0	3.741	7.424	11.143	14.919	18.762	22.685	26.703	30.829
40	0	3.792	7.525	11.297	15.127	19.025	23.009	27.087	31.272

TABLE 22

Comparisons of vapor pressure and osmotic pressure obtained by various workers

S(‰)	Δp (mm Hg)		Δπ (bar)			
	A	B	A	C	B	C
	0°C	25°C	0°C	0°C	25°C	25°C
5	0.009	—0.001	—0.119	—	0.044	—
10	0.007	—0.002	—0.312	0.51	0.034	0.74
15	0.015	—0.001	—0.509	—	0.025	—
20	0.013	0.000	—0.662	0.91	0.020	1.42
25	0.011	0.000	—0.799	—	0.016	—
30	0.008	0.001	—0.820	—	—0.006	—
35	0.008	0.001	—0.833	2.15	—0.044	1.66
40	0.013	0.000	—0.738	—	—0.086	—

A. Our results minus Miyake (1952) values.
B. Our results minus Robinson (1954) values.
C. Our results minus Wilson and Arons (1955) values.

The values P determined from freezing point measurements are in good agreement with direct measurements. The values of p and π determined from freezing point measurements are about three times more reliable than the direct measurements.

Activity of sea salt.—The activity of sea salt (a_2) or the mean activity of sea salt ($a_\pm = a_2^{1/2}$) can be calculated from the osmotic coefficient data by using the Gibbs-Duhem equation

$$-55.51 \text{ d ln } a_1 = 2\text{d}(m\phi) = m \text{ d ln } a_2 = 2m \text{ d ln } a_\pm \qquad (111)$$

By integrating this equation it is possible to determine the mean activity coefficient of seawater $\gamma_\pm = a_\pm/m = a_2^{1/2}/m$

$$\ln \gamma_2 = (\phi - 1) + \int_0^m (\phi - 1) \text{ d ln } m \qquad (112)$$

To determine reliable values of $\gamma_\pm$ and a_2 from equation (112), reliable values of ϕ are needed in dilute solutions. When dealing with isopiestic data, more reliable values of $\gamma_\pm$ and a_2 can be determined by using the relationship

$$m \text{ d ln } a_2 = m_{NaCl} \text{ d ln } a_{NaCl} \qquad (113)$$

$$\text{d ln } a_2 = R \text{ d ln } a_{NaCl} \qquad (114)$$

By integrating equation (114), the value of $\gamma_\pm$ can be determined from

$$\ln \gamma_\pm = \ln \gamma_\pm(\text{NaCl}) + \ln R + \int_0^m (R - 1) \times \text{d ln } \gamma(\text{NaCl}) \, m_{NaCl} \qquad (115)$$

Recently, Millero (1974a) calculated the values of $\gamma_\pm$ for sea salt from the isopiestic measurements of seawater of Robinson (1954) and Robinson and Stokes' (1959) results for NaCl solutions. The results are given in table 23. Since the isopiestic measurements used by Millero (1974a) were

TABLE 23

The mean activity coefficient of sea salt at 25°C

$\gamma_\pm$ (sea salt)

S(‰)	$\gamma_\pm$(NaCl)	A	B	C
20	0.705	0.690	0.628	0.625
25	0.692	0.675	0.614	0.610
30	0.682	0.664	0.604	0.600
35	0.675	0.656	0.598	0.592
40	0.670	0.651	0.593	0.587

A. From isopiestic data using equation (112).
B. From isopiestic data using equation (115) from Millero (1974a).
C. From freezing point data using equation (117).

not made in dilute solutions and the values of ϕ were not fitted to the limiting law, the values of $\gamma_{\pm}$ determined from equation (112) are not as reliable as those determined from equation (115).

Leyendekkers (1973) has recently determined the activity of sea salt by integrating equation (113). She obtained

$$\begin{aligned} k \log a_w = &-0.0131 \log [S(‰)10^{-3}] + 670.37 [S(‰)10^{-3}] \\ &-11480 [S(‰)10^{-3}]^2 + 86420 [S(‰)10^{-3}]^3 \\ &+ 49270 [S(‰)10^{-3}]^4 - 86820 [S(‰)10^{-3}]^5 + \text{const} \end{aligned} \tag{116}$$

where $k = (m/2)\ [10^3/S(‰)-1]$. The constant of integration was evaluated from single and two electrolyte solution activity data (−23.042 to −23.048). Since Leyendekkers (1973) treats sea salt as a mixture of salts, (while we treat sea salts as a mixture of ions), the values of a_w determined from equation (116) do not agree with those given in table 23. (They differ by a constant factor.)

Since the osmotic coefficients of seawater determined from freezing point data have been fitted to an extended Debye-Hückel equation that can be easily integrated, we can obtain the activity of sea salt by using equation (112). We obtain upon integration (using the ϕ's from equation 107)

$$\begin{aligned} \log \gamma_{\pm} = &- [S_\gamma' I^{1/2}/(1 + I^{1/2}) + 0.868\ B_\gamma' I + \\ &0.724\ C_\gamma' I^{3/2} + 0.651\ D_\gamma' I^2] \end{aligned} \tag{117}$$

Values of the activity coefficients of sea salt as a function of temperature and salinity determined from equation (117) are given in table 24, using the values of S_γ', B_γ', C_γ', and D_γ' given earlier. The activities of sea salt determined from $a_w = (\gamma_{\pm}\ m)^2$ are given in table 25. The values of $\gamma_{\pm}$ at 25°C determined from freezing point data are in good agreement with the values determined from the isopiestic data using equation (115) (see table 23).

TABLE 24

The main activity coefficient of sea salt

$\gamma_{\pm}$

Temp	Salinity 0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	1.0000	0.7327	0.6778	0.6459	0.6241	0.6081	0.5959	0.5865	0.5796
5	1.0000	0.7323	0.6779	0.6467	0.6254	0.6099	0.5982	0.5893	0.5827
10	1.0000	0.7315	0.6776	0.6468	0.6260	0.6109	0.5996	0.5911	0.5849
15	1.0000	0.7305	0.6769	0.6465	0.6261	0.6113	0.6003	0.5921	0.5862
20	1.0000	0.7293	0.6759	0.6458	0.6256	0.6111	0.6004	0.5924	0.5867
25	1.0000	0.7279	0.6746	0.6446	0.6247	0.6104	0.5999	0.5921	0.5866
30	1.0000	0.7263	0.6730	0.6432	0.6234	0.6093	0.5989	0.5912	0.5858
35	1.0000	0.7245	0.6712	0.6414	0.6217	0.6077	0.5974	0.5899	0.5846
40	1.0000	0.7226	0.6691	0.6394	0.6197	0.6058	0.5956	0.5881	0.5829

TABLE 25

The activity of sea salt

a_2

Temp	Salinity 0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	0.0034_7	0.0120_1	0.0247_8	0.0415_5	0.0622_3	0.0870_1	0.1159_2	0.1494_2
5	0	0.0034_7	0.0120_1	0.0248_4	0.0417_3	0.0626_5	0.0876_8	0.1170_3	0.1510_3
10	0	0.0034_6	0.0120_0	0.0248_5	0.0418_1	0.0628_5	0.0880_0	0.1177_5	0.1521_7
15	0	0.0034_5	0.0119_7	0.0248_3	0.0418_2	0.0629_3	0.0883_0	0.1181_5	0.1528_5
20	0	0.0034_4	0.0119_4	0.0247_7	0.0417_5	0.0628_9	0.0883_3	0.1182_7	0.1531_1
25	0	0.0034_3	0.0118_9	0.0246_8	0.0416_3	0.6027_5	0.0881_8	0.1181_5	0.1530_5
30	0	0.0034_1	0.0118_4	0.0245_7	0.0414_6	0.0625_2	0.0878_0	0.1177_9	0.1526_4
35	0	0.0033_9	0.0117_7	0.0244_1	0.0412_3	0.0621_0	0.0874_5	0.1172_7	0.1520_1
40	0	0.0033_5	0.0117_0	0.0242_8	0.0409_7	0.6018_1	0.0869_2	0.1165_6	0.1511_3

TABLE 26

The relative free energy of seawater

$-(G - G^\circ)$ (kj)

Temp	Salinity 0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	1.369	2.286	3.038	3.683	4.247	4.748	5.194	5.591
5	0	1.394	2.328	3.093	3.749	4.325	4.832	5.284	5.688
10	0	1.420	2.370	3.150	3.818	4.402	4.920	5.377	5.786
15	0	1.445	2.413	3.206	3.887	4.481	5.006	5.473	5.888
20	0	1.471	2.455	3.265	3.955	4.561	5.095	5.571	5.991
25	0	1.497	2.499	3.322	4.027	4.642	5.187	5.669	6.098
30	0	1.521	2.543	3.380	4.097	4.724	5.278	5.771	6.207
35	0	1.548	2.587	3.439	4.170	4.808	5.371	5.873	6.318
40	0	1.573	2.630	3.499	4.241	4.892	5.466	5.977	6.430

TABLE 27

The relative specific free energy of seawater

$-g$ (j g^{-1})

Temp	Salinity 0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	1.362	2.263	2.992	3.609	4.141	4.605	5.011	5.366
5	0	1.387	2.304	3.047	3.674	4.216	4.687	5.098	5.459
10	0	1.412	2.346	3.103	3.741	4.291	4.771	5.188	5.553
15	0	1.438	2.388	3.158	3.808	4.369	4.855	5.281	5.651
20	0	1.464	2.431	3.215	3.876	4.446	4.942	5.375	5.750
25	0	1.489	2.474	3.272	3.946	4.526	5.031	5.469	5.853
30	0	1.514	2.517	3.329	4.015	4.605	5.119	5.568	5.957
35	0	1.540	2.561	3.387	4.086	4.687	5.210	5.666	6.064
40	0	1.566	2.604	3.446	4.156	4.769	5.302	5.767	6.172

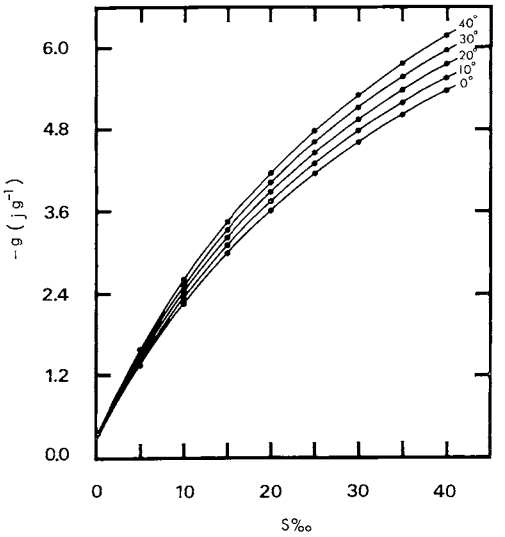

Fig. 4. The relative specific free energies of seawater solutions at various salinities and temperatures.

By combining the activity of water and sea salt using equation (80), the relative molal free energy of seawater can be determined. Values of $G - G^0$ determined from equation (80) are given in table 26. By expressing n_1 and n_2 in terms of moles per gram of solution, one can calculate the relative specific free energy of seawater (g). Values of (g) calculated in this manner are given in table 27. These values of g have been fitted to the equation (std deviation ± 0.002 j g^{-1})

$$g = A\ S(‰) + B\ S(‰)^{3/2} + C\ S(‰)^2 \tag{118}$$

where

$$A = -0.38346 - 1.42024 \times 10^{-3}t + 6.416 \times 10^{-8}t^2$$

$$B = 5.959 \times 10^{-2} + 2.170 \times 10^{-4}t - 1.714 \times 10^{-7}t^2$$

$$C = -3.1965 \times 10^{-3} - 1.0270 \times 10^{-5}t - 3.273 \times 10^{-8}t^2$$

The specific free energies of seawater solutions are shown in figure 4 as a function of salinity and temperature. The effect of pressure on the activity of water and sea salt can be determined from molal volume data (Millero, 1976) using the thermodynamic relations

$$(\partial \ln a_1/\partial P) = (\bar{V}_1 - \bar{V}_1^0) / RT \tag{119}$$

$$(\partial \ln a_2/\partial P) = (\bar{V}_2 - \bar{V}_2^0) / RT \tag{120}$$

The effect of pressure on the relative molal free energy is given by

$$\partial(G - G^0) / \partial P = (V - V^0) = 55.51\ (\bar{V}_1 - \bar{V}_1^0) / RT + 2m\ (\bar{V}_2 - \bar{V}_2^0) / RT \tag{121}$$

The Entropy of Seawater

The change in the entropy of seawater as a function of temperature, pressure, and composition can be expressed by

$$dS = (\partial S/\partial T)_P \, dT + (\partial S/\partial P)_T \, dP + \Sigma \, (\partial S/\partial n_i)_{T,P} \, dn_i \qquad (122)$$

The effect of temperature on the entropy is related to the heat capacity by

$$(\partial S/\partial T)_P = Cp \; / \; T \qquad (123)$$

while the effect of pressure on the entropy is related to the expansibility by

$$(\partial S/\partial P)_T = -V\alpha = -(\partial V/\partial T)_P \qquad (124)$$

where α is the expansibility. At constant pressure and temperature, the change in entropy as a function of composition is given by

$$dS = \bar{S}_1 \, dn_1 + \bar{S}_2 \, dn_2 \qquad (125)$$

where $\bar{S}_1$ is the partial molal entropy of water in seawater, and $\bar{S}_2$ is the partial molal entropy of sea salt. By using the thermodynamic relationship

$$G = H - TS \qquad (126)$$

the relative molal and relative specific entropy of seawater as well as the partial molal properties can be determined from free energy and enthalpy data given earlier

$$S - S^0 = [(H - H^0) - (G - G^0)] \; / \; T \qquad (127)$$

$$s = (h - g) \; / \; T \qquad (128)$$

$$\bar{S}_1 - \bar{S}_1^0 = [(\bar{H}_1 - \bar{H}_1^0) - (\overline{G}_1 - \overline{G}_1^0)] \; / \; T$$

$$= \bar{L}_1/T - R \ln a_1 \qquad (129)$$

$$\bar{S}_2 - \bar{S}_2^0 = [(\bar{H}_2 - \bar{H}_2^0) - (\overline{G}_2 - \overline{G}_2^0)] \; / \; T$$

$$= \bar{L}_2/T - R \ln a_2 \qquad (130)$$

Values for the relative molal entropy of seawater ($S - S^0$), the relative specific entropy of seawater (s), the relative partial molal entropy of water ($\bar{S}_1 - \bar{S}_1^0$) and sea salt ($\bar{S}_2 - \bar{S}_2^0$) determined from the enthalpy and free energy data are given in tables 28, 29, 30, and 31. Although the values given in these tables are relative values (to infinite dilution), unlike the enthalpy and free energy of seawater, it is possible to determine absolute values for the entropy of seawater. This is possible, since the entropy of an ideal solid is equal to zero at absolute zero degrees Kelvin

(−273.15°C). Thus, by using equation (123), the absolute entropy of a substance at any temperature can be determined from

$$S_T = \int_0^T (C_P/T)\, dT \qquad (131)$$

using heat capacity data as a function of temperature.

The molal entropy of water ($\bar{S}_1^0$) at 25°C is 70.00 j deg^{-1}mol^{-1} (Lewis and Randall, 1961). Since the molal entropy of salts (or ions) are known for the major sea salts, the partial molal entropy of sea salt at infinite dilution ($\bar{S}_2^0$) can be determined from

$$\bar{S}_2^0 = \Sigma\, N_i \bar{S}_i^0 \qquad (132)$$

where $\bar{S}_i^0$ is the absolute entropy of ionic constituent *i*. The calculation of the partial molal entropy of sea salt at 25°C using the data for ions tabulated by Lewis and Randall (1961) is shown in table 32. The $\bar{S}_2^0$ = 95.0 j mol^{-1}deg^{-1} for sea salt can be compared to a value of 115.4 j mol^{-1}deg^{-1} for NaCl.

TABLE 28

The relative molal entropy of seawater

$S - S°$ (j deg^{-1} mol^{-1})

	Salinity								
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	5.061_5	8.414_8	11.086_0	13.284_5	15.105_6	16.618_2	17.854_1	18.839_3
5	0	5.079_2	8.474_4	11.203_3	13.476_7	15.397_3	17.006_7	18.356_8	19.475_4
10	0	5.099_3	8.529_4	11.317_3	13.660_7	15.657_0	17.362_6	18.816_7	20.046_7
15	0	5.115_0	8.584_0	11.418_8	13.829_3	15.899_1	17.690_5	19.241_2	20.573_4
20	0	5.133_5	8.632_1	11.523_6	13.981_8	16.125_7	17.994_5	19.635_4	21.055_9
25	0	5.151_4	8.684_5	11.615_5	14.137_3	16.338_9	18.284_0	19.997_8	21.510_8
30	0	5.162_3	8.735_0	11.706_6	14.278_4	16.543_1	18.554_7	20.350_3	21.942_6
35	0	5.182_8	8.784_3	11.798_0	14.423_7	16.745_6	18.818_2	20.685_0	22.358_6
40	0	5.196_8	8.829_7	11.890_9	14.559_3	16.942_4	19.080_1	21.015_4	22.761_9

TABLE 29

The relative specific entropy of seawater

$10^2 \times s$ (j g^{-1} deg^{-1})

	Salinity								
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	0.503_5	0.833_1	1.091_8	1.301_3	1.471_8	1.609_5	1.718_4	1.801_6
5	0	0.505_4	0.838_8	1.103_8	1.320_7	1.500_5	1.648_5	1.735_4	1.865_3
10	0	0.507_1	0.844_5	1.115_1	1.338_0	1.526_5	1.684_3	1.814_9	1.922_4
15	0	0.509_1	0.849_7	1.125_2	1.355_5	1.151_1	1.716_7	1.857_5	1.975_1
20	0	0.512_0	0.855_0	1.135_3	1.371_2	1.573_3	1.747_3	1.896_7	2.023_1
25	0	0.512_5	0.860_1	1.144_8	1.386_6	1.595_0	1.776_2	1.932_7	2.068_9
30	0	0.513_0	0.864_9	1.153_8	1.400_8	1.615_1	1.803_0	1.968_1	2.011_8
35	0	0.515_7	0.869_0	1.162_0	1.415_1	1.635_3	1.829_6	2.001_3	2.120_9
40	0	0.517_5	0.874_7	1.172_2	1.428_8	1.655_0	1.855_7	2.034_5	2.193_8

TABLE 30

The relative partial molal entropy of water in seawater

$10^2 \times (\bar{S}_1 - \bar{S}_1^\circ)$ (j deg^{-1} mol^{-1})

Temp	Salinity 0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	2.239	4.599	7.123	9.805	12.635	15.602	18.694	21.909
5	0	2.216	4.523	6.977	9.570	12.304	15.155	18.124	21.214
10	0	2.196	4.455	6.849	9.366	12.003	14.761	17.621	20.596
15	0	2.177	4.395	6.729	9.181	11.739	14.399	17.177	20.052
20	0	2.160	4.341	6.631	9.009	11.500	14.087	16.779	19.559
25	0	2.144	4.291	6.535	8.863	11.287	13.809	16.414	19.127
30	0	2.121	4.245	6.438	8.723	11.088	13.543	16.093	18.723
35	0	2.107	4.203	6.356	8.593	10.904	13.299	15.785	18.356
40	0	2.093	4.153	6.278	8.462	10.731	13.072	15.498	18.007

TABLE 31

The relative partial molal entropy of sea salt

$\bar{S}_2 - \bar{S}_2^\circ$ (j deg^{-1} mol^{-1})

Temp	Salinity 0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	47.483_2	36.256_7	29.261_3	24.004_0	19.721_1	16.075_3	12.877_3	10.013_4
5	0	47.861_9	36.883_9	30.081_8	24.999_4	20.873_0	17.364_5	14.291_1	11.542_0
10	0	48.235_7	37.460_2	30.834_6	25.905_1	21.916_5	18.530_3	15.566_0	12.915_0
15	0	48.586_0	38.001_1	31.525_8	26.732_0	22.864_7	19.589_0	16.719_8	14.156_4
20	0	48.918_1	38.503_5	32.172_6	27.500_2	23.738_7	20.555_1	17.777_4	15.293_8
25	0	49.235_2	38.987_4	32.780_7	28.214_9	24.548_5	21.451_7	18.750_0	16.335_4
30	0	49.566_7	39.449_0	33.361_8	28.894_1	25.314_5	22.295_8	19.665_8	17.314_9
35	0	49.892_0	39.909_1	33.924_4	29.551_6	26.051_0	23.104_7	20.535_0	18.243_2
40	0	50.192_0	40.360_0	34.482_5	30.197_5	26.769_4	23.889_7	21.382_3	19.142_2

TABLE 32

Calculation of the partial molal entropy of sea salt at 25°C

Species	$\bar{S}_i^\circ$*	N_i	$N_i\bar{S}_i^\circ$
Na^+	60.2	0.83619	50.34
Mg^{2+}	—118.0	0.09509	—11.22
Ca^{2+}	— 55.2	0.01834	— 1.01
K^+	102.5	0.01822	1.87
Sr^{2+}	— 39.3	0.00016	— 0.01
Cl^-	55.2	0.97481	53.81
SO_4^{2-}	17.2	0.05042	0.87
HCO_3^-	95.0	0.00345	0.33
Br^-	80.8	0.00151	0.01
$B(OH)_3$	~ 50	0.0006	0.03
CO_3^{2-}	— 53.1	0.0004	— 0.02
$B(OH)_4^-$	~100	0.0001_5	0.01
F^-	— 9.6	0.0001	— 0.00_1
			95.01

* Based on $\bar{S}^\circ$ $(H^+) = 0$ and taken from Lewis and Randall (1961). The values of $B(OH)_4^-$ have been estimated by comparison with solutes of similar size and charge.

Since the S^0 is equal to $\bar{S}_1^0$, the relative molal entropies can be converted to absolute values by adding $\bar{S}_1^0$ at each temperature. The values of $\bar{S}_1^0$ as a function of temperature can be determined from heat capacity data and the 25°C value for $\bar{S}_1^0$

$$\bar{S}_1^0\ (T) = \bar{S}_1^0\ (273.15) + \int_{273.15}^{T} (\bar{C}p_1^0/T)\ dT \tag{133}$$

The values of $\bar{C}p_1^0$ from 0° to 40°C have been fitted to a function of T°K to simplify the integration (std deviation ± 0.0004 j $g^{-1}deg^{-1}$)

$$\bar{C}p_1^0 = 21.02343 - 1.198696 \times 10^{-1}\ T + 9.828769 \times 10^{-5}T^2 + 8.466352 \times 10^{-7}T^3 - 1.554175 \times 10^{-9}T^4 \tag{134}$$

Using integration, we obtain from equation (133) using the 25°C value of $\bar{S}_1^0$ to evaluate the constant of integration

$$\bar{S}_1^0\ (T) = 22.8218 + 21.02343\ \ln T - 1.198696 \times 10^{-1} \times T + 4.914384 \times 10^{-5}T^2 + 2.822117 \times 10^{-7}T^3 - 3.885437 \times 10^{-10}T^4 \tag{135}$$

which is only valid from 0° to 40°C.

Since future workers may wish to look at entropy surfaces in the oceans, the relative specific entropy of seawater has been fitted to a function of salinity (std deviation 0.0001 j $g^{-1}deg^{-1}$)

$$s = A_s\ S(‰) + B_s\ S(‰)^{3/2} + C_s\ S(‰)^2 \tag{136}$$

where

$$A_s = 1.4218_5 \times 10^{-3} - 3.1137 \times 10^{-7}t + 4.2446 \times 10^{-9}t^2$$

$$B_s = -2.1762 \times 10^{-4} + 4.1426 \times 10^{-7}t - 1.6285 \times 10^{-9}t^2$$

$$C_s = 1.0201 \times 10^{-5} + 1.5903 \times 10^{-8}t - 2.3525 \times 10^{-10}t^2$$

The specific entropy of seawater solutions is shown as a function of salinity and temperature in figure 5.

SUMMARY

In this paper the authors have attempted to summarize what they feel are the most reliable thermodynamic properties of seawater. These thermodynamic properties have been examined by using classical chemical thermodynamic methods developed by Lewis and Randall (1961), Harned and Owen (1958), and Robinson and Stokes (1959). It is hoped that this paper will lay the ground work for future studies on the thermodynamic properties of seawater. In a recent paper Bromley and others (1974) have also examined the thermodynamics of seawater solutions from 0° to 200°C and 0 to 120‰ salinity by using boiling point elevation

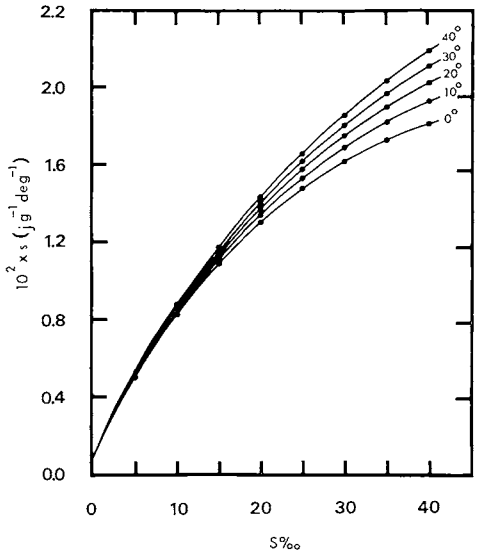

Fig. 5. The relative specific entropies of seawater solutions at various salinities and temperatures.

data. Over the oceanographic range of salinity and temperature, their results for ϕ, a_1, and π, respectively, agree on the average to ± 0.003 (max 0.004), ± 0.00003 (max 0.0001), and ± 0.3 percent (max 0.1 bar) with the results of this paper. This agreement is well within the combined accuracy of the two studies. Over the oceanographic range (0 to 40‰ and 0° to 40°C) the results of the present study are probably more accurate.

Little discussion has been made in this paper of the use of the thermodynamic data of seawater in understanding the ion-water and ion-ion interactions in seawater (Millero, 1974a). The use of the thermodynamic properties of seawater in obtaining information concerning the structure of seawater as a multicomponent electrolyte solution may eventually prove to be of great importance in understanding how seawater affects the bio- and geo-chemical processes occurring in the oceans. Although the ocean is a dynamic system and thermodynamics is really thermostatics, equilibrium chemical thermodynamics can still be quite useful in understanding the oceans.

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APPENDIX

Relationships between Partial Molal and Partial Specific Properties

In the oceanographic applications of thermodynamics to seawater, it is frequently more convenient to examine the physical chemical properties in terms of apparent and partial specific quantities (Fofonoff, 1962). In this section the relationship between these quantities will be developed. Throughout this discussion we will consider the mixture to be made up of two components: (1) water and (2) sea salt. It should be pointed out from the beginning that to obtain reliable relative thermodynamic properties of seawater, it is necessary to use molal properties to extrapolate the data to infinite dilution (that is, as a function of molal ionic strength not weight fraction).

The concentration unit used in treating the properties of one gram of solution (rather than a molal solution) is the weight fraction

$$X_1 = g_1/(g_1 + g_2) = g_1 \tag{1}$$

$$X_2 = g_2/(g_1 + g_2) = g_2 \tag{2}$$

where g_1 and g_2 are the grams of water and sea salt in one gram of solution ($g_1 + g_2 = 1.0$). As discussed in the composition section, g_1, g_2, and $g_1 + g_2$ are related to the salinity ($S‰ = 1.80655\ Cl‰$) by

$$X_1 = g_1 = 1.0 - 1.00488 \times 10^{-3}\ S(‰) \tag{3}$$

$$X_2 = g_2 = 1.00488 \times 10^{-3}\ S(‰) \tag{4}$$

In many cases one can obtain approximate values of X_1 and X_2 by equating the salinity and g_2 by

$$X_1 \cong 1.0 - 10^{-3}\ S(‰) \tag{5}$$

$$X_2 \cong 10^{-3}\ S(‰) \tag{6}$$

The g_1 and g_2 can be related to the moles of water (n_1) and sea salt (n_2) by

$$g_1 = n_1 M_1 \tag{7}$$

$$g_2 = n_2 M_2 \tag{8}$$

where M_1 and M_2 are the molecular weights of water (18.015) and sea salt (62.793). Since the total number of moles of water (n_1) and sea salt (n_2) are equal to the respective mole fractions (N_1 and N_2), the mole fraction and weight fraction of water and sea salt are related by

$$N_1 = M_1 X_1 = 18.015\ X_1 \tag{9}$$

$$N_2 = M_2 X_2 = 62.793\ X_2 \tag{10}$$

The thermodynamic partial specific properties of solutions can be developed in a manner similar to that used for molal properties. For example, the specific volume, v, (that is, the volume of one gram of solution) is related to the partial specific properties by

$$v = X_1 \bar{v}_1 + X_2 \bar{v}_2 \tag{11}$$

where the partial specific volumes are given by

$$\bar{v}_1 = (\partial v/\partial X_1)_{T,P,X_2} \tag{12}$$

$$\bar{v}_2 = (\partial v/\partial X_2)_{T,P,X_1} \tag{13}$$

As for partial molal properties, the evaluation of $\bar{v}_1$ and $\bar{v}_2$ for specific volume data can be conveniently made by using the apparent specific volume given by

$$\phi_v = (V_{Soln} - V_{H_2O}) / g_2 = (v - X_1 \bar{v}_1^0) / X_2 \tag{14}$$

where $\bar{v}_1^0$ is the specific volume of pure water. The differentiation of equation (14) with respect to X_2 gives

$$\bar{v}_2 = \phi_v + (\partial\phi_v/\partial X_2)\, X_2 \tag{15}$$

Combining equations (14), (15), and (11) gives

$$\bar{v}_1 = \bar{v}_1^0 - (X_2^2/X_1)\,(\partial\phi_v/\partial X_2) \tag{16}$$

The relationship between the apparent specific volume defined by equation (14) and the apparent molal volume given by

$$\Phi_v = (v - n_1\, \bar{V}_1^0) \,/\, n_2 \tag{17}$$

(where $\bar{V}_1^\circ = M_1\, \bar{v}_1^\circ$) is found to be:

$$\Phi_v = M_2\, \phi_v \tag{18}$$

Since $dn_i = dN_i = M_i\, dX_i$, $d\phi_V = M_2\, d\phi_v$, the partial molal specific properties are given by similar relationships

$$\bar{V}_1 = M_1\, \bar{v}_1 \tag{19}$$

$$\bar{V}_2 = M_2\, \bar{v}_2 \tag{20}$$

From these calculations, it is clear that partial molal properties (Y_i) of sea salt and water in seawater solutions are related to the partial specific properties ($\bar{y}_i$) by the general equations

$$Y_1 = M_1\, \bar{y}_1 \tag{21}$$

$$Y_2 = M_2\, \bar{y}_2 \tag{22}$$

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