Thermodynamic Properties of Sea Salt Solutions

Based on new experimental data presented for the boiling point elevation of natural sea water solutions, smoothed tabular values are presented for boiling point elevation (BPE), osmotic coefficient, water activity, osmotic pressure, and minimum separation energy to 200°C and 12% sea salt.

The concentration of sodium chloride solutions having the same water activities as sea salt solutions is also presented.

Rigorous thermodynamics and the equations for strong electrolytes by Bromley (1973) were used for the correlation together with previously obtained heat capacity and enthalpy data and equations. A simplified equation is presented for boiling point elevation.

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SCOPE

The dissolved solids composition of sea water on a dry basis is nearly uniform worldwide. Many desalination applications involve the use of this natural solution of strong electrolytes. Although there are some published experimental data on the boiling point elevation of synthetic sea salt solutions and estimates based on comparison with NaCl solutions, almost no data have been obtained on sea water from a natural source. The equipment designed for these measurements is briefly described.

In addition to the thermodynamic properties tabulated, the equations and constants presented can be used to calculate mean stoichiometric activity coefficients, activities, relative enthalpies, and heat capacities of sea salt solutions.

CONCLUSIONS AND SIGNIFICANCE

Boiling point elevation measurements made in two quite different boiling point apparati agreed to about 0.001°C.

At 25°C the one-constant extended Debye-Hückel equation presented by Bromley (1973), with the constant B calculated from the individual ion values, approximates the osmotic coefficient data of Rush and Johnson (1966) on synthetic sea water with a standard deviation of 0.007.

Using a second parameter C the boiling point data, together with heat capacity and heat of mixing data previously obtained in this laboratory, were correlated as a function of temperature. The resulting four-constant equation for parameter B and two-constant equation for C were used to calculate the tabular results presented. The correlated boiling point elevations should be accurate to 2%, and considerably better near 100°C and below 8% salt, where they should be accurate to 0.003°C.

The experimental and smooth derived values compare favorably with those obtained by others. At the highest temperatures and concentrations the equilibrium BPE values might be up to 1.0% lower due to $CaSO_4$ precipitation.

Besides boiling point elevation, the derived properties presented are of direct application in calculations involving evaporation or reverse osmosis. They are also of general interest to scientists and engineers studying physical, chemical, and biological processes involving saline solutions.

PREVIOUS WORK

Measurements, calculations, and estimates of the boiling point elevation of sea water of 3.5% salt as a function of temperature were summarized in the Bechtel Report (1964) to the Office of Saline Water. The reported values above 100°C differed by as much as a factor of two. Since then measurements on several different formulations of synthetic sea water, differing mainly in the amount of Ca^{++}, by Fabuss and Korosi (1966), Grunberg (1970), and Liu and Lindsey (1971) gave results differing in general by several hundredths of a degree. Based on sodium chloride solutions as a reference, Stoughton and Lietzke (1967) used rigorous thermodynamics, extended Debye-Hückel theory, and the osmotic coefficient data of Rush and Johnson (1966) at 25°C for synthetic sea water solutions to predict the boiling point elevations and osmotic pressures of sea salt solutions. These are also significantly different from the other reported values.

To resolve these discrepancies and to establish a firm foundation for the thermodynamics of natural sea water solutions, equipment was designed to measure directly the boiling point elevation of saline solutions. Measurements were made only in the limited range of 60° to 120°C.

For extrapolation over the wide temperature range reported, the data on heat capacity of sea salt solutions of Bromley et al. (1970) and the enthalpy data of Singh and

Bromley (1973) were used. These latter sets of data have been shown to be in good agreement with several sets of experimental measurements of enthalpy and heat capacity such as the recent data of Millero et al. (1973) and Connors (1970). They are in fair agreement with the data of Daley, Hilding, and Fisher (1970) although the latter use a different zero base for the enthalpy of the salt.

The theoretical basis for the correlation is the extended Debye-Hückel equations as modified by Bromley (1973). The recent equations of Pitzer (1973) and Pitzer and Mayorga (1973) could also be used as a theoretically sound basis for correlation of electrolyte data. The graphs and equations of Meissner and Kusik (1972, 1973) could also have been used.

Ray (1973) has shown that the values can be equally well correlated by using an assumed equilibrium ion association of sulfate ion with the bivalent positive ions somewhat as Pitzer (1972) has done for the pure bivalent sulfates. The percent associated increases with increasing temperature.

EXPERIMENT

The sea water used in this work was obtained from the end of Scripps Pier on the campus of the University of California, San Diego, California. This is at a point about 800 ft. off-shore and about midway between the ocean surface and bottom where the water averages about 12 ft. deep.

The sea water was acidified to *p*H 4.5 with about 120 ppm of concentrated ($\sim 36N$) sulfuric acid and then thoroughly degassed. Concentrated solutions were prepared by evaporation and dilute solutions by addition of distilled water.

Most solutions were analyzed by a Bissett-Berman Model 6230 Inductive Salinometer. The accuracy is claimed to be ±0.005 parts per thousand ($^0/_{00}$) in salinity. Some samples were analyzed by the Knudsen method using standardized silver nitrate solution in standard equipment.

The two differential ebulliometers used were similar in function but quite different in detail. The details of each have been recorded by Sridhar (1970) and Ray (1973).

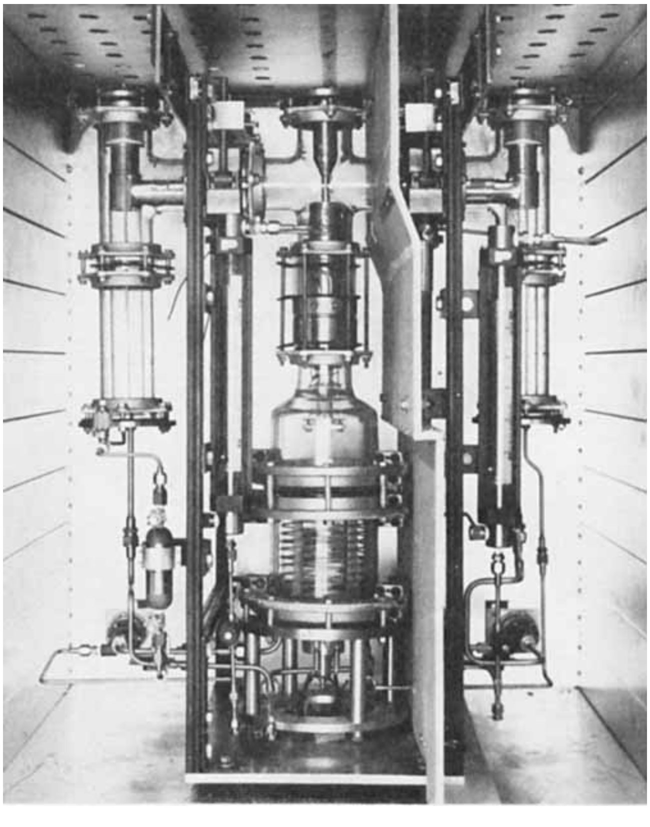

Fig. 1. Photograph of second boiling point apparatus.

The first used vapor lift pumps to raise the boiling solution whereas the second used mechanical pumps and was housed in a constant temperature oven held to ± 0.1°C.

Figure 1 is a photograph of the second apparatus. The temperatures of the solution and of pure water (from condensed vapor) at their boiling point were measured by means of calibrated Hewlett-Packard Model 2801A Quartz Thermometers, accurate to about 0.02°C, with the differential reading being accurate to 0.001°C.

The pressure within the equipment was controlled by a Texas Instrument Company Precision Pressure Test Set (Model 156-02) accurate to about 0.001 in. Hg at low pressure. Measurements were of such duration (several hours) that all carbon dioxide and other dissolved gases were removed and the vapor over the solutions was pure water. No precipitate was observed. Although not specifically measured, the *p*H of the resulting brines, based on other of our measurements, was 7.0 ± 1.0.

THEORY

The following equation for mean activity coefficient formed the basis of the correlation used.* (The logarithm is to the base 10.)

$$\log \gamma_\pm = \frac{-A_\gamma |Z_+Z_-| I^{1/2}}{1 + I^{1/2}} + \frac{(0.06 + 0.6B)|Z_+Z_-| I}{(1 + aI)^2} + BI + CI^n \quad (1)$$

where A_γ = Debye-Hückel constant. Values to 100°C are given by Lewis and Randall, Pitzer and Brewer (1961). Above 100° selected values are

t	A_γ
125°C	0.636
150°C	0.685
175°C	0.747
200°C	0.830

$$a = \frac{1.5}{Z_+Z_-}$$

and, for a multi-ion solution, the mean molal ionic activity coefficient for all ions,

$$\gamma_\pm = \gamma_1^{m_1/\Sigma m_i} \gamma_2^{m_2/\Sigma m_i} \gamma_3^{m_3/\Sigma m_i} \ldots$$

may be calculated if $|Z_+Z_-|$ is replaced by

$$\frac{\Sigma m_i Z_i^2}{\Sigma m_i}$$

which for sea salt has the value 1.2457 as given by Bromley (1968).

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* If Equation (1) with $C = 0$ were to apply exactly to pure solutions of all possible (2 ion) simple salts making up the complex solution, it can be shown that, neglecting interaction between like charged species and higher terms, the Debye-Hückel term (in $A\gamma$) and the term BI, with Z_+Z_- replaced by $\Sigma m_i Z_i^2/\Sigma m_i$, are correct for the calculation of the mean $\gamma_\pm$ for all the ions. The term in a, with B set equal to the B in the BI term, is rigorously correct only if all positively charged ions have the same charge and the negative ions have the same charge (the positive charge need not equal the negative, however). Otherwise the two B values would be somewhat different and the first one would be slightly concentration dependent.

Since Equation (1) is only approximate for simple salts and since the term involving a, where the first B occurs, is at most a few percent of the sum of the other terms, it is quite justified to use a single value of B for a given complex salt with constant ion composition ratios. This is especially true if the resulting equations represent the experimental data well. The relation between the values of B and the individual ion pair B_{MX} is given at the bottom of Table 2.

I (the apparent ionic strength) $= \dfrac{\Sigma m_i Z_i^2}{2}$

m_i = molality (moles/1000 g water) of ion i
Z_i = valence charge without regard to sign

The activity coefficient for a single salt in sea water solution at 25° may be calculated approximately by the equations of Bromley (1973). See Table 2 for ion values.

By rigorous thermodynamics, the corresponding equation for osmotic coefficient, which is defined as

$$\phi = \frac{-1000}{M_1 \Sigma m_i} \ln a_1 = 1 + \frac{1}{I} \int_0^I I \, d \ln \gamma_\pm \qquad (2)$$

where a_1 is the activity, and M_1 the molecular weight of water, becomes

$$\begin{aligned} 1 - \phi = {} & 2.303 A_\gamma |Z_+ Z_-| \frac{I^{1/2}}{3} \sigma(I^{1/2}) \\ & - 2.303(0.06 + 0.6B) |Z_+ Z_-| \frac{I}{2} \psi(aI) \\ & - 2.303B \frac{I}{2} - 2.303 \frac{n}{n+1} CI^n \qquad (3) \end{aligned}$$

Strictly, 2.303 should be written ln 10 and

$$\sigma(I^{1/2}) = \frac{3}{I^{3/2}} \left\{ 1 + I^{1/2} - \frac{1}{1 + I^{1/2}} - 2 \ln(1 + I^{1/2}) \right\} \qquad (4)$$

and

$$\psi(aI) = \frac{2}{aI} \left[\frac{1 + 2aI}{(1 + aI)^2} - \frac{\ln(1 + aI)}{aI} \right] \qquad (5)$$

For enthalpies and relative enthalpies, the following equations are useful. (All enthalpies and heat capacities in Equations (6) and (7) are on unit mass basis except $\overline{H}_1$ which is per mole.)

$$L = H - H^\circ = x(\phi L_s) = x\overline{L}_s + (1 - x)\overline{L}_w \qquad (6a)$$

The relative apparent enthalpy of the salt is

$$\begin{aligned} \phi L_s = {} & \frac{A_H}{2} \frac{\Sigma m_i Z_i^2}{\Sigma m_i M_i} I^{1/2} \left[\frac{1}{1 + I^{1/2}} - \frac{\sigma(I^{1/2})}{3} \right] \\ & - 2.303RT^2 \frac{\Sigma m_i}{\Sigma m_i M_i} I \Big\{ \left[\frac{1}{(1 + aI)^2} - \frac{\psi(aI)}{2} \right] \\ & (0.6 |Z_+ Z_-|) + \frac{1}{2} \Big\} \frac{dB}{dT} \\ & - 2.303RT^2 \frac{\Sigma m_i}{\Sigma m_i M_i} \left(\frac{1}{n+1} \right) I^n \frac{dC}{dT} \qquad (6b) \end{aligned}$$

The relative partial enthalpy of the salt is

$$\overline{L}_s = - \frac{\Sigma m_i}{\Sigma m_i M_i} RT^2 \frac{d \ln \gamma_\pm}{dT} \qquad (6c)$$

The relative partial enthalpy of the water is

$$\overline{L}_w = \frac{\Sigma m_i RT^2}{1000} \frac{d\phi}{dT} \qquad (6d)$$

The partial enthalpy is

$$\overline{H}_w = H_w^\circ + \overline{L}_w; \quad \overline{H}_1 = M_1 \overline{H}_w \qquad (6e)$$

where H_w° is the enthalpy of pure liquid water per unit mass and $\overline{H}_1$ is the partial molal enthalpy of water in solution and M_1 is the molecular weight of water.

For heat capacities per unit mass

$$C_p = C_{pw}^\circ (1 - x) + x(\phi C_{ps}) = \overline{C_{pw}}(1 - x) + x\overline{C_{ps}} \qquad (7a)$$

The apparent heat capacity of the salts is

$$\begin{aligned} \phi C_{ps} = {} & \overline{C_{ps}^\circ} + \frac{A_j}{2} \frac{\Sigma m_i Z_i^2}{\Sigma m_i M_i} I^{1/2} \left[\frac{1}{1 + I^{1/2}} - \frac{\sigma(I^{1/2})}{3} \right] \\ & - 2.303 \frac{\Sigma m_i}{\Sigma m_i M_i} RT^2 I \Big\{ \left[\frac{1}{(1 + aI)^2} - \frac{\psi(aI)}{2} \right] \\ & 0.6 |Z_+ Z_-| + \frac{1}{2} \Big\} \left(\frac{2}{T} \frac{dB}{dT} + \frac{d^2B}{dT^2} \right) \qquad (7b) \end{aligned}$$

The partial heat capacity of the salts is

$$\overline{C_{ps}} = \frac{d\overline{L_s}}{dT} + \overline{C_{ps}}^\circ \qquad (7c)$$

The partial heat capacity of the water is

$$\overline{C_{pw}} = \frac{d\overline{L_w}}{dT} + C_{pw}^\circ \qquad (7d)$$

The relative partial (specific) values of enthalpy and heat capacity of water and salts may also be written by reference to the equations of Bromley (1973). The value of $\overline{C_{ps}}^\circ$ for sea water solutions is given by

$$\begin{aligned} \overline{C_{ps}}^\circ = {} & \frac{-422.9}{(T - 243)^2} - 3.5214 \\ & + 0.0020582T - 0.00003228T^2 \qquad (7e) \end{aligned}$$

Equation (7e) gives values of $\overline{C_{ps}}^\circ$ consistent with the B values used later in this paper although individual values differ slightly from those given previously by Bromley et al. (1970). The equation can be integrated to give the enthalpy of the salt at infinite dilution relative to a convenient base such as 0 at 0°C.

The osmotic pressure π is related to the activity by (Lewis and Randall, Pitzer and Brewer, 1961)

$$\frac{\partial \pi}{\partial I} = - \frac{RT}{\overline{v}_1 M_1} \frac{\partial \ln a_1}{\partial I} \qquad (8)$$

where $\overline{v}_1$ is the partial specific volume of water in the solution. Then

$$\pi = \int_0^I \frac{RT}{1000\overline{v}_1} \cdot \frac{\Sigma m_i}{I} \cdot \frac{\partial (I\phi)}{\partial I} dI \qquad (9)$$

From Equations (3), (4), and (5)

$$\begin{aligned} \frac{\partial (I\phi)}{\partial I} = {} & 1 - 2.303 A_\gamma |Z_+ Z_-| \frac{I^{1/2}}{2(1 + I^{1/2})^2} \\ & + 2.303 (0.06 + 0.6B) |Z_+ Z_-| I \frac{(1 - aI)}{(1 + aI)^3} \\ & + 2.303BI + 2.303nCI^n \qquad (10) \end{aligned}$$

The value of the partial specific volume of water in sea salt solutions is found from the equation of Chen et al. (1973) to be

$$\begin{aligned} \overline{v}_1 = {} & v_0 - (2.654 \times 10^{-3} - 7.360 \times 10^{-5}t + 9.171 \\ & \times 10^{-7}t^2 - 2.718 \times 10^{-9}t^3)I^{3/2}/1.2457 \qquad (11) \end{aligned}$$

This approximate equation appears to be accurate to one part per thousand over the range in question.

The relation between ionic strength, the weight fraction of sea salt x, and the total molality of the ions Σm_i is

Table 1. Boiling Point Elevation Data

$T_0 = 60°C$[*]		$T_0 = 80°C$		$T_0 = 100°C$		$T_0 = 120°C$	
Wt. % salt[†]	BPE in °C	Wt. % salt	BPE in °C	Wt. % salt	BPE in °C	Wt. % salt	BPE in °C
0.6186	0.071	0.6239	0.081	0.7981	0.118	0.1901	0.0325
0.6369	0.072	1.2530	0.163	1.0010	0.147	0.6887	0.1160
1.1263	0.128	1.8504	0.241	1.2566	0.185	1.2813	0.2130
1.1735	0.134	2.5375	0.332	1.6830	0.248	1.9457	0.3240
1.5707	0.178	2.6430	0.347	1.7117	0.251	2.5357	0.4250
1.6867	0.192	3.4670	0.461	2.1510	0.318	2.6012	0.4370
2.2542	0.258	3.4690	0.461	3.0300	0.454	3.0582	0.5160
3.0542	0.356	4.0254	0.542	3.3541	0.505	3.3534	0.5670
3.7350	0.440	4.7790	0.654	3.4730	0.524	3.9086	0.6700
4.5285	0.542	5.3929	0.749	3.6180	0.547	4.4208	0.7640
5.1780	0.629	5.8352	0.816	4.2810	0.657	4.9110	0.8560
5.7635	0.709	5.9126	0.830	4.8760	0.756	5.4038	0.9510
6.4212	0.803	6.3231	0.894	5.0555	0.789	5.9291	1.0560
7.1354	0.907	6.4064	0.910	5.0648	0.790	6.4108	1.1540
		6.5710	0.937	5.4500	0.857	6.5937	1.1925
		6.5750	0.936	6.0340	0.960	6.8656	1.2455
		6.7474	0.964	6.5210	1.049		
		6.9931	1.008	6.5884	1.061		
				6.6215	1.062		
				6.7165	1.088		
				6.7369	1.090		
				7.0950	1.157		
				7.1360	1.167		

[*] T_0 is the boiling point of pure water at the pressure of measurement.

[†] The values listed are 0.1 of the salinity in parts per thousand. The true wt. % solids would be about a factor of 1.0046 larger because of the definition of salinity.

$$I = \frac{39.65}{2}\left(\frac{x}{1-x}\right) = 1.2457\,\frac{\Sigma m_i}{2} \tag{12}$$

Boiling Point Elevation. The boiling point elevation is related to the activity of the solvent a_1 at T_0 and the osmotic coefficient, also at T_0, by the following equation

$$-R\ln a_1 = \int_{T_0}^{T_0+\mathrm{BPE}} \frac{H_v - \overline{H}_1}{T^2}\,dT \tag{13}$$

together with Equation (2). H_v and $\overline{H}_1$ represent the molal enthalpy of pure water vapor and the partial molal enthalpy of water in the solution, respectively, between the temperatures of water and the solution, both at the boiling point at the chosen pressure. R is the universal gas constant.

MINIMUM SEPARATION ENERGY

At constant temperature and pressure this quantity, the Gibbs Free Energy, ΔG_{rec} may be calculated from the activities of water or the related osmotic coefficients. In terms of the latter (Stoughton and Lietzke 1965, 1967), for separation of one mole of water from a solution of ionic strength I_0 to produce a solution of ionic strength I

$$\frac{\Delta G_{\mathrm{rec}}}{RT} = \frac{100}{\%\ \mathrm{rec}}\,(I_0)\left(\frac{\Sigma m_i}{I}\right)\left(\frac{M_1}{1000}\right)\int_{I_0}^{I}\frac{\phi}{I}\,dI \tag{14}$$

The percent water recovered (% rec) is related to I by

$$(\%\ \mathrm{rec}) = 100\left(1 - \frac{I_0}{I}\right) \tag{15}$$

For sea water of 3.45% salt the ionic strength I_0 is

$$I_0 = 0.7084$$

and

$$\frac{\Delta G_{\mathrm{rec}}}{RT} = \frac{2.049}{\%\ \mathrm{rec}}\int_{I_0}^{I}\frac{\phi}{I}\,dI \tag{16}$$

For negligible recovery $I = I_0$ and this reduces to

$$\frac{\Delta G_{\mathrm{rec}}}{RT} = 0.02049\phi \tag{17}$$

EXPERIMENTAL RESULTS

Table 1 summarizes the experimental boiling point elevation data at temperatures from 60° to 120°C at various salinities (we will use wt. % salt rather than parts per thousand as used by oceanographers). No precipitation was observed for any of the experimental values reported. It should be mentioned that one experiment at 100°C was attempted at slightly over three times normal sea water concentration and that a slow downward drift of BPE and some small precipitation on the boiling heater element was observed. This precipitate redissolved on cooling.

SINGLE PARAMETER EQUATION

With the C term set equal to zero in Equation (3), the best value of the parameter B at 25°C was calculated from the osmotic coefficient results of Rush and Johnson (1966) on artificial sea water and found to be $B = 0.0622$. The data fit was only fair, showing a standard deviation in ϕ of 0.007 and a maximum deviation of 0.016.

The value of B at 25°C, predicted by the correlation of Bromley (1973) using individual ion values, is calculated, as shown in Table 2, to be $B = 0.0619$ in excellent agreement with the experimental value. Individual values of B ($C = 0$) were also evaluated from the BPE data shown in Table 1. The variation with temperature is correlated using

$$B = B^{*}\ln\frac{T-243}{T} + \frac{B_1}{T} + B_2 + B_3\ln T \tag{18}$$

It may be noted that

$$T^2 \frac{dB}{dT} = \frac{B^* T^2}{T - 243} - B_1 + (B_3 - B^*)T$$

$$= \frac{243 B^* T}{T - 243} - B_1 + B_3 T \quad (18a)$$

and

$$T^2 \left[\frac{2}{T} \frac{dB}{dT} - \frac{d^2B}{dT^2} \right] = B_3 - \frac{(243)^2 B^*}{(T - 243)^2} \quad (18b)$$

Equation (18), however, has four adjustable parameters and the data in Table 1 is insufficient and over too limited a range to accurately determine all of them. Consequently, the values for B^* and B_3 were obtained from the more extensive data to 200°C on heat capacities of Bromley et al. (1970), and B_1 from data on heats of mixing by Singh and Bromley (1973). Only B_2 was determined from the data in Table 1 and the data of Rush and Johnson (1966). The 25° data were given a weight of unity and the values at other temperatures weighted according to the number of measurements at each temperature. The weighting factor at each temperature varied between 0.8 and 1.3. The values found for the one parameter ($C = 0$) equations are

$$B^* = 0.031102$$

$$B_3 = -0.27491$$

$$B_2 = 1.94357$$

$$B_1 = -78.565$$

The calculated values of B are also given in Table 3. Although the results show only fair agreement, the extrapolation to high temperatures should be appreciably better than if heat capacity and enthalpy of mixing data had not been used.

TABLE 2. INDIVIDUAL ION VALUES FOR CALCULATION OF B FOR SEA WATER AT 25°C

Ion	m_i/m_{Na}*	Z_i	B_i	δ_i
Na^+	1.0	1	0	0.028
Mg^{++}	0.1139	2	0.0570	0.157
Ca^{++}	0.0217	2	0.0374	0.119
K^+	0.0212	1	−0.0452	−0.079
Cl^-	1.1656	1	0.0643	−0.067
SO_4^{--}	0.0600	2	0.000	−0.40
HCO_3^-	0.0051	1	(−0.05)	(0.2)
Br^-	0.0018	1	0.0741	0.064

$$B_{MX} = B_M + B_X + \delta_M \delta_X$$

$$B = \frac{4 \sum_M \sum_X B_{MX} \overline{Z}^2_{MX} \nu_M \nu_X}{\nu \Sigma \nu_i Z_i^2} = \frac{4 \sum_M \sum_X B_{MX} \overline{Z}^2_{MX} m_M m_X}{\Sigma m_i \Sigma m_i Z_i^2} = 0.0619$$

* Values given by Rush and Johnson (1966).

TABLE 3. ONE-PARAMETER FIT FOR ϕ SEA WATER

Temp., °C	Data source	B Exp. and Equation (3)	σ	B Correl. Equation (18)
25	Rush and Johnson (1966)	0.0622	0.007	0.0613
60	This work	0.0724	0.004	0.0703
80	This work	0.0717	0.002	0.0720
100	This work	0.0713	0.003	0.0723
120	This work	0.0703	0.005	0.0714

TABLE 4. TWO-PARAMETER FIT EXPERIMENTAL AND CORRELATED VALUES OF B & C

Temp., °C	B Expt'l.	B Correlated	C Expt'l.	C Correlated	σ*
25	0.0543	0.0618	+0.0029	−0.0008	0.003
60	0.0767	0.0756	−0.0034	−0.0047	0.001
80	0.0800	0.0797	−0.0064	−0.0065	0.002
100	0.0836	0.0820	−0.0092	−0.0082	0.002
120	0.0876	0.0830	−0.0136	−0.0097	0.001

* Note the σ value is the standard deviation in ϕ with the experimental best B and C values. 25° Data from Rush and Johnson (1966).

Using the correlated value of B (from experimental data at all temperatures) in Equation (3) for the one parameter fit ($C = 0$) at 100°C results in the smooth curve in Figure 2. The points are directly calculated from the experimental data. It will be noted that although the points lie moderately close to the line, clearly a better correlation is obtained by including the C parameter. This allows for some ion pair formation and its variation with temperature. However, except at the highest concentrations and temperatures, the single-parameter equation appears to adequately represent the data.

TWO-PARAMETER EQUATION

Consistent with values found in previous work, n was set equal to 1.5. The results of the least squares fit, using Equation (3) including the C term, are shown in Table 4. As with the one parameter fit, heat capacity and heat of mixing data were used to obtain the temperature dependence of B and C. Since the heat capacity is not significantly improved by the addition of the C term, B^* and B_3 remain the same as for the one parameter fit. The new values of B_1 and B_2 for use in Equation (18) are

$$B_1 = -92.220$$

$$B_2 = 1.98989$$

In correlating heats of mixing data it was observed that within the accuracy of the data, a constant value for $T^2 \frac{dC}{dT}$ could be used over the entire temperature range 0-75°C. Therefore the form of the equation used for the temperature dependence of C is

$$C = \frac{C_1}{T} + C_2 \quad (19)$$

A least squares fit on the heat of mixing data gives

$$C_1 = 11.05$$

and from the values in Table 4

$$C_2 = -0.03782$$

The correlated values of B and C are also given in Table 4.

It will be observed that the individual B and C values show rather poor agreement and an apparent drift with temperature. Fortunately the changes are at least partially self-compensating and as may be seen in Figure 2 the smooth curve using the correlated B and C values is a rather good representation of the data.

Further, extrapolation to 200°C with the correlated values should be much more accurate as it uses the heat capacity data previously obtained to 200°C.

SMOOTHED VALUES

Osmotic Coefficient. Tables 5a and 5b contain the values of the calculated osmotic coefficient and activity of water respectively, using the two-parameter equation [Equation (3)] and the 6 constants (B^*, B_1, B_2, B_3, C_1, C_2) determined from experimental data and used in Equations (3), (18), and (19). The values were calculated on a Hewlett-Packard Model 9820A calculator.

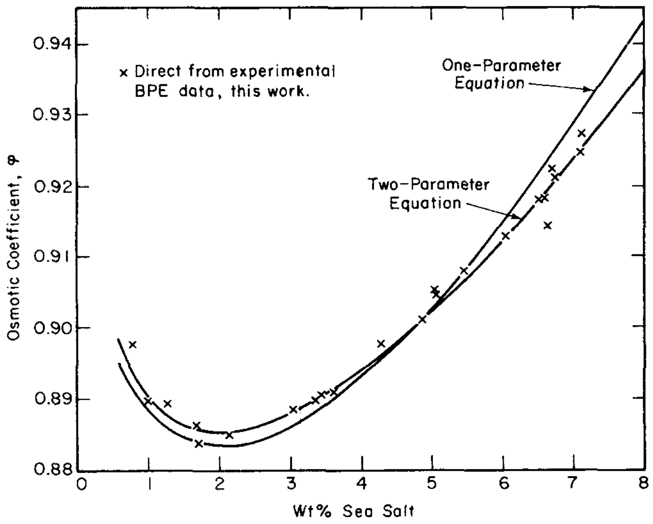

Fig. 2. Osmotic coefficient at 100°C.

NaCl Equivalent. For research purposes it is frequently desirable to make up a sodium chloride solution which has the same water activity as a sea water solution in question. Figure 3 is a plot of the weight fraction ratio, $x_{\mathrm{NaCl}}/x_{\mathrm{Sea\ Salt}}$, versus weight percent sea salt for various temperatures which give solutions of equal water activity. In the calculation of these, the values summarized by Stoughton and Litzke (1967); Robinson and Stokes (1968), together with the Debye-Hückel limiting law, were used. The values at various $x_{\mathrm{Sea\ Salt}}$ were first smoothed with temperature using an equation of the form

$$\frac{x_{\mathrm{NaCl}}}{x_{\mathrm{Sea\ Salt}}} = A + Bt + \frac{C}{t - D}$$

and then smoothed with concentration using

$$\frac{x_{\mathrm{NaCl}}}{x_{\mathrm{Sea\ Salt}}} = 0.930\,[1 - 1.195A_\gamma x^{1/2} + ---].$$

using a power series in $x^{1/2}$ to $x^{5/2}$.

The weight ratios shown in Figure 3 should be accurate to about 0.002. The graph suggests that one should not try to approximate sea water solution with NaCl solution at concentrations below one percent salt because of the large effect of bivalent ions at low concentrations.

It should be noted that both the 0° and 40°C, and

Table 5a. Osmotic Coefficients of Sea Salt Solutions

	Wt. % sea salt							
Temp., °C	1.0	2.0	3.45	4.0	6.0	8.0	10.0	12.0
0	0.9037	0.8956	0.8951	0.8966	0.9075	0.9246	0.9462	0.9715
10	0.9050	0.8988	0.9006	0.9030	0.9171	0.9373	0.9621	0.9905
20	0.9053	0.9003	0.9038	0.9068	0.9229	0.9452	0.9720	1.0023
25	0.9052	0.9007	0.9048	0.9080	0.9249	0.9479	0.9754	1.0065
40	0.9042	0.9006	0.9058	0.9095	0.9280	0.9524	0.9813	1.0135
60	0.9010	0.8976	0.9035	0.9073	0.9266	0.9517	0.9810	1.0134
80	0.8962	0.8924	0.8981	0.9019	0.9210	0.9458	0.9745	1.0061
100	0.8902	0.8855	0.8904	0.8940	0.9122	0.9360	0.9636	0.9938
120	0.8828	0.8767	0.8804	0.8836	0.9005	0.9229	0.9488	0.9711
140	0.874	0.866	0.868	0.870	0.886	0.906	0.930	0.956
160	0.863	0.852	0.852	0.854	0.867	0.886	0.908	0.932
180	0.849	0.836	0.833	0.835	0.845	0.862	0.881	0.902
200	0.832	0.815	0.810	0.810	0.818	0.832	0.849	0.868

Table 5b. Activity of Water in Sea Salt Solutions

	Wt. % sea salt							
Temp., °C	1.0	2.0	3.45	4.0	6.0	8.0	10.0	12.0
0	0.99478	0.98957	0.98183	0.97881	0.96733	0.95494	0.94149	0.92685
10	0.99477	0.98954	0.98172	0.97866	0.96699	0.95434	0.94054	0.92547
20	0.99477	0.98952	0.98165	0.97857	0.96679	0.95396	0.93995	0.92462
25	0.99477	0.98951	0.98163	0.97854	0.96671	0.95383	0.93974	0.92432
40	0.99478	0.98952	0.98161	0.97850	0.96661	0.95362	0.93939	0.92381
60	0.99480	0.98955	0.98166	0.97855	0.96665	0.95365	0.93941	0.93282
80	0.99482	0.98961	0.98177	0.97868	0.96685	0.95394	0.93980	0.92434
100	0.99486	0.98969	0.98192	0.97887	0.96716	0.95440	0.94045	0.92524
120	0.99490	0.98979	0.98212	0.97911	0.96758	0.95503	0.94134	0.92644
140	0.9950	0.9899	0.9824	0.9794	0.9681	0.9558	0.9424	0.9280
160	0.9950	0.9901	0.9827	0.9798	0.9688	0.9568	0.9438	0.9297
180	0.9951	0.9903	0.9831	0.9803	0.9695	0.9580	0.9454	0.9319
200	0.9952	0.9905	0.9835	0.9808	0.9705	0.9594	0.9473	0.9344

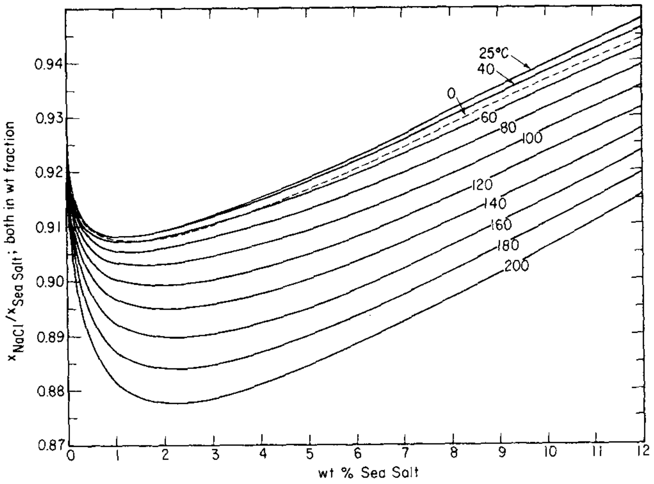

Fig. 3. Weight fraction ratio $x_{NaCl}/x_{sea\ salt}$ vs. weight percent sea salt for equal water activity.

higher temperature curves, lie below the 25° curve which is near the maximum above one percent salt.

Osmotic Pressure. Table 6 contains the values of the calculated osmotic pressure using Equations (3), (9), (10), (11), (18), and (19) and the values of B and C of the two-parameter equation as used for osmotic coefficient The numerical integration was accomplished using 16-point Gaussian Quadrature on a Hewlett-Packard 9820A calculator.

BOILING POINT ELEVATION

Table 7 contains values of the calculated boiling point elevation using Equations (2) and (13) and the osmotic coefficient using the same B and C parameters previously fitted to the experimental data. Pure water properties were obtained from the National Engineering Laboratory (1964) Steam Tables. Relative enthalpies were taken from Singh and Bromley (1973). The equations were solved by successive approximation and numerical integration using

TABLE 6. OSMOTIC PRESSURE IN ATMOSPHERES

	Wt. % sea salt							
Temp., °C	1	2	3.45	4	6	8	10	12
0	6.51	13.04	22.83	26.67	41.37	57.46	75.2	94.9
10	6.76	13.56	23.80	27.83	43.32	60.35	79.2	100.2
20	6.99	14.05	24.69	28.89	45.06	62.89	82.7	104.7
25	7.10	14.27	25.11	29.38	45.86	64.06	84.3	106.8
40	7.41	14.92	26.27	30.76	48.09	67.26	88.6	112.3
60	7.79	15.67	27.63	32.35	50.62	70.85	93.4	118.4
80	8.12	16.33	28.77	33.70	52.73	73.79	97.2	123.2
100	8.40	16.88	29.73	34.80	54.42	76.12	100.2	126.9
120	8.64	17.33	30.48	35.67	55.72	77.85	102.4	129.5
140	8.82	17.66	31.00	36,27	56.6	78.9	103.6	130.9
160	8.95	17.86	31.28	36.6	56.9	79.3	103.9	131.0
180	9.00	17.91	31.27	36.5	56.7	78.8	103.1	129.7
200	8.98	17.78	30.94	36.1	55.9	77.5	101.1	126.9

TABLE 7. BOILING POINT ELEVATIONS OF SEA SALT SOLUTIONS, °C

	Wt. % sea salt						
Temp., °C	2.0	3.45	4.0	6.0	8.0	10.0	12.0
0	0.144	0.253	0.295	0.459	0.637	0.835	1.053
10	0.157	0.276	0.323	0.503	0.701	0.920	1.164
20	0.170	0.300	0.351	0.547	0.765	1.006	1.275
25	0.177	0.312	0.365	0.570	0.797	1.049	1.330
30	0.184	0.324	0.380	0.593	0.830	1.093	1.386
40	0.198	0.350	0.409	0.640	0.896	1.181	1.499
50	0.213	0.376	0.440	0.689	0.965	1.272	1.614
60	0.228	0.403	0.472	0.739	1.035	1.364	1.731
70	0.244	0.431	0.505	0.790	1.107	1.459	1.851
80	0.261	0.460	0.538	0.843	1.180	1.556	1.973
90	0.278	0.489	0.573	0.897	1.256	1.655	2.098
100	0.295	0.520	0.609	0.953	1.334	1.756	2.225
110	0.314	0.552	0.647	1.011	1.414	1.860	2.355
120	0.333	0.585	0.685	1.070	1.496	1.967	2.488
130	0.352	0.619	0.725	1.131	1.580	2.076	2.623
140	0.372	0.654	0.765	1.194	1.666	2.187	2.762
150	0.393	0.690	0.807	1.258	1.754	2.300	2.902
160	0.415	0.727	0.850	1.324	1.844	2.416	3.045
170	0.437	0.765	0.894	1.391	1.935	2.533	3.189
180	0.461	0.804	0.940	1.459	2.028	2.652	3.335
190	0.484	0.844	0.986	1.529	2.122	2.772	3.482
200	0.509	0.885	1.033	1.600	2.218	2.893	3.630

Table 8a. Boiling Point Elevation in °C of Sea Salt† Solutions by Different Workers at 100°C

Wt. % salt	Bechtel,* (1964)	S & L (1965)	F & K (1966)	S & L (1967)	G (1970)	L & L (1972)	Present work
2		0.295	0.297	0.296	0.28	0.270	0.295
3.45	0.4-0.75	0.520	0.530	0.524	0.50	0.486	0.520
4		0.609	0.624	0.615	0.59	0.572	0.609
6		0.949	0.981	0.964	0.92	0.909	0.953
8		1.322	1.369	1.348	1.29	1.285	1.334

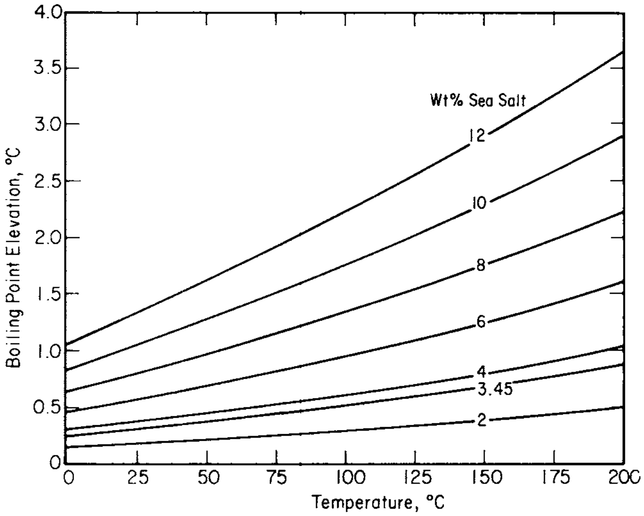

Fig. 4. Boiling point elevation of sea salt solutions [from Equation (21)].

eight-point Gauss until the desired convergence (10^{-5} in ϕ) was obtained. Between 60° and 120° and below 8% salt, the values should be accurate to 0.003°C. Other values should be accurate to 2%.

Simplified Equation. For boiling point elevation, the following equation gives a maximum deviation from the values in Table 7 of 0.001°C below 150°. The maximum deviation is 0.004°C at 200° and 12% salt.

$$\mathrm{BPE} = \frac{xT^2}{13832}\left[1 + 0.001373T - 0.00272\sqrt{x}T + 17.86x - 0.0152xT\left(\frac{T-225.9}{T-236}\right) - \frac{2583\,x(1-x)}{T}\right] \tag{21}$$

x is the wt. fraction sea salt and T is in °K

Equation (21) is plotted in Figure 4.

Since no precipitation occurred during any of the BPE measurements and yet many of the correlated values at high concentration and high temperatures are for conditions under which some $CaSO_4$ may be expected, the equilibrium values might be somewhat smaller than given. The reduction should not exceed 1.2% as estimated by Stoughton and Lietzke (1965) for complete $CaSO_4$ precipitation at 12% and 200°C. Since we would estimate from the data that at most 85% of the $CaSO_4$ would be precipitated under these conditions, the reduction should be at most 1.0%.

Comparison of BPE. The results of recent investigators for the boiling point elevation at 100°C are compared in Tables 8a and 8b. It is interesting to note that the original values of Stoughton and Lietzke (1965) which are based on sodium chloride appear to be the closest to our own. In general, most values appear to be within the accuracy claimed by each author.

Table 8b. Temperature Effect on BPE of Normal Sea Water (~3.45% Salt)

Temp., °C	S & L (1965)	F & K (1966)	S & L (1967)	G (1970)	L & L (1972)	This work
25	0.311	—	0.312	—	—	0.312
40	0.348	0.34	0.350	0.36	—	0.349
80	0.459	0.47	0.463	0.47	0.422	0.460
120	0.585	0.59	0.590	0.60	0.555	0.585
160	0.730	0.71	0.735	0.75	0.707	0.727
200	0.900	—	0.906	—	0.880	0.885

* This is a summary of numerous workers' values. S & L denotes Stoughton and Lietzke; F & K denotes Fabuss and Korosi; G denotes Grunberg; L & L denotes Lindsey and Liu.

† Most of the solutions used were artificially made and had compositions usually reduced in Ca^{++}. S & L values were based on comparison with NaCl solutions.

Table 9. $\Delta G_{\mathrm{rec}}/RT$ for Separation of Pure Water from Normal Sea Water of 3.45 Wt. % Salt

	% recovery of water			
Temp., °C	0	25	50	75
0	0.01834	0.02114	0.02560	0.0349
25	0.01854	0.02141	0.02600	0.0356
50	0.01855	0.02143	0.02606	0.0358
75	0.01844	0.02131	0.02591	0.0356
100	0.01824	0.02108	0.02562	0.0352
125	0.01798	0.02076	0.02521	0.0345
150	0.01763	0.02034	0.02468	0.0337
175	0.01718	0.0198	0.0240	0.0327
200	0.01659	0.0191	0.0231	0.0314

MINIMUM SEPARATION ENERGY

Table 9 gives computed values of the dimensionless group $\Delta G/RT$ for 0, 25, 50, and 75% recovery of water from sea water of 3.45% salt. The values compare quite favorably with those computed by Stoughton and Lietzke (1965, 1967). At 25° the value of 0.01854 for $\Delta G_{\mathrm{rec}}/RT$ corresponds to a value of 0.709 kWh/1000 kg or 2.68 kWh/1000 gal. This compares very favorably with Spiegler's (1962) value of 2.65 kWh/1000 gal.

ENTHALPY AND HEAT CAPACITY

The various enthalpies may be calculated by reference to Equations (6) to (6e) together with a knowledge of the heat capacity of the salts at infinite dilution $\overline{C}_{p_s}{}^\circ$, Equation (7e), and Equation (18) for B. Values of enthalpy previously published by Bromley et al. (1970) are essentially correct, however. At 25°C, the value calculated from Equation (7e) for $\overline{C}_{p_s}{}^\circ$ is −0.393 cal/g°C which is slightly more negative than given previously [−0.370 Bromley (1968) and −0.363 Bromley et al. (1970)] and is in excellent agreement with the value of −0.40 calculated from the individual tabulated ion values of Criss and Cobble (1964). Other heat capacity values may be calculated by reference to Equations (7) to (7d). Again the tabulated values of Bromley et al. (1970) are essentially correct to within the accuracy of the experimental data although values calculated by the equations in this present paper should be slightly better.

ACKNOWLEDGMENT

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NOTATION

A_γ = Debye-Hückel constant for activity coefficient, see Equation (1) and Lewis and Randall (1961), $kg^{1/2}mol^{-1/2}$
A_H = Debye-Hückel constant for enthalpy, see Equation (6b) and Lewis and Randall (1961), cal/mol
A_j = Debye-Hückel constant for heat capacity, see Equation (7b), Lewis and Randall (1961), and Bromley et al. (1970), cal/deg-mol
a = constant in Equation (1); found to be $1.5/Z_+Z_- = 1.5\,\Sigma m_i/\Sigma m_i Z_i^2$
a_1 = activity of water in solution
B = temperature-dependent but concentration-independent parameter, see Equation (18)
B_1, B_2, B_3, B^* = constants in Equation (18)
B_i, B_M, B_X = ionic values, see Table 2; i for any ion, M for cation, and X for anion
BPE = boiling point elevation, °C
C = temperature-dependent but concentration-independent parameter, see Equation (19)
C_1, C_2 = constants in Equation (19)
C_p = heat capacity at constant pressure, cal/g °C
$\overline{C}_{ps}$ = partial (specific) heat capacity of salt in solution, see Equations (7a) and (7c), cal/g °C
$\overline{C_{ps}}^\circ$ = heat capacity of salts at infinite dilution, cal/g °C
C_{pw}° = heat capacity of pure water, cal/g °C
$\overline{C}_{pw}$ = partial (specific) heat capacity of water in solution, see Equations (7a) and (7d), cal/g °C
d, ∂ = derivative, partial derivative
ΔG_{rec} = Gibbs free energy of recovery of pure water from sea water of 3.45% salt = reversible isothermal work of recovery
H = enthalpy of the solution, cal/g
H° = enthalpy of pure water and salts at infinite dilution, (Standard States)
H_v = enthalpy of vapor, cal/mole
$\overline{H}_w$ = partial (specific) enthalpy of water in solution, see Equation (6e). cal/g
H_w° = specific enthalpy of pure water, usually referred to 0°C, cal/g
$\overline{H}_1$ = partial molal enthalpy of water in solution, cal/mole
I = apparent ionic strength = $\dfrac{\Sigma m_i Z_i^2}{2}$, see Equation (12)
L = relative (specific) enthalpy of solution, see Equation (6a), cal/g
$\overline{L}_s$ = relative partial (specific) enthalpy of salt in solution, see Equation (6c), cal/g
$\overline{L}_w$ = relative partial (specific) enthalpy of water in solution, see Equation (6d), cal/g
ln = logarithm to base e
log = logarithm to base 10
M_i = molecular weight of ionic species i
M_1 = molecular weight of water
m_i = molality of ionic species i; moles/1000 g water
n = constant taken as 3/2
R = universal gas constant = 1.9873 defined cal/deg-mol = 82.06 cc atm/deg mol; 1 joule = 4.1840 defined calories; = 0.12831 kWh per 1000 kg water per °K
T = absolute temperature, °K = t + 273.16°
t = temperature, °C
$\overrightarrow{v}_1$ = partial specific volume of water in solution, cc/g
v_0 = specific volume of pure water, cc/g
x = weight fraction salts
$|Z_+Z_-|$ denotes absolute value of charge product = $\Sigma m_i Z_i^2/\Sigma m_i$
Z_i denotes valence charge (without regard to sign)
$\overline{Z}_{MX}$ = arithmetic average charge of cation and anion = $\dfrac{Z_M + Z_X}{2}$
$\gamma_\pm$ = mean stoichiometric ionic activity coefficient $= \gamma_1^{m_1/\Sigma m_i}\,\gamma_2^{m_2/\Sigma m_i}\,\gamma_3^{m_3/\Sigma m_i}\ldots$
$\delta_i, \delta_M, \delta_X$ = ionic values, see Table 2.
ν, ν_M, ν_X = stoichiometric ion sum, cations, and anions, respectively
π = osmotic pressure, atm
σ = standard deviation
$\sigma(I^{1/2})$ = function of $I^{1/2}$, see Equation (4)
ϕ = osmotic coefficient, see Equations (2) and (3)
ϕL_s = apparent relative (specific) enthalpy of sea salt in solution, cal/g
ϕC_p = apparent heat capacity of sea salts in solution, cal/g-°C
$\psi(aI)$ = function of (aI), see Equation (5)

LITERATURE CITED

Bechtel Corporation, "Cost Studies of Large Multi-Stage Flash Saline Water Conversion Plants," Office of Saline Water, USDI, page IX-16, Report No. 116 (1964).

Bromley, L. A., "Thermodynamic Properties of Strong Electrolytes in Aqueous Solutions," *AIChE J.*, **19**, 313 (1973).

———., "Heat Capacity of Sea Water Solutions, Partial and Apparent Values for Salts and Water," *J. Chem. Eng. Data*, **13**, 60 (1968).

———., A. E. Diamond, E. Salami, and D. G. Wilkins, "Heat Capacities and Enthalpies of Sea Salt Solutions to 200°C," *ibid.*, **15**, 246 (1970).

Chen, S. F., R. C. Chan, S. M. Read, and L. A. Bromley, "Viscosity of Sea Water Solutions," *Desalination*, **13**, 37 (1973).

Connors, D. N., "On the Enthalpy of Sea Water," *Limnology Oceanography*, **15**, 587 (1970).

Criss, C. M., and J. W. Cobble, "Thermodynamic Properties of Aqueous Solutions," *J. Am. Chem. Soc.*, **86**, 5390 (1964).

Daley, J. G., W. E. Hilding, and D. A. Fisher, "Thermodynamic Properties of Sea Water Concentrates," *Proc. 5th Symp. on Thermo-phys. Properties*, A.S.M.E., C. F. Bonilla (ed.), 134 (1970).

Fabuss, B. M., and A. Korosi, "Boiling Point Elevation of Sea Water and its Concentrates," *J. Chem. Eng. Data*, **11**, 606 (1966).

Grunberg, L., "Properties of Seawater Concentrates," *3rd Intern. Symp. Fresh Water from Sea*, **1**, 31 (1970).

Lewis, G. N., and M. Randall, revised by K. S. Pitzer and L. Brewer, *Thermodynamics*, 2nd edit., McGraw-Hill, New York (1961).

Liu, S., and W. T. Lindsey, Jr., Westinghouse Corp., "Thermodynamic Properties of Aqueous Solutions at High Temperatures," Office of Saline Water, U.S.D.I. Report No. 722 (1972).

Meissner, H. P., and C. L. Kusik, "Activity Coefficients of Strong Electrolytes in Multicomponent Aqueous Solutions," *AIChE J.*, **18**, 294 (1972).

———., "Aqueous Solutions of Two or More Strong Electrolytes. Vapor Pressures and Solubilities," *Ind. Eng. Chem. Process Design Develop.*, **12**, 205 (1973).
Millero, F. J., "The Enthalpy of Seawater from 0 to 30°C and from 0 to 40% Salinity," *J. Marine Research*, **31**, 1 (1973).
NEL Steam Tables 1964, Her Majesty's Stationary Office, Edinburgh, Scotland.
Pitzer, K. S., "Thermodynamic Properties of Aqueous Solutions of Bivalent Sulfates," *J. Chem. Soc. Faraday Trans. II*, **68**, 101 (1972).
———., "Thermodynamics of Electrolytes, I. Theoretical Basis and General Equations," *J. Phys. Chem.*, **77**, 268 (1973).
———., and G. Mayorga, "Thermodynamics of Electrolytes, II. Activity and Osmotic Coefficients for Strong Electrolytes with one or both Ions Univalent," *ibid.*, **77**, 2300 (1973).
Ray, P., "Thermodynamic Properties of Sea Salt Solutions by Boiling Point Elevation Method," Ph.D. dissertation, Univ. California, Berkeley (1973).
Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions*, 2nd Rev. Edit., Butterworths, London (1968).
Rush, R. M., and J. S. Johnson, "Osmotic Coefficients of Synthetic Sea Water Solutions at 25°C," *J. Chem. Eng. Data*, **11**, 590 (1966).
Singh, D., and L. A. Bromley, "Relative Enthalpies of Sea Salt Solutions at 0 to 75°C," *ibid.*, **18**, 174 (1973).
Spiegler, K. S., *Salt Water Purification*, Wiley, New York (1962).
Sridhar, S., "Boiling Point of Sea Salt Solutions," M.S. thesis, Univ. California, Berkeley (1970).
Stoughton, R. W., and M. H. Lietzke, "Calculation of Some Thermodynamic Properties of Sea Salt Solutions at Elevated Temperatures from Data on NaCl Solutions," *J. Chem. Eng. Data*, **10**, 254 (1965).
Stoughton, R. W., and M. H. Lietzke, "Thermodynamic Properties of Sea Salt Solutions," *ibid.*, **12**, 101 (1967).

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Boundary-Layer Skimming: Calculational Curiosity or Promising Process?

It is suggested that the productivity of ultra-filtration and reverse osmosis can be increased substantially where the desired product is concentrated in the diffusional boundary layer adjacent to the membrane. This increase can be achieved by removing product preferentially from the boundary-layer region. The possible concentration increase and yield of such a skimming process are predicted to be very significant for the constant-property approximation and stagnation flow considered in this exploratory paper.

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SCOPE

This paper suggests the possibility of substantially increasing the capacity of ultra-filtration equipment by skimming off the concentrated boundary layers which form adjacent to the filtration membrane. It builds on two previous papers from our laboratory (Kozinski et al., 1971, 1972) which are devoted to description of protein boundary layers, and on the generalized boundary-layer analysis of Stewart (1963).

The skimming process is described schematically in Figure 1, and a specific example, two-dimensional stagnation flow, is shown in Fig. 2. Behavior is described in terms of a concentration factor f and an effectiveness e defined by

$$f = c_{sk}/c_\infty \qquad (1)$$

where c_{sk} is the cup-mixing concentration of solute in the skimmed layer and c_∞ is that in the approaching fluid, and

$$e = fQ_{sk}/(Q_{sk} + Q_{uf}) \qquad (2)$$

where Q_{sk} is the volumetric rate at which the boundary layer is skimmed off, and Q_{uf} is the volumetric rate of ultrafiltration.

The effectiveness is just the ratio of (hypothetical) effective protein concentration in the solution removed, by a combination of ultra-filtration and skimming, to that outside the boundary layer. Its significance can perhaps be seen most clearly in a simple closed system operating continuously, as shown in Figure 3. For this situation

$$e = c_F/c_\infty \qquad (3)$$

where c_F is feed concentration. Clearly $0 \leq e \leq 1$. The concentration factor on the other hand will always be greater than unity.

CONCLUSIONS AND SIGNIFICANCE

The results of this preliminary analysis, summarized in Figures 4 and 5, are very encouraging for concentration of solutes by boundary-layer skimming, in either ultra-filtration or reverse osmosis. Efficient fractionation based on differences in solute diffusivity also appear possible, but the picture here is less clear.