Part II

Calculation of Some Thermodynamic Properties of Sea Salt Solutions at Elevated Temperatures from Data on NaCl Solutions

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Literature values of osmotic coefficients of NaCl solutions from 1 to 4*m* and 25° to 100° C. and from 1 to 3*m* and 125° to 270° C. were fitted to an extended Debye-Hückel equation. By the use of the parameters of fit and the required theoretical change in the limiting slope, vapor pressures of sea salt solutions from 25° to 175° C. and 1 to 28 wt. % solids were calculated and compared with experimental values. In addition, boiling point elevations were calculated for the ranges 2 to 28 wt. % salts and 25° to 260° C., theoretical minimum energies of recovery of water from sea water were calculated for the ranges 0 to 100% recovery and 25° to 200° C., and osmotic pressures were calculated for sea salt solutions of 1 to 25 wt. % solids and for 0.01 to 5*m* NaCl solutions over the temperature range 25° to 100° C. Where NaCl solutions were desirable as a stand-in for sea salt solutions, the thermodynamic properties appear to be much more alike for solutions of the same total concentration of ions than for those of the same ionic strength (at least at the lower temperatures).

VAPOR PRESSURES of sea salt solutions (*18*) have been calculated at 25°, 40°, 60°, 80°, and 100° C. and from 1 to 28 wt. % solids by the use of activity (*8*) and osmotic (*15*) coefficient data for NaCl solutions. More recently, osmotic coefficients for NaCl at 1, 2, and 3*m* and to 270° C. have been published by Gardner, Jones, and de Nordwall (*7*). The purpose of this paper is to use the values of osmotic coefficients of NaCl reported in the literature in order to extend the comparison of calculated and observed vapor pressures of sea salt solutions to as high a temperature as such measurements were made (175° C.), to calculate boiling point elevations over a wide range of concentration and temperature, to calculate minimum energies to 200° C. for recovery of water from sea water, and to calculate osmotic pressures to 100° C. for sea salt and NaCl solutions.

CALCULATIONS AND RESULTS

The osmotic coefficient ϕ of NaCl or of a salt mixture was expressed as a function of concentration and temperature as a Debye-Hückel term [with κa set equal to 1.5 $(I)^{1/2}$] plus a linear and quadratic term in ionic concentration.

$$\phi = 1 - \frac{S}{3.375\,I}\left\{[1 + 1.5\,(I)^{1/2}] - 2\ln[1 + 1.5\,(I)^{1/2}] - \frac{1}{1 + 1.5\,(I)^{1/2}}\right\} + BI' + CI'^2 \quad (1)$$

In this equation, S is the limiting slope, I is the ionic strength on a molality basis$(\frac{1}{2}\sum_i m_iZ_i^2)$, and I' is defined as half the sum of molalities of all ions $\frac{1}{2}(\sum_i m_i)$. The parameters B and C were assumed to have the temperature dependence shown in Equation 2 for B,

$$B = \frac{B_1}{T} + B_2 + B_3 \ln T \quad (2)$$

the functional form of which is consistent with a constant ΔC_p. The limiting slope varies inversely as the product of the dielectric constant D of the solvent and the absolute temperature T raised to the $\frac{3}{2}$ power. The temperature variation of D with T was assumed to be given by the equation of Akerlöf and Oshry (*1*).

$$D = 5321/T + 233.76 - 0.9297T + 0.001417T^2 - 8.292 \times 10^{-7}\,T^3 \quad (3)$$

Since the Debye-Hückel equation was derived on a volume basis whereas the ionic strength I was expressed in terms of molalities, S was assumed to contain the factor $(\rho)^{1/2}$, where ρ is the density of water. Equation 4 gives the density of water as a function of centigrade temperature t, based on data in Lange's Handbook (*12*).

$$\rho = 1.00157 - 1.56096 \times 10^{-4}t - 2.69491 \times 10^{-6}t^2 \quad (4)$$

The limiting slope for a 1-1 electrolyte (e.g., NaCl) S_1 and for an electrolyte mixture S as a function of temperature is, in terms of the values of D and T at 25° C.,

$$S = \left(\sum_i m_iZ_i^2/\sum_i m_i\right) S_1 = 1.17202 \left(\sum_i m_iZ_i^2/\sum_i m_i\right) \rho^{1/2}(D_{25}T_{25}/DT)^{3/2} \quad (5)$$

By using the osmotic coefficients at 1, 2, 3, and 4m NaCl and 25°, 60°, 80°, and 100° C. from (*15*) and those at 1, 2, and 3m NaCl from 125° to 270° C. from (*7*), the following values of the B and C parameters (Equation 2) were obtained by the method of least squares.

$B_1 = -348.662$	$C_1 = 40.5016$
$B_2 = 6.72817$	$C_2 = -0.721404$
$B_3 = -0.971307$	$C_3 = 0.103915$

These parameters were used in all the subsequent calculations. A plot of the deviations of the values of ϕ calculated by using these parameters from the measured values is shown in Figure 1. Also shown are similar values calculated from the parameters obtained in previous calculations (*18*).

The following calculations were carried out on a digital computer.

Vapor Pressures of Sea Salt Solutions. At low temperatures, the osmotic coefficient for an electrolyte or an electrolyte mixture may be expressed by Equation 7 to a good approximation.

$$\left(\sum_i m_i\right)\phi \equiv -\frac{1000}{W}\ln a_1 \quad (6)$$

$$\cong -\frac{1000}{W}\ln\frac{p}{p_0} \quad (7)$$

where a_1, W, and p_0 are the activity, molecular weight, and vapor pressure of water, respectively, while p is the vapor pressure of the electrolyte solution. Equation 7 was used in the previous calculations (*18*) to 100° C.

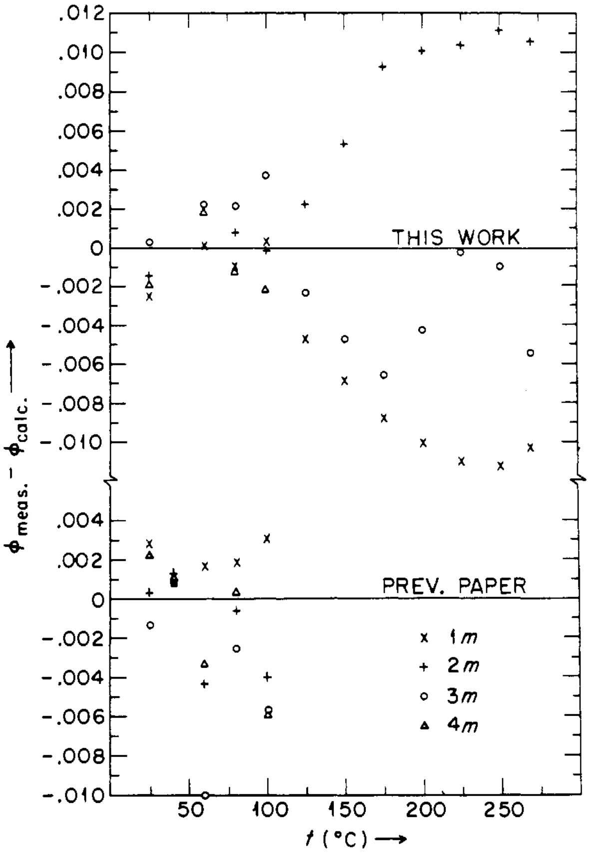

Figure 1. Deviations of calculated values of osmotic coefficients from measured values

At higher temperatures a more nearly exact equation should be used (*7*):

$$\phi = -\frac{1000}{(\sum_i m_i)WRT}\left[\int_{p_0}^{p} V_g\,dp + V_l(p_0 - p)\right] \quad (8)$$

$$= -\frac{1000}{(\sum_i m_i)W}\left\{\ln\frac{p}{p_0} + \frac{1}{RT}\left[\int_{p}^{p_0}\left(\frac{RT}{p} - V_g\right)dp + V_l(p_0 - p)\right]\right\} \quad (9)$$

where V_g and V_l are the molal volumes of water vapor and liquid water, respectively, and R is the molal gas constant.

The value of ϕ for a particular sea salt concentration and temperature was calculated using Equation 1, where B and C were obtained using the above parameters. To evaluate S for the sea salt mixture, it was necessary to know the charges and relative concentrations of all the ions in the mixture. The composition of "standard" sea water in parts per million of each constituent was taken from Spiegler (*17*); these values along with corresponding molalities are shown in Table I. They give $(\sum_i m_iZ_i^2/\sum_i m_i) = 1.2457$ for sea water.

Each value of ϕ obtained from Equation 1 was inserted in Equation 9, and the value of p was obtained by successive approximations. Values of p_0 at any temperature were calculated using Equation 10 which gives the pressure in atm.

$$\ln p_0 = 82.1159 - \frac{7720.13}{T} + 0.00966520\,T - 10.9812\ln T \quad (10)$$

The parameters in Equation 10 were determined by the method of least squares from the data of Keenan and Keyes

(*11*) over the range 10° to 300° C. The central term in the brackets of Equation 9 was integrated analytically using the equation of state of Keenan and Keyes (*11*); in their symbology, this term becomes

$$\frac{1}{RT}\int_{p}^{p_0}\left(\frac{RT}{p} - V_g\right)dp = \frac{-W}{RT}\left[B_0p + \frac{g_1T}{2}\left(\frac{B_0p}{T}\right)^2 + \frac{g_2T}{4}\left(\frac{B_0p}{T}\right)^4 - \frac{g_3T}{13}\left(\frac{B_0p}{T}\right)^{13}\right]_p^{p_0} \qquad (11)$$

where p is in atmospheres and R is in cc.-atm./degree. Values of V_l were obtained from Equation 4 since $V_l = W/\rho$.

In Figure 2, vapor pressures calculated in this manner are compared directly with the experimental values of Arons and Kientzler (*2*) and of Higashi, Nakamura, and Hara (*10*), and with corrected, interpolated values of Forrest and Worthley (*6*). The latter authors did not make measurements at the exact concentrations shown in the figure and their relative concentrations of ions were not exactly the same as those for standard sea water. The experimental data are seen to scatter badly about the calculated curves; generally the values of Arons and Kientzler are higher than, and those of Forrest and Worthley lower than, the calculated values. Hence, if vapor pressures of sea salt solutions of greater accuracy than the calculated values are needed, much more accurate experimental measurements will have to be made.

As a comparison, vapor pressures of the solutions were also calculated by the use of Raoult's law. These values (which are independent of temperature) are shown in Table II along with values of the current calculations averaged over the temperature range and with the range of experimental vapor pressures. The values calculated by means of Raoult's law are within the experimental discrepancy to a concentration of about 15 wt. %, above which they show too small a deviation from the vapor pressure of water. The current calculations using experimental osmotic coefficients should certainly be expected to be more accurate than those based on Raoult's law.

Boiling Point Elevations. Boiling point elevations (BPE's) were calculated from 25° to 260° C. and from 1 to 28 wt. % sea salts by computing the difference between the temperature at which p_0 (Equation 10) was equal to p (Equation 9). The results are shown in Table III.

The calculated values of BPE were approximately linear in temperature but with the slope (d BPE/dt) increasing with both concentration and temperature under all condition.

For comparison, values of BPE were calculated by the use of Raoult's law and the assumption that water vapor behaves as a perfect gas. Some of these values are compared with those of the current calculation in Table III-A. As in the case of the vapor pressure calculations, under all conditions the values based on Raoult's law and the perfect gas assumption were higher at lower concentrations and lower at higher concentrations than those presented in Table III.

Values of BPE have also been calculated by Clark, Nabavian, and Bromley (*4*) and by Hickman (*3, 9*). Values taken from these two references are compared in Table IV with those of the present calculation. The values reported here in general lie between those of Clark *et al.* (*4*) and Chambers and Hickman (*3, 9*). Also, the most reliable values of Clark *et al.* (*4*) would appear to be those at 25° C. where there is good agreement with those reported in this paper.

Theoretical Minimum Energy (Free Energy Change) Required for Recovery of Water from Sea Water. The free energy change $d(\Delta G)_{rec}$ on removing a small amount of pure water dn_1 from a mixture of n_1 moles of water and n_2 moles of salt(s) is equal in magnitude but opposite in sign to that for adding dn_1 moles of water to the mixture,

$$-d(\Delta G)_{rec} = d(\Delta G)_{mix} = RT[(\ln a_1)\,dn_1 + (\ln a_2)dn_2] = RT(\ln a_1)\,dn_1 \qquad (12)$$

since $dn_2 = 0$. Here a represents activity, and the subscripts 1 and 2 refer to solvent and solute, respectively. Equation 12 may be expressed in terms of the osmotic coefficient ϕ and the molal concentration of the solute I'.

If n_1 moles of water are removed from that amount of solution containing 1 kg. of water when the concentration of ions is I_0'.

Table I. Major Constituents of Sea Water

Constituent	P.P.M.	m_i
Sodium (Na^+)	10,561	0.47564
Magnesium (Mg^{-2})	1,272	0.05417
Calcium (Ca^{+2})	400	0.01034
Potassium (K^+)	480	0.01007
Chloride (Cl^-)	18,980	0.55441
Sulfate (SO_4^{-2})	2,649	0.02856
Bicarbonate (HCO_3^-)	142	0.00241
Bromide (Br^-)	65	0.00084
Other solids	34	. . .
Total dissolved solids	34,583	1.13644
Specific gravity (20° C.)	1.0243	. . .
Water (balance)	965,417	. . .

Table II. Calculated *vs.* Measured Vapor Pressures of Sea Salt Solutions

Wt. % Salts	−log (p/p_0) Calculated Raoult's Law		Measured (*2, 6, 10*)
	Raoult's Law	ϕ's of NaCl	
3.5	0.0089	0.0082 ± 0.0000	0.005 to 0.016
9.6	0.0257	0.0253 ± 0.0002	0.022 to 0.034
16.5	0.0466	0.0510 ± 0.0008	0.040 to 0.062
21.6	0.0637	0.0773 ± 0.0011	0.065 to 0.091
28.2	0.0883	0.124 ± 0.005	0.110 to 0.143

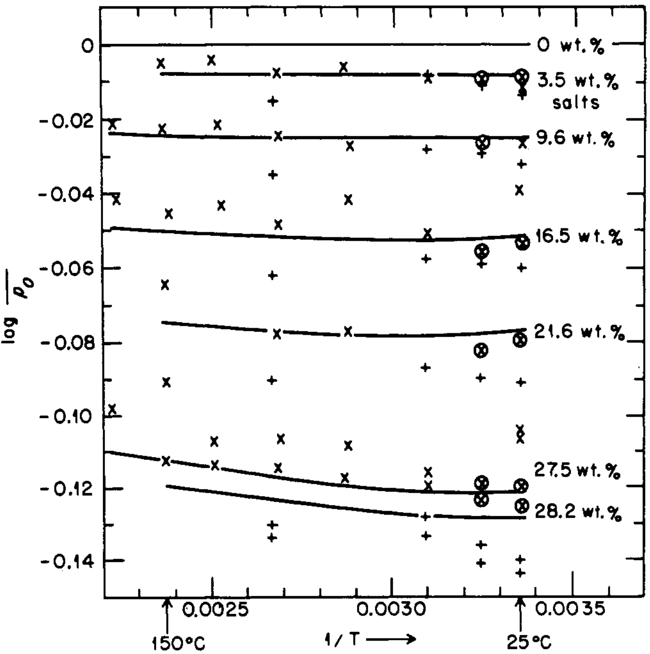

Figure 2. Deviations of vapor pressures of sea salt solutions from measured values

— Calculated
⊗ Arons and Kientzler
x Higashi et al.
+ Forrest and Worthley (interpolated)

Table III. Calculated Boiling Point Elevations for Sea Salt Solutions, ° C.

		Wt. % Sea Salts									
t, ° C.	p_0, Atm.	2.0	3.45[a]	4.0	6.0	8.0	12.0	16.0	20.0	25.0	28.0
25	0.031	0.177	0.311	0.363	0.564	0.783	1.285	1.901	2.675	3.96	4.98
30	0.042	0.183	0.323	0.378	0.587	0.816	1.340	1.983	2.788	4.12	5.17
40	0.073	0.198	0.348	0.407	0.634	0.882	1.452	2.149	3.018	4.45	5.56
50	0.122	0.213	0.374	0.439	0.683	0.951	1.566	2.318	3.252	4.78	5.95
60	0.197	0.228	0.402	0.470	0.734	1.021	1.684	2.491	3.490	5.11	6.35
70	0.309	0.244	0.430	0.503	0.786	1.094	1.803	2.667	3.731	5.45	6.76
80	0.469	0.260	0.459	0.537	0.839	1.168	1.925	2.845	3.976	5.79	7.17
90	0.694	0.277	0.489	0.572	0.893	1.244	2.050	3.026	4.225	6.14	7.59
100	1.003	0.295	0.520	0.609	0.949	1.322	2.176	3.210	4.475	6.50	8.02
110	1.418	0.313	0.552	0.646	1.007	1.402	2.305	3.396	4.729	6.85	8.45
120	1.965	0.332	0.585	0.685	1.067	1.483	2.437	3.586	4.99	7.22	8.89
130	2.673	0.352	0.619	0.724	1.128	1.568	2.571	3.778	5.25	7.58	9.34
140	3.577	0.373	0.655	0.766	1.191	1.654	2.708	3.973	5.51	7.95	9.79
150	4.711	0.394	0.691	0.808	1.256	1.742	2.848	4.171	5.78	8.33	10.26
160	6.119	0.417	0.730	0.853	1.324	1.834	2.991	4.373	6.05	8.72	10.73
180	9.931	0.464	0.811	0.947	1.466	2.025	3.287	4.789	6.61	9.50	11.70
200	15.407	0.517	0.900	1.049	1.618	2.229	3.600	5.222	7.18	10.32	12.72
220	22.993	0.575	0.998	1.162	1.785	2.450	3.932	5.675	7.78	11.17	13.80
240	33.184	0.641	1.106	1.287	1.967	2.688	4.286	6.153	8.41	12.07	14.94
260	46.520	0.714	1.228	1.425	2.168	2.950	4.665	6.657	9.07	13.01	16.15

[a] Standard sea water.

Table III A. Calculated BPE Values, ° C., Compared with Those Based on Raoult's and Perfect Gas Laws

	Wt. % Salts									
	2.0		3.45		8.0		16.0		25.0	
t, ° C.	SL[a]	RP[b]	SL[a]	RP[b]	SL[a]	RP[b]	SL[a]	RP[b]	SL[a]	RP[b]
25	0.177	0.195	0.311	0.340	0.783	0.818	1.901	1.748	3.96	2.96
60	0.228	0.252	0.402	0.439	1.021	1.056	2.491	2.257	5.11	3.83
100	0.295	0.326	0.520	0.569	1.322	1.369	3.210	2.931	6.50	4.98
150	0.394	0.434	0.691	0.757	1.742	1.822	4.171	3.902	8.33	6.63
200	0.517	0.556	0.900	0.970	2.229	2.336	5.222	5.006	10.3	8.5
260	0.714	0.717	1.228	1.253	2.950	3.015	6.657	6.466	13.0	11.0

[a] This work. [b] Based on Raoult's Law and perfect gas assumption.

Table IV. Boiling Point Elevations, ° C., of Sea Salt Solutions vs. Temperature and Wt. % Salts

	Wt. % Salts													
	2			4			6			8			10	
t, ° C.	SL[a]	CNB[b]	KCDH[c]	SL[a]	CNB[b]	KCDH[c]	SL[a]	CNB[b]	KCDH[c]	SL[a]	CNB[b]	KCDH[c]	SL[a]	KCDH[c]
25	0.177	0.16	...	0.363	0.34	...	0.564	0.56	...	0.783	0.79	...	1.02	...
40	0.198	0.17	0.22	0.407	0.36	0.45	0.634	0.59	0.72	0.882	0.84	1.00	1.15	1.31
60	0.228	0.17	0.26	0.470	0.39	0.52	0.734	0.63	0.81	1.02	0.91	1.14	1.34	1.50
70	0.244	0.18	0.33	0.503	0.39	0.58	0.785	0.66	0.92	1.09	0.94	1.22	1.43	1.58
100	0.295	0.21	...	0.609	0.44	...	0.949	0.72	...	1.32	1.04	...	1.73	...
120	0.332	0.22	...	0.685	0.46	...	1.07	0.77	...	1.48	1.11	...	1.94	...
140	0.373	0.23	...	0.766	0.49	...	1.19	0.81	...	1.65	1.17	...	2.16	...

[a] This work. [b] Reference (*4*). [c] References (*3, 9*).

$$n_1 = \frac{1000}{W}\left(1 - \frac{I'_0}{I'}\right) \tag{13}$$

On differentiation,

$$\mathrm{d}n_1 = \frac{1000}{W}\,\frac{I'_0}{I'^2}\,\mathrm{d}I' \tag{14}$$

By using the definition of ϕ (Equation 6) and of I' and inserting Equations 14 and 1 into 12 and integrating,

$$\Delta G_{rec} = 2RT\int_{I'_0}^{I'} \frac{I'_0}{I'}\,\phi\,\mathrm{d}I' \tag{15a}$$

$$= 2RTI'_0\Big[\ln I' + BI' + \frac{CI'^2}{2} + \frac{2S}{2.25\,(I)^{1/2}}\left\{1 - \frac{\ln[1 + 1.5\,(I)^{1/2}]}{1.5\,(I)^{1/2}}\right\}\Big]_{I'_0}^{I'} \tag{15b}$$

where B and C may be assumed equal for NaCl and sea salt solutions.

The maximum work obtainable from an isothermal process is actually equal to the negative of the change in Helmholtz free energy, $-\Delta A$. Hence ΔA is equal to the minimum energy required for making an isothermal process occur. The difference $\Delta G_{rec} - \Delta A_{rec} = \Delta(pV)$ is small, since the initial and final states involve liquids (and a solid in the case of 100% recovery), and amounts to not more than about 0.01%. at 100° C. Although density data for NaCl solutions are not available above 100° for an accurate calculation of $\Delta(pV)$, this term should amount to no more than about 1% of ΔG_{rec} at 200° C. Hence, values of ΔG_{rec} are sufficiently close to the values of minimum energy required (being within the accuracy of the calculations) that no corrections were made.

Equation 15b may be used to calculate values of ΔG_{rec} for any finite per cent recovery up to saturation of the salt (or salt mixture). For zero % recovery—i.e., the removal of a relatively small amount of water from a very large amount of sea water—the integral of Equation 12 was used where $\ln a_1$ has the constant value of standard sea water. For 100% recovery, Equation 15b was used to the point of saturation; the integral of Equation 12 with $\ln a_1$ having its value at saturation of NaCl (given by Equation 16) was used for the remaining water—i.e., the "effective" solubility of the sea salt mixture was taken as the solubility of NaCl at the same total concentration of ions. While this effective solubility involves some error, we know of no certain improvement in view of the scatter and discrepancies in the experimental measurements shown in Figure 2. Solubilities of NaCl *vs.* temperature from near 0° to 344° C. reported by Seidell (*16*) were fitted to a cubic equation in the centigrade temperature t by the method of least squares; the parameters are given in Equation 16 in which s is the molal solubility of NaCl.

$$s = 6.033 + 6.403 \times 10^{-3} t - 7.384 \times 10^{-6} t^2 + 1.049 \times 10^{-7} t^3 \quad (16)$$

The minimum energies of recovery are presented in Table V. They show an increase with temperature for any per cent recovery and with per cent recovery for any temperature. There is a large increase in minimum energy requirement between 75 and 100% recovery, which is not surprising since the concentration goes from 13.8 to about 28 wt. % in this range. Spiegler (*17*) calculated a minimum energy of recovery of 0.70 kw.h. per cubic meter of water at zero % recovery and 25° C. which agrees well with the value of 0.706 kw.h. per 1000 kg. in Table V. Dodge (*5*) presented a curve indicating about 0.80, 0.89, 1.09, 1.5, and 3.1 kw.h. per 1000 kg. water for 0, 25, 50, 75 and 100% recovery at 25° C.; these values agree reasonably well with the first row of minimum energies in Table V.

Table V. ΔG_{rec} (Kw.H./1000 Kg. Water)[a] for Recovery from Standard Sea Water (3.45 Wt. % Salts)

	% Recovery				
t, ° C.	0	25	50	75	100
25	0.706	0.814	0.987	1.342	2.91
50	0.765	0.884	1.073	1.463	3.19
75	0.820	0.948	1.151	1.571	3.45
100	0.871	1.006	1.222	1.667	3.69
125	0.917	1.059	1.285	1.750	3.90
150	0.958	1.105	1.340	1.820	4.10
175	0.99	1.15	1.39	1.88	4.28
200	1.02	1.18	1.42	1.92	4.45

[a] One kw.h. per 1000 kg. water = 0.0155 kcal. per mole.

Table VI. ΔG_{rec} (Kw.H./1000 Kg. Water)[a] for Recovery from NaCl Solutions in which the Concentration of Ions = Total Concentration of Ions in Standard Sea Water (3.45 Wt.% Salts)

	% Recovery				
t, ° C.	0	25	50	75	100
25	0.724	0.835	1.012	1.374	2.94
50	0.786	0.908	1.101	1.499	3.24
75	0.844	0.975	1.183	1.613	3.50
100	0.898	1.037	1.259	1.714	3.74
125	0.948	1.094	1.327	1.804	3.96
150	0.994	1.146	1.388	1.882	4.17
175	1.035	1.192	1.441	1.948	4.36
200	1.070	1.232	1.486	2.000	4.55

[a] One kw.h. per 1000 kg. water = 0.0155 kcal. per mole.

Table VII. Parameters for Equation 19

t, ° C.	α	γ
25	1.00267	2.1045×10^{-5}
40	1.00762	1.8967×10^{-5}
60	1.01684	1.7636×10^{-5}
80	1.02876	1.7654×10^{-5}
100	1.04323	2.1729×10^{-5}

Values of ΔG_{rec} were also calculated for NaCl solutions with the same total concentration of ions and with the same ionic strength as standard sea water. The former are shown in Table VI; in all cases the values are higher than but within 5% of those for standard sea water. In the case of solutions of the same ionic strength, the values for .the NaCl solutions were larger by some 20 to 30%. Thus, where it is desirable to use NaCl solutions for a standin for sea salt solutions, a solution of the same total concentration of ions is preferable to one of the same ionic strength.

Osmotic Pressures of NaCl and Sea Salt Solutions. Equation 1 and the associated parameters were also used to calculate osmotic pressures of sea salt solutions and of NaCl solutions. The partial derivative of the osmotic pressure Π of a solution in terms of the molality m of the solute and of the partial molal volume $\bar{V}_1$ and activity a_1 of the solvent is given (*13*) by Equation 17.

$$\frac{\partial \Pi}{\partial m} = -\frac{RT}{\bar{V}_1}\frac{\partial \ln a_1}{\partial m} \qquad (17)$$

On changing the concentration variable to $I' \equiv \frac{1}{2}\sum_i m_i$ and using the definition of ϕ (Equation 6), one obtains for either NaCl or the sea salt mixture,

$$\frac{\partial \Pi}{\partial I'} = \frac{RTW}{1000\,\bar{V}_1}\frac{\partial}{\partial I'}(2I'\phi)$$

$$= \frac{2RT}{1000\,\tilde{V}_1}\frac{\partial}{\partial I'}(I'\phi) \qquad (18)$$

where $\tilde{V}_1$ is the partial specific volume of the solvent. Values of $\tilde{V}_1$ were calculated at 25°, 40°, 60°, 80°, and 100° C. from NaCl solution densities given in the ICT; 100° C. is the highest temperature for which the density data are given. These values were expressed by equations of the form of Equation 19,

$$\tilde{V}_1 = \alpha - \gamma\ (\text{wt. \%})^2 \qquad (19)$$

and the values of α and γ are given in Table VII. It was assumed that the values in Table VII are satisfactory for sea salt mixtures as well as for NaCl.

By inserting Equation 1 into 18 and integrating one obtains

$$\Pi = \frac{2RT}{1000}\int_0^{I'} \frac{1}{\tilde{V}_1}\left\{1 + 2BI' + 3CI'^2 - \frac{S(I)^{1/2}}{2[1 + 1.5\,(I)^{1/2}]^2}\right\} dI' \qquad (20)$$

Table VIII. Osmotic Pressures (in Atm.) of Sea Salt Solutions

	Wt. % Salts								
t, ° C.	1.00	2.00	3.45[a]	5.00	7.50	10.00	15.00	20.00	25.00
25	7.10	14.25	25.02	37.17	58.43	82.12	139.0	214.0	317
40	7.41	14.88	26.17	38.96	61.40	86.46	146.6	225.1	331
60	7.78	15.64	27.54	41.05	64.82	91.40	155.1	237.5	347
80	8.11	16.30	28.71	42.81	67.64	95.40	161.7	247.1	359
100	8.40	16.86	29.68	44.25	69.87	98.50	166.7	254.1	368

[a] 3.45 wt. % solids is taken as the value for standard sea water.

Table IX. Osmotic Pressures (in Atm.) of NaCl Solutions

	Molality NaCl								
t, ° C.	0.01	0.10	0.50	1.00	1.50	2.00	3.00	4.00	5.00
25	0.47	4.56	22.55	45.80	70.25	96.2	153.2	218.9	295.2
40	0.49	4.76	23.60	48.08	73.93	101.3	161.6	230.5	309.4
60	0.52	5.00	24.85	50.76	78.17	107.3	171.0	243.3	325.2
80	0.54	5.23	25.94	53.02	81.69	112.1	178.5	253.3	337.4
100	0.57	5.42	26.87	54.87	84.49	115.9	184.2	260.8	346.5

Table X. Per Cent Decrease in BPE if All $CaSO_4$ Precipitates

	Wt. % Salts		
t, ° C.	3.45	12.0	25.0
25	1.5	1.6	2.2
100	1.4	1.6	2.1
150	1.2	1.4	2.0
200	1.0	1.2	1.8

Table XI. Approximate Temperatures for Inception and 80% Completion of $CaSO_4$ Precipitation [a]

	t, ° C.	
Wt. % Salts	Beginning Ppt'n.,	80% Ppt'd.,
3.45	110	180
10.0	80	120
15.0	<25	110
20.0	<25	100
25.0	<25	80

[a] Based on measurements of reference (*14*).

Table XII. Per Cent Decrease in ΔG_{rec} if All $CaSO_4$ Precipitates

	% Recovery				
t, ° C.	0	25	50	75	100
25	1.3_0	1.3_3	1.3_6	1.4_5	1.1_6
100	1.2_1	1.2_3	1.2_7	1.3_7	1.1_0
200	0.8_9	0.9_0	0.9_3	1.0_3	0.9_6

Table XIII. Per Cent Decrease in Osmotic Pressure if All $CaSO_4$ Precipitates

	Wt. % Salts					
t, ° C.	2.0	3.45	5.0	10.0	20.0	25.0
25	1.2_6	1.3_2	1.3_5	1.5_6	2.0_3	2.3_3
60	1.2_8	1.2_7	1.3_4	1.5_4	1.9_7	2.2_0
100	1.1_9	1.2_1	1.2_9	1.4_9	1.8_8	2.1_0

Equation 20 was integrated numerically by using 8 point Gaussian Quadrature to evaluate the osmotic pressures of sea salt solutions from 1 to 25 wt. % solids and of NaCl solutions from 0.01 to 5m. Some of the results are shown in Tables VIII and IX.

EFFECT OF SOLUBILITYOF $CaSO_4$

The calculations in this paper were based upon the assumption that all the salts remained in solution at all concentrations and temperatures. Marshall, Slusher, and Jones (*14*) have recently reported solubilities of $CaSO_4$ in NaCl solutions to 200° C. and 6m. Their results show that at equilibrium most of the $CaSO_4$ will have precipitated at the higher temperatures and concentrations reported here.

If all the $CaSO_4$ were removed by precipitation, a Raoult's law correction indicates that the differences between the vapor pressures of sea salt solutions and that of pure water as calculated here would be decreased by about 1.8, 1.7, and 1.5% for 3.45, 12, and 25 wt. % salts, respectively, at any temperature. The corresponding decrease in calculated BPE's would be the same. A more accurate calculation based upon the methods of the previous sections indicates a somewhat lower correction at the lower concentrations and a somewhat higher correction at the higher concentrations, with all (percentage) corrections decreasing with increasing temperature, as given in Table X.

While it is very doubtful that the BPE's reported in this paper are accurate to within 2% or that precipitation to equilibrium conditions will necessarily occur, nevertheless, corrections for precipitation of $CaSO_4$ can be made if desired by the use of Tables X and XI. Table XI gives at several concentrations the approximate temperatures at which precipitation should begin and should reach 80% completion.

To a first approximation the minimum energy of recovery and osmotic pressure would be decreased about the same amount as the vapor pressure and BPE according to the Raoult's law calculation, should all the $CaSO_4$ precipitate. Typical decreases with the more accurate calculation are shown in Tables XII and XIII.

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NOMENCLATURE

a_1 = activity of solvent (water)
a_2 = activity of solute
A = Helmholtz free energy
B_0 = parameter in Keenan and Keyes' equation of state for water vapor
B = coefficient of linear term in expression for osmotic coefficient *vs.* concentration (Equation 1)
B_1, B_2, B_3 = coefficients in expression of B *vs.* temperature (Equation 2)
C = coefficient in quadratic term in expression for osmotic coefficient *vs.* concentration (Equation 1)
C_1, C_2, C_3 = coefficients in expression of C *vs.* temperature (see Equation 2)
D = dielectric constant of water
D_{25} = dielectric constant of water at 25° C.
G = Gibbs free energy
i = subscript index
I = ionic strength $\equiv (1/2)\sum_i m_i Z_i^2$
I' = half the sum of ionic molalities $\equiv (1/2)\sum_i m_i$
I_0' = initial value of I'
m = molality (moles solute/kg. water)
p = vapor pressure of solution, atm.
p_0 = vapor pressure of water, atm.
R = molal gas constant, cm.^{3} – atm./° K. – mole. In Equation 12, 15a, and 15b, units are watt-hr./° K. – mole
s = molal solubility of NaCl
t = temperature, ° C.
T = temperature, ° K.
T_{25} = absolute temperature corresponding to 25° C. = 298.15° K.
V = total volume
V_g = molal volume of water vapor, cm.^{3}
V_l = molal volume of liquid water, cm.^{3}
$\bar{V}_1$ = partial molal volume of solvent (water), cm.^{3}/mole

$\bar{V}_1$ = partial specific volume of solvent (water), cm.^{3}/gram
W = molecular weight of water
Z = ionic charge
S = Debye-Hückel limiting slope for an ionic mixture
S_1 = Debye-Hückel limiting slope for a 1-1 electrolyte
α, γ = coefficients in expression of partial specific volume of water *vs.* wt. % salt (Equation 19)
Δ = change in a quantity, e.g., ΔG = change in the Gibbs free energy
ΔC_p = change in heat capacity between that at an arbitrary concentration and that in the standard state
κa = expression involving concentration in the Debye-Hückel equation, here set equal to $1.5\ (I)^{1/2}$
Π = osmotic pressure, atm.
ρ = density of water, gram/cm^3.

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Ternary Systems of Glycols

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This paper presents experimental graphs for 33 new ternary or quaternary systems of ethylene glycol, 13 for diethylene glycol, 16 for triethylene glycol, and four involving higher glycols. Some show unusual types; and certain requirements for three separate binodal curves are discussed. A novel concept of "shadow graphs" is applied to triangular graphs showing three components completely miscible and a fourth practically immiscible with the other three.

ETHYLENE GLYCOL is not usually suitable as a single solvent for separation of hydrocarbons because of its low miscibilities with all hydrocarbons, even the most aromatic. However, its complete miscibility with water and with many alcohols and some other organic compounds makes it unique in some solubility relations. It is a convenient and higher boiling substitute for water as a diluent for certain solvents. For some of these—e.g., sulfur dioxide—it is better, because it mixes while water does not mix (*3, 10*).

About 135 critical solution temperatures (CST) (some with > or < signs) have been compiled (*1*, pp. 87-9; *8*, pp. 225-61). Published ternary systems involving ethylene glycol include 26 aqueous and about 61 nonaqueous systems (*3*, graphs 29 to 33, 62, 64, 66; *4*, graphs 55 to 62; *8*, pp. 155-6, 205; *9*, pp. 941, 1078-83, 1117).

Diethylene glycol dissolves somewhat larger volumes of hydrocarbons, and at elevated temperatures is considered very selective as to type. It is a favorite solvent (Udex process) because of convenient adjustment of solubility with temperature and water concentration (*12, 13*, and numerous technical papers). CST with 39 hydrocarbons and 14 nonhydrocarbons are listed (*1*, pp. 70-1) for diethylene glycol; and about 16 ternary systems are published (*3*, graphs 2, 27, 28; *4*, graphs 30, 38, 49, 50, 51, 124; *8*, pp. 148, 203).

Triethylene glycol is one of the most selective water miscible solvents for hydrocarbons. CST have been observed for 34 hydrocarbons (*1*, pp. 174-5); and about 16 ternary systems have been published (*4*, graphs 96, 97; *8*, pp. 192, 220). Several systems of propylene glycol and 2,3-butene glycol also have been published (*3*, graph 2; *8*, pp. 137, 183, 217; *9*, pp. 1006-7, 1089).

This paper presents observations on 33 new ternary (or quaternary) systems of ethylene glycol, 13 of diethylene glycol, 16 of triethylene glycol, and four systems of other glycols (Figure 1). All are plotted in concise form as in previous papers (*3, 4, 7*) to save space.

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