delivered the amines in an easy manner, however, with yields of 15 to 35% only.

The *N*-nitroso compounds were obtained from aqueous hydrochloric acid solutions of secondary amines by reaction with sodium nitrite. After the addition of sodium nitrite, the mixture was heated to 50° C. for 1 hour, extracted with dichloromethane after cooling, and the solutions were dried with calcium chloride. The solvent was evaporated, and the *N*-nitroso compounds were purified by vacuum distillation.

The *N*-amino compounds—unsymmetrical hydrazines—have been prepared by reduction of the corresponding *N*-nitroso compounds with lithium aluminum hydride as described earlier (*1-4*).

5-Nitro-2-hydroxybenzal derivatives have been obtained from the reaction with 5-nitro-2-hydroxybenzaldehyde—Schuchardt, Munich, Germany—in ethanol (*3*). UV and visible measurements were taken with a spectrophotometer Beckman DK 1. The ultraviolet spectra and elemental analyses are given in Table I. Boiling and melting points are uncorrected.

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Thermodynamic Properties of Sea Salt Solutions

R. W. STOUGHTON AND M. H. LIETZKE
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Thermodynamic properties of sea salt solutions have been recalculated in view of re-evaluations of the properties of NaCl solutions as a function of temperature and an experimental comparison of the osmotic coefficients of NaCl and sea salt solutions at 25° C. Boiling point elevations (BPE's) were evaluated in the ranges 2 to 28 wt. % salts and 25° to 260° C.; theoretical minimum energies of recovery of water from sea water, in the ranges of 0 to 100% recovery and 25° to 200° C.; and osmotic pressures, in the ranges 1 to 25 wt. % solids and 25° to 100° C. The new values show greatest deviations from the previous calculations at high concentrations and low temperatures. The largest change is a 12% increase in BPE at 25° C. and 28 wt. % solids. In general, where there is a change, the new values are higher; the values of BPE at the highest concentrations and temperature are exceptions—e.g., a 2% decrease at 28 wt. % solids at 260° C.

IN PREVIOUS WORK (*15, 16*) vapor pressures of sea salt solutions were calculated from 25° to 175° C. and from 1 to 28 wt. % solids by using the following extended Debye-Hückel equation and parameters obtained from measured osmotic coefficients of sodium chloride solutions.

$$\phi = 1 - \frac{S}{A^3 I}\left\{\left[1 + A\,(I)^{1/2}\right] - 2\ln\left[1 + A\,(I)^{1/2}\right] - \frac{1}{1 + A\,(I)^{1/2}}\right\} + BI' + CI'^2 \quad (1)$$

In Equation 1, S is the appropriate Debye-Hückel limiting slope for either a single electrolyte or an electrolyte mixture, A is the Debye-Hückel parameter (here set equal to 1.5), I is the ionic strength, I' is a concentration term discussed below, while B and C are adjustable parameters. The latter parameters for NaCl solutions were evaluated to 270° C. (*15, 16*) from osmotic or activity coefficients from the literature up to 4*m* to 100° (*11*) and up to 3*m* from 100° to 270° C. (*4*).

In applying Equation 1 to sea salt solutions, the values of B and C for NaCl solutions were used with three different concentration terms for I':

$$I' = \tfrac{1}{2}\sum_i m_i Z_i^2 = I \quad (2a)$$

$$= \tfrac{1}{2}\sum m_i\,|Z_i| \quad (2b)$$

$$= \tfrac{1}{2}\sum m_i \quad (2c)$$

where m_i is the molality and Z_i the charge of any ionic constituent. (For a 1-to-1 electrolyte all three expressions are equal to the molality.)

The calculated vapor pressures were compared with the measured values of Arons and Kientzler (*1*) at 25° and 35° C. and those of Higashi, Nakamura, and Hara (*8*) from 25° to 175° C. and to 28 wt. % solids. The agreement was best when Equation 2c was used and poorest when 2a was used. Vapor pressure measurements of Forrest and Worthley (*2*) from 25° to 100° C. gave better agreement with Equation 2a than with 2b or 2c, although the scatter of the various experimental values (*1, 2, 8*) was much greater than the difference between the values calculated using Equations 2a and 2c; even at 28 wt. % solids the scatter was greater by at least a factor of two than the difference between the two sets of calculated values. Because the measurements of Arons and Kientzler (*1*) appeared to be the most precise ones available, the authors concluded (*15, 16*) that Equation 2c gave best results for the thermodynamic properties of sea salt solutions.

Recently, Rush and Johnson (*12*) have measured osmotic coefficients of synthetic sea salt solutions in the ionic strength range 0.6 to 7.0 at 25° C. by using NaCl as a standard and the osmotic coefficients of reference (*11*) for the standard. These were compared with values of ϕ calculated by using Equations 2a and 2c and Equation 1 with the addition of a cubic term DI'^3 in which the B, C, and D parameters were evaluated from osmotic coefficients at 25° C. only. Throughout the whole concentration range, Equation 2a gave best agreement, showing a maximum deviation of 0.003. By contrast, Equation 2c showed a deviation of 0.001 at the lowest and about 0.1 at the highest concentration.

The authors believe the measurements of Rush and Johnson are the best available and, hence, now conclude that Equation 2a should be used to calculate the thermodynamic properties of sea salt solutions, at least at and near room temperature. The authors, therefore, recommend that, unless and until good experimental measurements suggest otherwise, Equation 2a be used at all temperatures—i.e., it is best to set $I' = I = \frac{1}{2} \sum m_i Z_i^2$ at all temperatures.

The current change in recommendation for the concentration term to be used for I does not change the authors' previous conclusion (*15*) concerning the use of NaCl solutions for a stand-in for sea salt solutions—i.e., where NaCl solutions are used for a stand-in for sea salt solutions, a solution of the same total concentration of ions is preferable to one of the same ionic strength. The reason is that in thermodynamic calculations the most important concentration term is the coefficient of ϕ in the definition of the osmotic coefficient:

$$\left(\sum m_i\right)\phi \equiv -\frac{1000}{W}\ln a_1 \quad (3)$$

where a_1 and W are the activity and molecular weight of water. The authors' current change in recommendation does not affect this concentration term.

Table I. Parameters of Fit of ϕ_{NaCl} vs. T

B_1 =	− 330.332	C_1 =	32.6806
B_2 =	6.31446	C_2 =	− 0.553679
B_3 =	− 0.909395	C_3 =	0.0790215

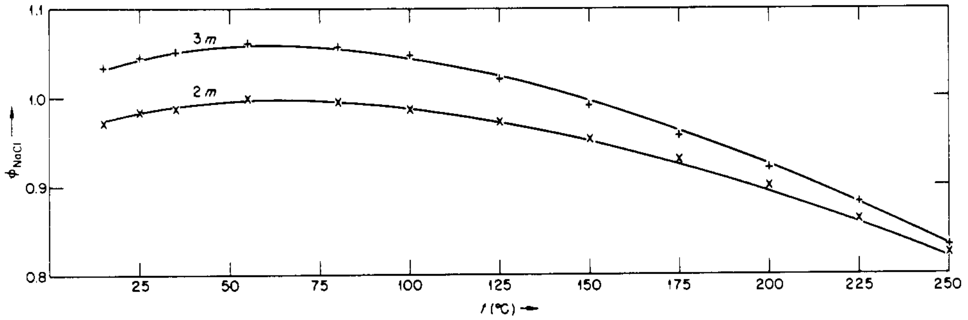

Figure 1. Osmotic coefficients of NaCl as a function of temperature from 25° to 250° C.

ACCURACY OF EXISTING NaCl OSMOTIC COEFFICIENTS

The test of the applicability of Equations 2a, 2b, and 2c to calculations of osmotic coefficients of sea salt solutions ϕ_{SS} is approximately independent of the accuracy of the osmotic coefficients of NaCl providing the same values of ϕ_{NaCl} are used for the standard in isopiestic measurements and for the evaluation of the B and C (and D) parameters of Equation 1. However, the accuracy of the calculated values of ϕ_{SS} is essentially the same as the accuracy of the values of ϕ_{NaCl} at 25° C. (being not more than about 0.003 of a unit different at any concentration).

Lanier (*9*) has shown that different investigators have reported activity coefficients of NaCl at 25° C. which differ by 1.5% at 3*m* and 2% at 6*m*. The corresponding difference in osmotic coefficients is a little less than this. Hence there is an uncertainty of at least 1% even at 25° C. at the higher concentrations.

The authors have re-evaluated the B and C parameters of Equation 1 by the method of least squares on the assumption that their variation with absolute temperature T was the same as that given in Equation 4 for B

$$B = \frac{B_1}{T} + B_2 + B_3 \ln T \quad (4)$$

At 15° and 35° C. the authors used osmotic coefficients at 0.5, 1.0, 2.0, 3.0, and 4.0*m* which had been calculated (*10*) from activity coefficients presented by Harned and Owen (*7*). At 60°, 80°, and 100° C. the authors used osmotic coefficients at the same concentrations, while at 25° C. the value at 5*m* was included also—all from reference (*11*). Between 125° and 250° C. (inclusive) at every 25° interval the results of reference (*4*) were used, plus some additional and some corrected experimental values (*3*). Unit weights were assigned to all values except those at 25° C.; at 25° statistical weights of 3.0 were assigned in the least squares fit since these were the result of a critical evaluation of measurements from different sources. The resulting values of the B and C parameters are given in Table I.

Figure 1 shows a typical plot of ϕ_{NaCl} *vs.* temperature at 2.0 and 3.0*m*. Figure 2 shows the deviations of calculated from experimental values at 0.5, 1.0, 2.0, 3.0, and 4.0*m*. At lower temperatures, the deviations are within those between different experimental measurements. The region of most consistency appears to be that of 60° to 100° C. where the observed values were those calculated by Smith and Hirtle (*14*) to give best reasonable agreement with the boiling point elevation measurements of Smith and Hirtle (*13, 14*) between 60° and 100° C. and the e.m.f.

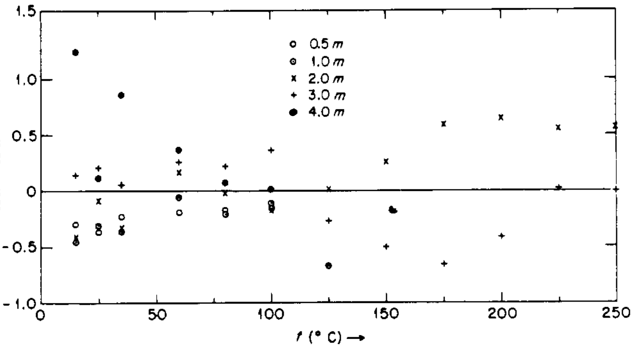

Figure 2. Deviations between observed and calculated osmotic coefficients of NaCl

measurements of Harned, Cook, and Nims (*5*, *6*) between 0° and 40° C.

Additional fits were made by using different weights, by fixing the values of the parameters at 25° C. to be consistent with the 25° data, and by using seven temperature-dependent parameters—i.e., by adding a term B_4 T. None of these gave a fit to the measured values which was significantly better than that using the parameters of Table I. They all appeared to fit the data well within the apparent uncertainties.

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

		Wt. % Sea Salt									
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	0.312	0.366	0.570	0.795	1.324	1.991	2.858	4.36	5.58
30	0.042	0.184	0.325	0.380	0.594	0.829	1.381	2.077	2.977	4.52	5.77
40	0.073	0.198	0.350	0.410	0.642	0.898	1.497	2.250	3.216	4.86	6.16
50	0.122	0.214	0.377	0.442	0.692	0.969	1.616	2.426	3.458	5.19	6.56
60	0.197	0.229	0.405	0.474	0.744	1.041	1.737	2.604	3.704	5.53	6.96
70	0.309	0.245	0.433	0.508	0.797	1.115	1.860	2.786	3.952	5.88	7.36
80	0.469	0.262	0.463	0.542	0.851	1.191	1.986	2.969	4.202	6.22	7.77
90	0.694	0.279	0.493	0.578	0.907	1.269	2.113	3.155	4.454	6.57	8.18
100	1.003	0.296	0.524	0.615	0.964	1.348	2.242	3.342	4.708	6.92	8.60 -
110	1.418	0.315	0.556	0.652	1.022	1.429	2.374	3.532	4.963	7.27	9.01
120	1.965	0.334	0.590	0.691	1.082	1.512	2.508	3.723	5.22	7.62	9.43
130	2.673	0.354	0.624	0.731	1.144	1.597	2.643	3.917	5.48	7.98	9.86
140	3.577	0.375	0.660	0.773	1.208	1.684	2.782	4.113	5.74	8.34	10.28
150	4.711	0.396	0.697	0.816	1.274	1.774	2.923	4.311	6.00	8.70	10.71
160	6.119	0.418	0.735	0.861	1.341	1.866	3.066	4.511	6.27	9.06	11.15
180	9.931	0.466	0.817	0.955	1.484	2.057	3.361	4.920	6.81	9.79	12.03
200	15.407	0.519	0.906	1.058	1.637	2.261	3.670	5.342	7.36	10.54	12.94
220	22.993	0.577	1.003	1.170	1.802	2.480	3.995	5.777	7.92	11.30	13.87
240	33.184	0.642	1.111	1.293	1.983	2.715	4.338	6.231	8.49	12.08	14.84
260	46.520	0.716	1.232	1.431	2.181	2.971	4.703	6.700	9.08	12.88	15.83

[a] Standard sea water.

Thus at least at 25° C., the uncertainties in the calculated values of the thermodynamic properties of sea salt solutions result from the uncertainties in the measured values of NaCl solutions.

RECALCULATED BPE's, MINIMUM ENERGIES OF RECOVERY, AND OSMOTIC PRESSURES

The authors have recalculated the boiling point elevations (BPE's) of sea salt solutions, the minimum energies of recovery of water from standard sea water, and the osmotic pressures of sea salt solutions over wide ranges of temperature using the current recommendation (Equation 2a), and the new NaCl parameters (Table I). These are presented, respectively, in Tables II, III, and IV.

The minimum energies of recovery are expressed in the dimensionless form $\Delta G_{rec}/RT$ in Table III. In this form (rather than as ΔG_{rec}) their variation with temperature over the range 25° to 200° C. is reduced from some 45% to about 10%.

Table III. $\Delta G_{rec}/RT$ for Recovery from Standard Sea Water

3.45 Wt. % Salts

	Recovery, %				
T, ° C.	0	25	50	75	100
25	0.0185	0.0214	0.0260	0.0356	0.081
50	0.0186	0.0215	0.0261	0.0359	0.082
75	0.0185	0.0214	0.0261	0.0358	0.081
100	0.0183	0.0212	0.0258	0.0354	0.080
125	0.0181	0.0209	0.0254	0.0348	0.079
150	0.0178	0.0205	0.0250	0.0341	0.078
175	0.0174	0.0201	0.0244	0.0331	0.076
200	0.0170	0.0195	0.0236	0.0320	0.074

$RT = 0.12831\ T$ kw.h. per 1000 kg. water

$= 1.9866\ T$ cal. per mole water

$= 82.057\ T$ cc.-atm. per mole water

where T is in ° K.

The current calculations assume no precipitation of $CaSO_4$. Corrections for precipitation should be made as indicated previously (*15*)—i.e., the same percentage variation—if so desired.

The new values all show the greatest deviations from the previous calculations (*15*) at low temperatures and high concentrations (100% recovery in the case of the free energy of recovery). The largest change is a 12% increase

Table IV. Osmotic Pressures of Sea Salt Solutions, Atm.

	Wt. % Salts								
T, ° C.	1.00	2.00	3.45[a]	5.00	7.50	10.00	15.00	20.00	25.00
25	7.11	14.29	25.15	37.49	59.30	83.97	144.93	228.59	348
40	7.42	14.93	26.34	39.35	62.41	88.53	152.81	239.86	362
60	7.80	15.70	27.74	41.51	65.98	93.69	161.53	252.06	376
80	8.13	16.37	28.94	43.32	68.89	97.82	168.27	261.17	386
100	8.42	16.94	29.92	44.79	71.17	100.97	173.16	267.47	393

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

in BPE at 25° C. at 28 wt. % solids. The largest change at 12 wt. % solids and below is a 4% increase in BPE at 25° C. In general, where there is a change the new values are higher. The BPE values at the highest concentrations and temperatures are exceptions to this general observation; a 2% decrease occurs at 28 wt. % solids at 260° C.

ANALYTICAL EXPRESSIONS for BOILING POINT ELEVATIONS

Attempts were made to get an analytical expression for the BPE's *vs.* concentration and temperature given in Table II so that intermediate values could be calculated directly without resorting either to graphical interpolation or to the elaborate iteration procedure used in the original calculations (*15*). The authors' general approach to the problem was to express the BPE's as $\mathrm{BPE}_{\mathrm{ideal}}$, or some approximation thereof, times a function of temperature and concentration. The ideal BPE is given by Equation 5.

$$\mathrm{BPE}_{\mathrm{ideal}} = (RT^2 \textstyle\sum m_i)/\Delta H_{\mathrm{vap}}, \tag{5}$$

where R is the molal gas constant and ΔH_{vap} is the heat of vaporization of a kilogram of water. In this equation, the mole fraction of solute in Raoult's law has been replaced by the mole ratio of solute to solvent. Equation 5 may be expressed in terms of the absolute temperature T and the ionic strength I as follows.

$$\mathrm{BPE}_{\mathrm{ideal}}\ (^\circ\mathrm{C.}) = 0.24048\ T^2 I / (93{,}467.7 - 6{,}189{,}790/T - 96.5849\ T), \tag{6}$$

where

$$I = 0.19819 \times \mathrm{wt.}\ \% / (1 - 0.01 \times \mathrm{wt.}\ \%) \tag{7}$$

Equation 6 may be used as a rough approximation. The BPE values obtained are good to within about 10% at concentrations below about 16 wt. % and temperatures below about 125° C. At 260° C. the values obtained are about 30% low at all concentrations to about 20 wt. %. The ideal BPE's (Equation 6) showed in general a greater deviation from the more accurately calculated ones (*15*) than did those based on Raoult's law and the authors' previous equation (*15*) for the vapor pressure of water as a function of temperature, particularly at the higher temperatures. However, the latter calculations involved an iteration to evaluate the BPE such that the vapor pressure of the solution at temperature T + BPE was equal to the vapor pressure of pure water at temperature T.

Because of the peculiar way in which the calculated BPE's (*15*) deviated from the ideal values, it was difficult to get a suitable analytical expression by the method of least squares. When only a few parameters—e.g., five or six—were used, the agreement was not as good as desired. Equation 8 is the equation of best fit that was obtained with six parameters.

$$\mathrm{BPE} = \mathrm{BPE}_{\mathrm{ideal}} \times (0.205648 + 3.49091 \times 10^{-3}\,T + 0.150005\ I - 2.86240 \times 10^{-4}\,I\ T - 4.61964 \times 10^{-6}\,T^2 + 2.78176 \times 10^{-3}\ I^2) \tag{8}$$

In the range 0 to 20 wt. % solids the maximum deviation (4%) of Equation 8 from the accurate values is at 2 wt. % at both 25° and 260° C. For weight per cents between 3.45 (standard sea water) and 20 for temperatures between 30° and 240° C., the maximum deviations are about 2.5%.

When seven to ten parameters were used to get better agreement, convergence difficulties were encountered. Equation 9 was obtained by a combination of adjusting the temperature dependence of ΔH_{vap} and of evaluating a few parameters, fixing these, and then evaluating additional ones.

$$\mathrm{BPE} = [565.757/T - 9.81559 + 1.54739 \times \ln T - (337.178/T - 6.41981 + 0.922753 \times \ln T)\ I + (32.681/T - 0.55368 + 0.079022 \times \ln T)\ I^2] \times I / (266{,}919.6/T^2 - 379.669/T + 0.334169) \tag{9}$$

Equation 9 shows deviations from the more accurate calculation of about 1% or less in the ranges 3.45 to 20 wt. % and 30° to 250° C. At 2 wt. % and at 25° C., many of the deviations are about 2%. Thus, this equation reproduces the BPE's to well within the accuracy to which they are known, except at the lowest concentration and at the lowest temperature.

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