Relative Enthalpies of Sea Salt Solutions at 0° to 75°C

Daljit Singh and LeRoy A. Bromley[1]
Department of Chemical Engineering, University of California, Berkeley, Calif. 94720

The relative enthalpy of seawater, its solutions, and concentrates, the apparent enthalpy of sea salts, and the relative partial enthalpies of sea salts and water in seawater solutions, in the temperature range 0–75°C and salinity range 0–12%, have been evaluated from accurate calorimetric measurements of heats of mixing of sea salt solutions. The data were correlated by an extended Debye-Hückel theory. The results are consistent with the published data on heat capacity and heat of mixing.

In order to tap the oceans successfully as a source of fresh water and raw materials, the chemical engineer needs accurate information as to the properties of seawater and their variation with temperature, pressure, and salinity.

This paper provides such information on heats of mixing and relative enthalpies of seawater, its solutions and concentrates, in the temperature range 0–75°C, and means of accurate interpolation and fairly reliable extrapolation of the reported data. Apart from its immediate usefulness in desalination-related studies, the data are useful for calculating the change of free energy of seawater with temperature, for temperature variation of activity coefficients and osmotic coefficients, and will be useful in the calculation of the variation of boiling point elevation with temperature.

Theory

The most abundant constituent of seawater is water, and many of its characteristics and properties are close to those of water *(14)*, although the salt content makes a difference in many ways that are of engineering importance. The chemical and physicochemical differences are almost wholly attributable to 11 major constituents that make up over 99.9% of the material dissolved in seawater. The ratio of these materials to each other varies only slightly in the open ocean, so that the salt that might be obtained by dehydrating seawater would have almost exactly the same composition *(7, 10)*, no matter where in the ocean the water came from *(1)*, provided it was reasonably remote from the mouths of major rivers. The composition of these salts, hereinafter referred to as sea salts, is given in Table I.

The properties of seawater depend upon the temperature, pressure, and concentration (and relative amounts) of ions present. If we regard seawater as a binary mixture of sea salts and water, the relative enthalpy of solution, at constant temperature and pressure, is given by

$$L = x\phi L_s = x\bar{L}_s + (1 - x)\bar{L}_w \tag{1}$$

where ϕL_s is the apparent enthalpy of salts in solution, cal/g salts; $\bar{L}_s$ is the relative partial enthalpy of salts in solution, cal/g salts; $\bar{L}_w$ is the relative partial enthalpy of water in solution, cal/g water; and x is the mass fraction of salts in solution.

At very dilute concentrations, the enthalpies of electrolyte solutions may be calculated from the well-known Debye-Hückel theory. Lange *(12)* has shown that this theory, despite its shortcomings, represents the heat of dilution data fairly well for 1-1, 1-2, 2-1, 1-3, and 1-4 salts in the 0.001–0.01 molal range. The deviations become large as the concentration increases.

To extend the validity of this theory to higher concentration ranges, many approaches have been published. These "extended" theories invariably introduced additional empirical parameters. In principle, similar results can be obtained mathematically by adding a power series to the expression derived from Debye-Hückel theory. Although possible physical significance is lost, the extended Debye-Hückel theory, as developed by Guggenheim *(8, 9)* and Lewis et al. *(13)* and modified by Bromley *(3)*, provides a good correlation of the experimental data. The pertinent equations, based on the extended Debye-Hückel theory, are summarized below.

For unit mass:

$$\phi L_s = \frac{A_H}{2}\left(\frac{\Sigma m_i Z_i^2}{\Sigma m_i M_i}\right) I^{1/2}\left(\frac{1}{1 + I^{1/2}} - \frac{\sigma(I^{1/2})}{3}\right) - B''\frac{\Sigma m_i}{2} - \frac{2}{n+1}C''\left(\frac{\Sigma m_i}{2}\right)^n \tag{2}$$

$$\bar{L}_w = -\frac{A_H}{2}\left[\frac{\sigma(I^{1/2})}{3}\right]\left(\frac{2I^{3/2}}{1000}\right) + \frac{B''}{1000}\left(2\frac{\Sigma m_i M_i}{\Sigma m_i}\right)\cdot\left(\frac{\Sigma m_i}{2}\right)^2 + \frac{2n}{n+1}\left(\frac{C''}{1000}\right)\left(2\frac{\Sigma m_i M_i}{\Sigma m_i}\right)\left(\frac{\Sigma m_i}{2}\right)^{n+1} \tag{3}$$

and

$$\bar{L}_s = \frac{A_H}{2}\left(\frac{\Sigma m_i Z_i^2}{\Sigma m_i M_i}\right)\frac{I^{1/2}}{1 + I^{1/2}} - 2B''\frac{\Sigma m_i}{2} - 2C''\left(\frac{\Sigma m_i}{2}\right)^n \tag{4}$$

where the function $\sigma(u)$ is given by

$$\sigma(u) = \frac{3}{u^3}\left(1 + u - \frac{1}{1 + u} - 2\ln(1 + u)\right) \tag{5}$$

B'' and C'' are related (for 1-1 salts) to B and C of Lewis et al. *(13)* by

$$\frac{B''}{dB/dT} = \frac{C''}{dC/dT} = 2.303\,RT^2\left(\frac{\Sigma m_i}{2\,\Sigma m_i M_i}\right)\left(\frac{4\,\Sigma m_+ \Sigma m_-}{(\Sigma m_i)^2}\right) \tag{6}$$

For seawater *(2)*,

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[1] To whom correspondence should be addressed.

$$\frac{2\,\Sigma m_i M_i}{\Sigma m_i} = 62.83 \qquad (7)$$

and

$$\frac{4\,(\Sigma m_+)(\Sigma m_-)}{(\Sigma m_i)^2} = 0.998 \qquad (8)$$

Equipment

The equipment used for measuring the heats of mixing is similar to that used previously at 25°C *(3)* and consisted essentially of a calorimeter vessel (Dewar) with its mixing, stirring, and heating accessories, a constant temperature circulation bath, and a temperature-measuring and recording system. An auxiliary unit for controlled and metered heat input was available for heat capacity determinations and for calibration of the equipment.

The calorimeter was operated under isothermal conditions wherein the temperature of the surroundings was kept constant. However, the temperature changes during measurement were kept small and the calorimeter was well insulated, so that the result approximated that from an adiabatic calorimeter *(16)*. In the present equipment, this was achieved by using a low dilution ratio (180:4000 approximately). The extent to which the dilution ratio could be reduced was limited by the precision of the temperature-measuring equipment available.

A detailed description of the calorimeter has been given by Singh *(15)*; the main units are described below.

Calorimeter vessel. The calorimeter vessel, shown in Figure 1, consisted of a well-stirred Dewar flask of about 4-liter capacity, which contained an accurately weighed amount of one of the solutions to be mixed. A hollow Teflon stopper surrounding the Dewar neck supported a 2-ft high vertical glass column by means of an O-ring seal. A neoprene tube was cemented to the outside of the glass column and the Dewar flask with silastic 892 RTV to prevent further accidental leakage of fluids to or from the Dewar vessel. The Dewar was surrounded by a jacket, basically a 20-liter pressure cooker, with an inlet for circulating liquid at the bottom. A second vertical glass column rested on the top of this jacket. The two concentric glass columns were connected at the top with a brass flange having an outlet for the circulating liquid. Liquid is circulated through the jacket and the annular space between the two columns to maintain a constant temperature within and above the calorimeter. The circulating liquid used was tap water for measurements at room temperature and above, and glycerol–water for low temperature measurements.

Stirring within the calorimeter is effected by a three-blade propeller attached to a 316 stainless steel rod revolving at 300 rpm and controlled by a synchronous motor through a flexible drive.

The second solution to be mixed was contained in a stainless steel pipet of about 180-cm^3 capacity (Figure 2) fixed with stainless steel supports to a Teflon stopper. The latter is equipped with holes for a stirrer, a heater, and a thermometer. The pipet was essentially cylindrical with rounded top and bottom to prevent local accumulation of liquid within the pipet and to reduce the time lag on mixing. Two disc plugs were fitted into either end with Viton O-rings. The two plugs could be opened simultaneously to facilitate adequate circulation and fast mixing.

Constant temperature bath. The constant temperature bath was controlled by a Hallikainen thermotrol unit composed of a sensing probe and a regulator with a controlling sensitivity of better than 0.001°C. A Brinkman-Lauda constant temperature circulator, Model NS, was used for preliminary heating of the bath liquid and as an aid to efficient control. For low-temperature measurements, this was replaced by a Brinkman-Lauda K-4/R circulator. A modified soft drink cooler with a high-capacity compresser was used for preliminary cooling of the sample.

Temperature measuring and recording unit. The primary temperature sensing element was a Rosemount platinum resistance thermometer calibrated by the National Bureau of Standards. A Leeds & Northrup Type G-2 Mueller bridge was used for measuring the resistance of the thermometer. The Mueller bridge was housed in a thermally insulated and magnetically shielded enclosure, and the thermometer leads were magnetically shielded to reduce electrical noise and interference from stray electrostatic fields. A Keithley Model 147 Nanovolt null detector, connected to a Leeds & Northrup Speedomax recorder, was used in conjunction with the Mueller bridge. By interpolating the null detector needle

TABLE I. Composition of Sea Salts (Assuming complete ionization)

Ion	Wt % in sea salts
Cl^-	55.082
SO_4^{2-}	7.691
HCO_3^-	0.406
Br^-	0.174
Na^+	30.646
Mg^{2+}	3.686
Ca^{2+}	1.161
K^+	1.103
Sr^{2+}	0.029
	99.978

Apparent molecular weight (2) = 62.83

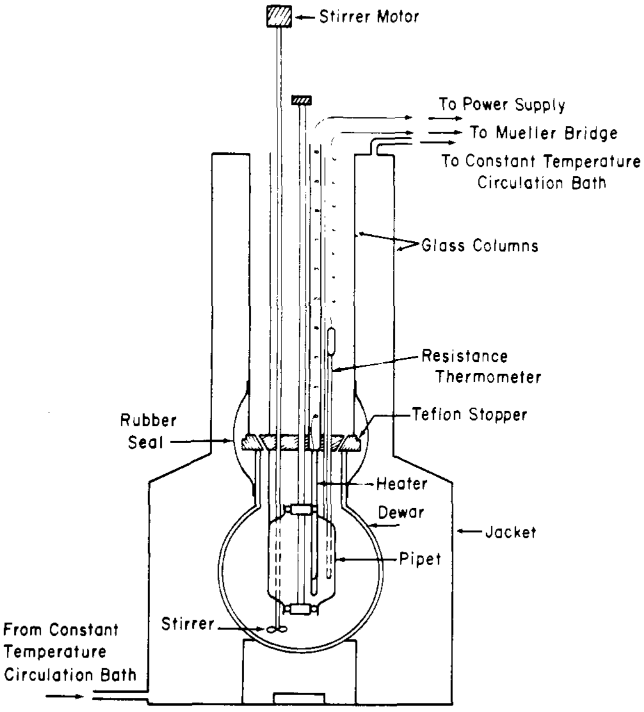

Figure 1. Sectional view of calorimeter

deflection, resistances could be estimated to within ±2.5 $\times 10^{-6}$ ohm, corresponding to about 2.5×10^{-5}°C.

A schematic of the entire calorimeter is shown in Figure 3.

Heat-capacity equipment. Auxiliary equipment for a metered energy input was available for heat capacity runs. The electrical energy input to the system was 60-cycle held constant at 110 V by a Sola regulator, and measured by a Sangamo rotating standard, J-5. Its absolute accuracy was 0.17% and reproducibility was ±0.02%. The heating time was variable up to 120 sec by a variable timer and was measured by means of a fixed timer that can be read to 0.001 sec.

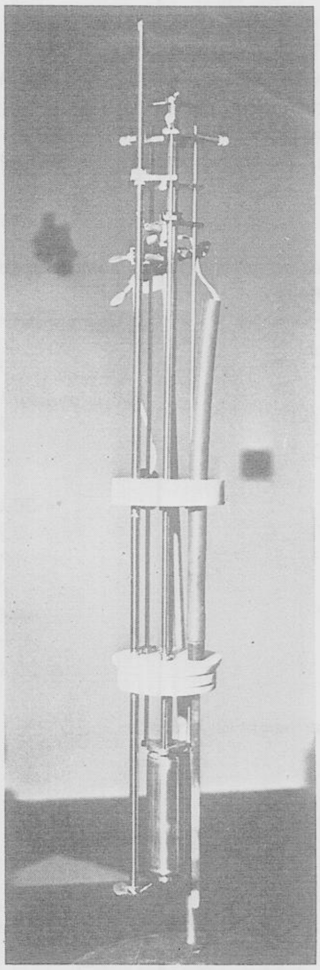

Figure 2. Calorimeter pipet

Further details have been described by Wilkins *(17)*.

Salinity measurements. A single parameter, salinity, was used to describe the concentration of salts in sea water, following the recommendation of the Unesco Joint Panel of Oceanographic Table and Standards *(6)* (JPOTS). This value of salinity is related fo chlorinity by

$$S(^0/_{00}) = 1.80655\, Cl(^0/_{00}) \qquad (9)$$

Chlorinity, as used here, is defined as the total amount of chlorine, bromine, and iodine, in grams, contained in 1 kg of seawater, assuming that bromine and iodine have been replaced by chlorine. The salinity, so defined, is about 4 parts per thousand less than the total dissolved solids.

The salinity of the sea salt solutions was measured by the conductometric method using a Bissett-Berman Model 6230 salinometer. The salinity, S, is related to the conductivity by

$$S(^0/_{00}) = 0.08996 + 28.29720\, R_{15} + 12.80832\, R_{15}^2 - 10.67869\, R_{15}^3 + 5.98624\, R_{15}^4 - 1.32311\, R_{15}^5 \qquad (10)$$

where R_t is the ratio of conductivity of sample water to that of standard water having a salinity of exactly $35^0/_{00}$, both samples being at the same temperature, t°C, and under a pressure of 1 atm.

If measurements are made at a temperature other than 15°C—e.g., at room temperature—R_{15} may be computed by

$$R_{15} = R_t + 10^{-5} R_t (R_t - 1)(t - 15)\,[96.7 - 72.0\, R_t + 37.3\, R_t^2 - (0.63 + 0.21\, R_t^2)(t - 15)] \qquad (11)$$

The Bissett-Berman Co. provides standard tables for direct evaluation of salinity from conductivity ratio, as well as for temperature corrections.

The Knudsen method *(11)* of titrating with silver nitrate solution in standard equipment was used in the initial stages of the experiment. This method had a relatively lower accuracy. The measured chlorinity is converted to salinity by

$$S(^0/_{00}) = 0.030 + 1.805\, Cl(^0/_{00}) \qquad (12)$$

The G. M. Manufacturing Co. provides standard tables for direct conversion of titration readings to chlorinity and salinity.

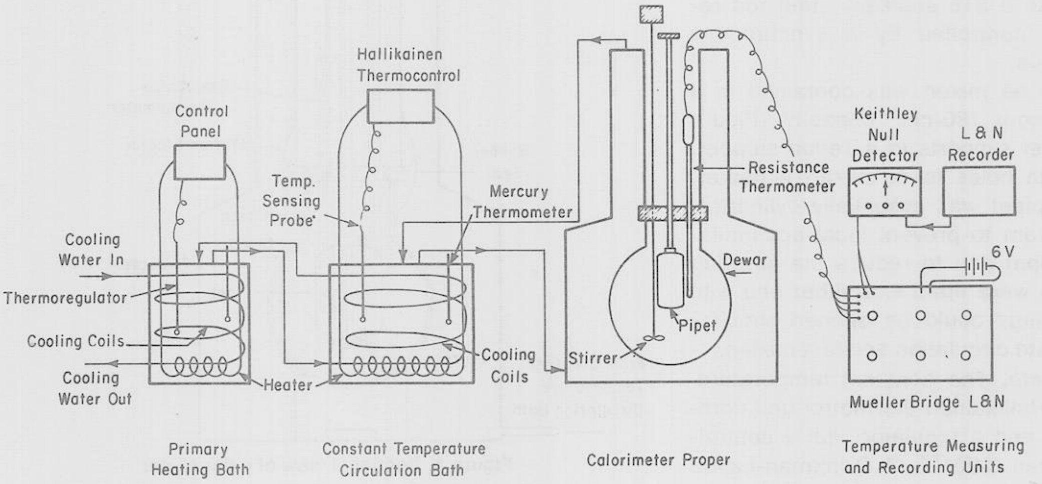

Figure 3. Schematic of heat of mixing Calorimeter

Since the range of both the conductometric and Knudsen methods is limited, samples with higher concentration were diluted with distilled water, by weight, to normal concentrations. The salinity was then determined by the aforementioned procedure.

I.A.P.S.O. (Denmark) standard seawater having a chlorinity of $19.375^0/_{00}$ was used for standardization.

Procedure

The seawater used was obtained from the Scripps Institution of Oceanography, La Jolla, Calif. The Pacific Ocean water, obtained from about 800 ft offshore, is pumped from a point midway between the ocean floor and the ocean surface, collected, and delivered in plastic bottles. The pH of the water is about 8.2.

To prevent precipitation of calcium carbonate or magnesium hydroxide, concentrates of seawater are prepared by acidifying seawater to a pH of about 4.5 and then boiling it to the desired concentration. This approximates the usual procedure used as a pretreatment for seawater conversion. It is anticipated that as long as no solids precipitate, the heat effects would not be too sensitive to initial pH, but this was not investigated. About 3.2 ml of concentrated sulfuric acid (sp gr 1.84) are required for approximately 45 liters of seawater. Dilute solutions are prepared by addition of distilled water.

TABLE II. Observed and Correlated Heats of Mixing of Sea Water Solutions at 3°, 50°, and 73°C

	Weight, g		Salinity, %		Heat of mixing, cal	
No.	Dewar	Pipet	Dewar	Pipet	Obsd.	Correlated
			At 3°C			
1	3803.2	174.3	0.407	3.338	13.90	12.12
2	3801.1	174.9	1.329	3.338	7.27	6.56
3	3799.0	177.4	1.096	6.700	52.55	53.48
4	3805.4	178.2	1.612	6.700	45.07	45.13
5	3799.0	178.8	2.278	6.700	35.46	34.66
6	3797.9	174.7	0.000	3.338	14.27	11.22
7	3797.2	174.5	0.000	3.338	14.53	11.20
8	3800.3	173.9	0.149	3.338	15.47	12.62
9	3801.2	182.4	1.290	9.425	109.59	118.11
10	3893.1	183.0	1.680	9.425	118.31	108.39
11	3805.1	183.0	1.542	9.425	104.12	111.89
12	3800.2	178.5	3.350	6.522	16.53	17.98
13	3800.5	179.2	1.563	6.595	42.43	44.29
14	3804.7	178.1	3.350	6.522	16.10	17.95
			At 50°C			
1	4049.8	254.2	0.000	3.360	−24.60	−24.20
2	4058.0	260.0	0.000	3.360	−25.60	−24.61
3	4021.4	185.2	0.157	3.340	−11.76	−11.73
4	4036.3	190.7	0.434	3.340	−7.93	−6.68
5	4017.8	188.8	0.000	3.340	−23.30	−19.29
6	4081.6	226.5	3.360	0.000	−3.93	−5.61
7	4011.2	185.6	3.666	0.000	−4.18	−4.61
8	4050.7	189.8	0.567	3.340	−3.57	−5.17
9	4054.8	189.7	0.691	3.340	−2.91	−4.12
10	4058.3	189.9	0.809	3.340	−1.64	−3.33
11	4061.4	190.2	0.922	3.340	−1.81	−2.72
12	4123.8	185.8	3.366	0.000	−6.06	−4.61
13	4016.6	188.8	0.297	3.340	−8.42	−8.71
14	4064.5	190.0	1.030	3.340	−1.11	−2.24
15	4065.4	195.5	0.000	6.966	−38.69	−38.10
16	4074.6	195.1	0.320	6.966	−20.97	−19.67
17	4085.4	220.0	3.360	10.080	−1.30	−1.80
18	3999.3	151.3	0.000	10.620	−48.56	−45.50
			At 73°C			
1	3808.0	169.1	0.000	3.382	−31.98	−30.93
2	3812.0	172.1	0.855	5.068	−20.68	−17.46
3	3798.1	171.1	1.535	5.047	−12.18	−9.48
4	3799.5	172.1	1.686	5.047	−10.03	−8.38
5	3789.2	179.0	0.000	9.864	−108.12	−119.52
6	3800.4	179.3	0.443	10.275	−78.89	−85.98
7	3790.8	168.9	0.000	3.350	−31.86	−30.52
8	3790.4	170.0	0.143	3.350	−22.84	−21.44
9	3792.4	169.5	0.281	3.350	−19.81	−16.72
10	3697.5	173.1	0.861	6.736	−34.96	−29.76
11	3700.5	173.2	1.124	6.736	−27.72	−24.77
12	3703.7	173.8	1.375	6.736	−22.55	−21.08
13	3799.7	174.5	1.832	6.735	−18.55	−15.96
14	3790.1	172.4	0.671	5.118	−27.02	−21.21

TABLE III. B" Values for Seawater

Temp., °C	$B''\left(\frac{\text{cal}}{\text{g}} \cdot \frac{\text{kg}}{\text{mol}}\right)$
3.0	9.4529
25.0	6.0993[a]
50.0	4.5254
73.0	3.3296

[a] From *(3)*.

To determine the thermal capacity of the calorimeter, the Dewar is filled with an accurately weighed amount of distilled water or a seawater sample of known salinity and heat capacity. The pipet, along with the stirrer, heater, and resistance thermometer, is then placed in the calorimeter. The contents of the Dewar are allowed to come to thermal equilibrium with the surroundings, maintained at a fixed temperature by the control unit described ear-

TABLE IV. Relative Enthalpies of Sea Salt Solutions at 0°, 25°, 50°, and 75°C (Calories/gram)

Salinity, %	Apparent enthalpy of sea salts, ϕL_s	Partial enthalpy of salts, $\bar{L}_s$	Partial enthalpy of water, $\bar{L}_w$	Relative enthalpy of solution, L	Salinity, %	Apparent enthalpy of sea salts, ϕL_s	Partial enthalpy of salts, $\bar{L}_s$	Partial enthalpy of water, $\bar{L}_w$	Relative enthalpy of solution, L
		At 0°C					At 25°C		
0	0	0	0	0	0	0	0	0	0
0.001	0.084	0.125	−0.00000	0.00000	0.001	0.126	0.187	−0.00000	0.00000
0.005	0.181	0.266	−0.00000	0.00001	0.005	0.275	0.407	−0.00001	0.00001
0.01	0.249	0.362	−0.00001	0.00002	0.01	0.382	0.562	−0.00002	0.00004
0.05	0.494	0.685	−0.00009	0.00025	0.05	0.795	1.140	−0.00017	0.00040
0.1	0.634	0.842	−0.00021	0.00063	0.1	1.065	1.497	−0.00043	0.00106
0.2	0.772	0.949	−0.00035	0.00154	0.2	1.392	1.900	−0.00102	0.00278
0.3	0.832	0.943	−0.00033	0.00250	0.3	1.604	2.134	−0.00159	0.00481
0.4	0.853	0.883	−0.00012	0.00341	0.4	1.757	2.286	−0.00212	0.00703
0.5	0.850	0.790	0.00031	0.00425	0.5	1.874	2.387	−0.00258	0.00937
0.6	0.831	0.674	0.00095	0.00498	0.6	1.966	2.454	−0.00295	0.0118
0.7	0.799	0.541	0.00182	0.00559	0.7	2.039	2.496	−0.00322	0.0143
0.8	0.757	0.396	0.00291	0.00606	0.8	2.098	2.519	−0.00339	0.0168
0.9	0.708	0.242	0.00424	0.00638	0.9	2.146	2.526	−0.00346	0.0193
1	0.653	0.080	0.00579	0.00653	1	2.184	2.522	−0.00341	0.022
2	−0.091	−1.762	0.0341	−0.00182	2	2.274	2.125	0.00304	0.046
3	−0.999	−3.761	0.0854	−0.0300	3	2.114	1.463	0.0201	0.063
4	−1.974	−5.796	0.159	−0.0789	4	1.852	0.730	0.0467	0.074
5	−2.982	−7.827	0.255	−0.149	5	1.541	−0.0106	0.0817	0.077
6	−4.010	−9.839	0.372	−0.241	6	1.205	−0.730	0.124	0.072
7	−5.047	−11.822	0.510	−0.353	7	0.858	−1.412	0.171	0.060
8	−6.090	−13.773	0.668	−0.487	8	0.510	−2.046	0.222	0.041
9	−7.134	−15.687	0.846	−0.642	9	0.165	−2.626	0.276	0.015
10	−8.178	−17.563	1.043	−0.818	10	−0.171	−3.146	0.331	−0.017
11	−9.219	−19.397	1.258	−1.014	11	−0.495	−3.601	0.384	−0.054
12	−10.257	−21.188	1.491	−1.231	12	−0.804	−3.989	0.434	−0.097
		At 50°C					At 75°C		
0	0	0	0	0	0	0	0	0	0
0.001	0.180	0.269	−0.00000	0.00000	0.001	0.249	0.372	−0.00000	0.00000
0.005	0.396	0.587	−0.00001	0.00002	0.005	0.549	0.815	−0.00001	0.00003
0.01	0.552	0.815	−0.00002	0.00006	0.01	0.767	1.134	−0.00003	0.00008
0.05	1.167	1.692	−0.00027	0.00058	0.05	1.634	2.381	−0.00037	0.00082
0.1	1.584	2.265	−0.00068	0.00158	0.1	2.231	3.214	−0.00098	0.00223
0.2	2.115	2.965	−0.00170	0.00423	0.2	3.007	4.264	−0.00252	0.00601
0.3	2.480	3.423	−0.00284	0.00744	0.3	3.552	4.980	−0.00430	0.0107
0.4	2.761	3.762	−0.00402	0.0110	0.4	3.982	5.529	−0.00621	0.0159
0.5	2.990	4.028	−0.00522	0.0150	0.5	4.339	5.976	−0.00823	0.0217
0.6	3.182	4.244	−0.00641	0.0191	0.6	4.646	6.352	−0.0103	0.0279
0.7	3.348	4.423	−0.00758	0.0234	0.7	4.915	6.677	−0.0124	0.0344
0.8	3.493	4.573	−0.00871	0.0280	0.8	5.155	6.962	−0.0146	0.0412
0.9	3.622	4.702	−0.00981	0.0326	0.9	5.372	7.216	−0.0168	0.0484
1.0	3.736	4.813	−0.0109	0.0374	1.0	5.570	7.444	−0.0190	0.0557
2	4.453	5.378	−0.0189	0.0891	2	6.941	8.946	−0.0409	0.139
3	4.798	5.519	−0.0223	0.144	3	7.781	9.815	−0.0629	0.233
4	4.986	5.520	−0.0223	0.200	4	8.391	10.452	−0.0859	0.336
5	5.093	5.480	−0.0204	0.255	5	8.878	10.996	−0.112	0.444
6	5.157	5.442	−0.0182	0.309	6	9.295	11.514	−0.142	0.558
7	5.200	5.433	−0.0176	0.364	7	9.672	12.041	−0.178	0.677
8	5.233	5.468	−0.0204	0.419	8	10.028	12.600	−0.224	0.802
9	5.266	5.557	−0.0288	0.474	9	10.375	13.208	−0.280	0.934
10	5.306	5.710	−0.0449	0.531	10	10.722	13.876	−0.350	1.072
11	5.357	5.932	−0.0710	0.589	11	11.078	14.612	−0.437	1.219
12	5.424	6.230	−0.110	0.651	12	11.446	15.425	−0.543	1.374

lier. A measured amount of heat is then added to the Dewar contents, and the temperature rise is recorded. The thermal capacity of the calorimeter is calculated therefrom.

For the heat of mixing runs, the Dewar is filled with an accurately weighed amount of one of the samples (of known salinity) to be mixed, at approximately the temperature of operation. The pipet, containing a known amount of a known salinity sample, at approximately the temperature of the experiment, is then inserted in place along with the resistance thermometer, heater, and stirrer. The two samples are allowed to equilibrate while the surroundings are maintained at a constant temperature. At steady state, the heat input due to stirring is equivalent to the heat leak from the Dewar flask. A continuous temperature record is maintained on the Speedomax recorder. When equilibrium is attained, the pipet is opened, the samples are allowed to mix, and the change of temperature is recorded. This is corrected for the heat of opening, and the net heat of mixing is computed.

The procedure used for determining the heat of opening of the pipet is identical, except that the Dewar and pipet are both filled with the same sample.

Results and Discussion

Relative, partial, and apparent enthalpies. The heats of mixing data were correlated through the use of extended Debye-Hückel Equations 1 through 4. The observed and correlated values for various temperatures are given in Table II; data at 25°C have been reported *(3)*. The agreement between the observed and correlated values appears to be good in most cases.

The standard states chosen at any temperature were pure water and sea salts at infinite dilution. The value used for n was 1.5, following the general discussion given by Bromley *(3)*.

B'' and C'' were treated as constants in these calculations, to be evaluated from the experimental data at any particular temperature. C'' was very slightly dependent upon temperature, but the best value selected at 25°C, −2.2359, was used at all temperatures. B'' varied with temperature, and the various values are given in Table III.

B'' is also related to the parameter B', used in heat-capacity work *(4)* by Equation 13

$$\frac{B''}{dB/dT} = \frac{\mathrm{B}'}{\frac{2}{T}\frac{dB}{dT} + \frac{d^2B}{dT^2}} = 2.303\,RT^2 \left(\frac{\Sigma m_i}{2\,\Sigma m_i M_i}\right)\cdot\left(\frac{4\,\Sigma m_+ \Sigma m_-}{(\Sigma m_i)^2}\right) \quad (13)$$

The value of B' found from heat capacity data is given by

$$B' = -\,(272)(0.171253 \times 10^{39})T^{-17} - 0.072070739 + (1.05884208 \times 10^{-4})T \quad (14)$$

Combining Equations 15 and 17, we get

$$B'' = 17(0.171253 \times 10^{39})\,T^{-16} - (0.072070739)\,T + (0.52942104 \times 10^{-4})\,T^2 + BK \quad (15)$$

where BK is a constant to be evaluated from the experimental data.

A computer program was written to find the best value of BK from the data given in Table III. The best value chosen was 22.20429, leading to

$$B'' = 17(0.171253 \times 10^{39})\,T^{-16} - (0.072070739)\,T + (0.52942104 \times 10^{-4})\,T^2 + 22.20429 \quad (16)$$

These values of B'' were used in Equations 1 through 4 to evaluate the relative enthalpy of sea salt solutions, relative partial enthalpy of water in seawater, relative partial enthalpy of sea salts, and relative apparent enthalpy of sea salts in the temperature range 0–75°C.

The calculated values of the relative, partial, and apparent enthalpies at 0°, 25°, 50°, and 75°C are reported in Table IV; results at 25°C are based on the data from Bromley *(3)*. The smoothed values differ slightly, in that the value of B'' from Equation 16 was used. Plots of these quantities vs. salinity may be found in Figures 4 through 7. Salinity, as used in these graphs, is expressed in percent, not in parts per thousand.

Comparison with heat capacity data. An estimate of the relative enthalpies may also be obtained from the heat capacity data of Bromley et al. *(4)*. In the temperature range involved, the heat capacity of seawater is given by

$$C_P = C_{P(w)}^{*}\,(1 - x) + x(\phi C_{P(s)}) \quad (17)$$

$$(\phi C_{P(s)}) = \overline{C^{\circ}_{P(s)}} + \frac{A_j}{2}\left(\frac{\Sigma m_i Z_i^2}{\Sigma m_i M_i}\right) I^{1/2}\left(\frac{1}{1 + I^{1/2}} - \frac{\sigma(I^{1/2})}{3}\right) - B'\,\frac{\Sigma m_i}{2} \quad (18)$$

$$A_j = 7.858661 + 0.04424799\,t + (0.2129136 \times 10^{-2})\,t^2 - (0.1837382 \times 10^{-4})\,t^3 + (0.7077757 \times 10^{-7})\,t^4 \quad (19)$$

and B' is given by Equation 14. $\overline{C^{\circ}_{P(s)}}$ is a sixth-degree polynomial in t which cancels while evaluating relative enthalpies.

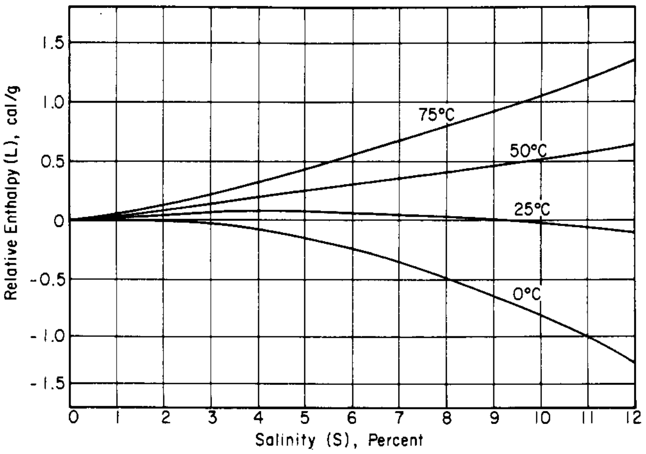

Figure 4. Relative enthalpies of sea salt solutions

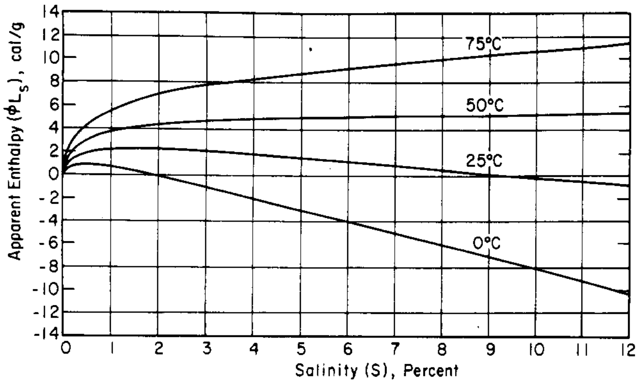

Figure 5. Apparent enthalpy of sea salt solutions

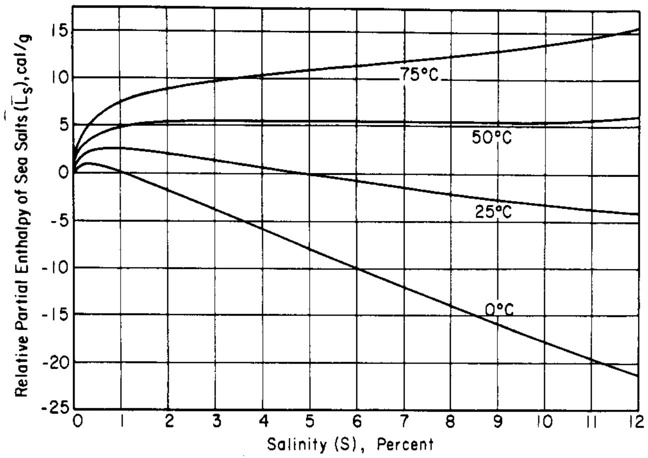

Figure 6. Relative partial enthalpy of sea salts in seawater

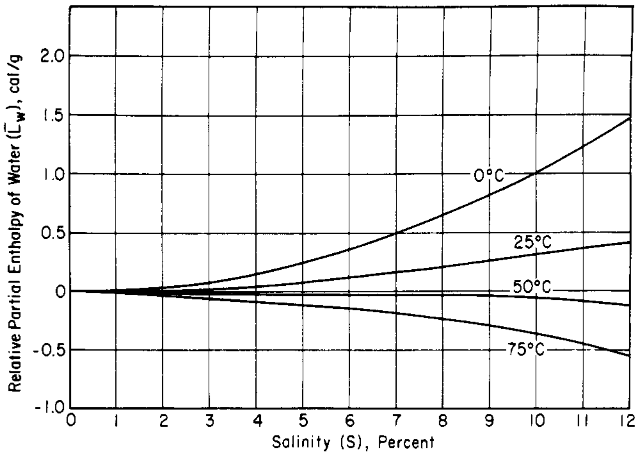

Figure 7. Relative partial enthalpy of water in seawater

TABLE V. Relative Enthalpy of Sea Salt Solutions at Various Temperatures

Salinity, %	25°C, obsd.	50°C		75°C		0°C	
		Obsd.	Calcd. from heat capacity data	Obsd.	Calcd.	Obsd.	Calcd.
1	0.022	0.037	0.037	0.056	0.056	0.007	0.007
2	0.046	0.089	0.089	0.139	0.141	−0.002	−0.002
3	0.063	0.144	0.144	0.233	0.246	−0.030	−0.030
4	0.074	0.199	0.199	0.336	0.349	−0.079	−0.078
5	0.077	0.255	0.255	0.444	0.449	−0.149	−0.149
6	0.072	0.309	0.309	0.558	0.565	−0.241	−0.240
7	0.060	0.364	0.364	0.677	0.686	−0.353	−0.353
8	0.041	0.419	0.419	0.802	0.813	−0.487	−0.487
9	0.015	0.474	0.474	0.934	0.946	−0.642	−0.642
10	−0.017	0.531	0.531	1.072	1.087	−0.818	−0.818
11	−0.054	0.589	0.589	1.219	1.235	−1.014	−1.015
12	−0.097	0.651	0.651	1.374	1.392	−1.231	−1.232

TABLE VI. Comparison with Connors' (*5*) Data at Various Temperatures and Concentrations

Temp., °C	Solution 1		Solution 2		Heat of mixing, cal.	
	Salinity, ‰	Weight, g	Salinity, ‰	Weight, g	Obsd. (Connors)	Estd. (from our data)
25.3	10.24	0.5	60.50	0.5	0.024	0.023
24.6	10.24	0.5	60.50	0.5	0.024	0.023
21.4	10.24	0.5	60.50	0.5	0.027	0.028
20.0	10.24	0.5	60.50	0.5	0.028	0.029
15.0	10.24	0.5	60.50	0.5	0.035	0.036
14.2	10.24	0.5	60.50	0.5	0.036	0.037
9.15	10.24	0.5	60.50	0.5	0.047	0.046
3.10	10.24	0.5	60.50	0.5	0.063	0.058
2.75	10.24	0.5	60.50	0.5	0.065	0.059
2.00	10.24	0.5	60.50	0.5	0.064	0.061
1.93	10.0	0.5	60.0	0.5	0.064	0.061
1.90	10.0	0.5	60.0	0.5	0.060	0.061
2.05	15.0	0.5	54.6	0.5	0.039	0.038
2.02	15.0	0.5	54.6	0.5	0.037	0.038
2.86	15.0	0.5	54.6	0.5	0.038	0.038
2.00	20.0	0.5	49.6	0.5	0.020	0.021
1.99	20.0	0.5	49.6	0.5	0.021	0.021
2.08	24.8'	0.5	45.4	0.5	0.010	0.010
2.03	24.8	0.5	45.4	0.5	0.010	0.010

The relative enthalpy at any temperature $(RH)^t$, is given by

$$(RH)^t - (RH)^{25} = \int_{25}^{t} (C_P - C_{P(w)}{}^* (1 - x) - \overline{C^\circ{}_{P(s)}}\, x)dt$$
$$= \int_{25}^{t} (\phi C_{P(s)} - \overline{C^\circ{}_{P(s)}})\, x dt$$
$$= x \cdot \frac{1}{2} \left(\frac{\Sigma m_i Z_i{}^2}{\Sigma m_i M_i} \right) I^{1/2} \cdot$$
$$\left(\frac{1}{1 + I^{1/2}} - \frac{\sigma(I^{1/2})}{3} \right) \cdot \int_{25}^{t} A_j\, dt -$$
$$x \frac{\Sigma m_i}{2} \int_{25}^{t} B' dt \qquad (20)$$

which can conveniently be evaluated.

These calculated values at various temperatures are compared with the observed values in Table V. The agreement between the two values is very good.

Comparison with Connors' (5) data. Some data on heats of mixing of seawater solutions in the temperature range, 0-30°C, and salinity range, 10-40$^0/_{00}$, have also been reported by Connors *(5)*. Connors' reported temperature changes were converted to heats of mixing and compared with our estimated values, using the extended Debye-Hückel theory. The two values are compared at various temperatures and at various concentrations in Table VI. In most cases, the two values agree within his error estimates. This represents rather good agreement and gives a high degree of confidence to our relative enthalpy data.

Nomenclature

A_H = Debye-Huckel constant for enthalpy
A_j = Debye-Huckel constant for heat capacity
B', B'', C'' = constants defined in Equations 6 and 13
$Cl(^0/_{00})$ = chlorinity, parts per thousand
C_p = heat capacity of solution at constant pressure, cal/g °C
$\bar{C}_{P(s)}$ = partial heat capacity of salts in solution, cal/g salts °C
$\bar{C}^\circ{}_{P(s)}$ = partial heat capacity of salts at infinite dilution, cal/g salts °C
$\phi C_{P(s)}$ = apparent heat capacity of salts, cal/g salts °C
$\bar{C}_{P(w)}$ = partial heat capacity of water in solution, cal/g water °C
$C_{P(w)}{}^*$ = heat capacity of pure water at constant pressure, cal/g water °C
I = ionic strength (= $\Sigma m_i Z_i{}^2/2$)
L = relative enthalpy, cal/g
$\bar{L}_s$ = relative partial enthalpy of salts in solution, cal/g salts
$\bar{L}_w$ = relative partial enthalpy of water in solution, cal/g water
ϕL_s = apparent enthalpy of salts in solution, cal/g salts
M_i = molecular weight of ion i
m_i = molality of species i, g mol/1000 g water
m_+ = total molality of positive ions
m_- = total molality of negative ions
n = constant in Equations 2, 3, and 4 = 1.5
$(RH)^t$ = relative enthalpy at t°C, cal/g
R_t = conductivity ratio at t°C, in Equations 10 and 11
$S(^0/_{00})$ = salinity, parts per thousand
T = temperature, K
t = temperature, °C
x = mass fraction salts in solution
Z_i = charge on ion i

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

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Received for review July 18, 1972. Accepted December 14, 1972. Work supported by a grant from the Office of Saline Water, U.S. Department of the Interior.