Heat Capacity of Sea Water Solutions

Partial and Apparent Values for Salts and Water

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Consistent values from 0° to 80° C. and 0 to 12% salinity of the partial (unit mass basis) heat capacities of water and sea salts as well as apparent values of sea salts have been calculated from published data by use of extended Debye-Hückel theory applied to multi-ion solutions. Sea salts are treated as a single component. As an aid to calculations involving small changes in salinity, values are given to five decimal places for each 5° C. and 0.1% salinity, although absolute accuracy of the heat capacities is about 1 part in 1000.

MEASURED and smoothed values of the heat capacity of sea water solutions have been reported (*1, 2*), but shed no light on whether the extended Debye-Hückel theory could also be used to correlate the data adequately. Furthermore, there is a need for the partial and apparent heat capacity value for use in calculating accurate changes with temperature in thermodynamic quantities, including enthalpies, activities, and vapor pressure. A single set of values, expressed as a function of temperature and salinity, will suffice for ocean waters because, to a first approximation, the oceans' salts are of constant composition. Because of the multiplicity of ions in sea water, a unit mass basis proved considerably less confusing or ambiguous than a molal basis.

In all cases the defined calorie is used: 1 defined calorie = 4.1840 absolute joules

The heat capacity values for pure water were taken from Osborne *et al.* (*6*).

The composition of sea water given by Sverdrup, Johnson, and Fleming (*8*) was used in all calculations. For calculations of ionic strength, the major salt components, except boric acid, were assumed to be completely ionized.

The salt content of ocean water is related to salinity. Salinity is strictly defined (*8*) as "the total amount of solid material in grams contained in 1 kg. of sea water when all the carbonate has been converted to oxide, the bromine and iodine replaced by chlorine, and all organic matter completely oxidized."

We use per cent salinity to be 0.1 times the defined salinity in parts per thousand, ‰, and mass fraction salts to be 0.01 times the per cent salinity.

THEORY

The extended Debye-Hückel theory as summarized by Lewis *et al.* (*5*) was generalized for multi-ion solution to give the following equations for heat capacity. All equations are written on a unit mass basis.

From the definition of apparent and partial heat capacities, one may write for a two-component system of water and dissolved salts:

$$C_p = C_{p_1}^*(1-x) + x(\phi C_{p_2}) = \overline{C}_{p_1}(1-x) + xC_{p_2} \qquad (1)$$

where x is the mass fraction salts. We use the salinity expressed in mass fraction (or in per cent) for x.

A few other mathematical relationships relating the above quantities are:

$$\overline{C}_{p_1} = C_p - x\frac{dC_p}{dx} = C_{p_1}^* - x^2\frac{d(\phi C_{p_2})}{dx} \qquad (2)$$

$$\overline{C}_{p_2} = C_p + (1-x)\frac{dC_p}{dx} = \overline{C}_{p_1} + \frac{dC_p}{dx} = (\phi C_{p_2}) + x(1-x)\frac{d(\phi C_{p_2})}{dx} \qquad (3)$$

also

$$\frac{\dfrac{d\overline{C}_{p_1}}{dx}}{\dfrac{d\overline{C}_{p_2}}{dx}} = \frac{-x}{1-x} \qquad (4)$$

Since x = mass fraction salts,

$$x = \frac{\sum m_iM_i}{1000 + \sum m_iM_i} \qquad (5)$$

Values of the apparent and partial quantities from the extended Debye-Hückel theory for a multi-ion solution may be written:

For the apparent heat capacity of salts,

$$(\phi C_{p_2}) = \overline{C}_{p_2}^\circ + \frac{A_J}{2}\left(\frac{\sum m_iZ_i^2}{\sum m_iM_i}\right)I^{1/2}\left(\frac{1}{1+I^{1/2}} - \frac{\sigma I^{1/2}}{3}\right) - B'\frac{\sum m_i}{2} + \dots \qquad (6)$$

For the partial heat capacity of water,

$$\overline{C}_{p_1} = C_{p_1}^* - \frac{A_J}{2}\left(\frac{\sigma I^{1/2}}{3}\right)\left(\frac{2I^{3/2}}{1000}\right) + \frac{B'}{1000}\left(\frac{2\sum m_iM_i}{\sum m_i}\right)\left(\frac{\sum m_i}{2}\right)^2 + \dots \qquad (7)$$

For the partial heat capacity of salts,

$$\overline{C}_{p_2} = \overline{C}_{p_2}^\circ + \frac{A_J}{2}\left(\frac{\sum m_iZ_i^2}{\sum m_iM_i}\right)\frac{I^{1/2}}{1+I^{1/2}} - 2B'\frac{\sum m_i}{2} + \dots \qquad (8)$$

Here

$$B' = 2.303RT^2\left(\frac{\sum m_i}{2\sum m_i M_i}\right)\left[\frac{4\left(\sum m_{\cdot}\right)\left(\sum m\right)}{\sum m_i^2}\right]\left(\frac{2}{T}\frac{dB}{DT}+\frac{d^2B}{dT^2}\right) \qquad (9)$$

which for a given water-salt system is a function of temperature only. B' will be evaluated from experimental data on heat capacity using Equations 1 and 6.

PROCEDURE

The values of the constant, A_j, given by Lewis and Randall (*5*) were fitted to a smooth curve, and the smoothed values used are given in Table I. These values are uncertain, but, except for the extrapolations to infinite dilution, the results are rather insensitive to changes in A_j.

The experimental values for heat capacity (*1*) for each salinity were fitted by the least squares method to a cubic equation in temperature. A fourth-power equation was also tried, but with essentially no better fit of the data. At each temperature the values calculated from these equations were fitted to the extended Debye-Hückel Equation 6 together with Equation 1. The constants $\overline{C_p}^\circ$ and B' were evaluated by the method of least squares. The method of least squares was also applied using higher terms in molality, but the agreement with experimental data was only slightly better, and hence the simpler two-constant equation was retained.

The term in Equation 6, involving $1 + I^{1/2}$, is frequently written as $1 + AI^{1/2}$; $\sigma I^{1/2}$ is also written $\sigma A I^{1/2}$. The revised equation, with A set equal to 1.5, was tried. The resulting fit of the data was slightly poorer, and hence the form with $A = 1.0$ was retained.

At high concentrations, it has presumably been well established (*5, 7*) that the apparent heat capacity of the salts in many aqueous salt solutions, above the Debye-Hückel range in concentration, is proportional to the square root of concentration. Our data were computer-analyzed for both square root dependence and first-power dependence. Within the accuracy of the data ($\sim$1 part per 1000) either could have been equally well used to fit the data. It was therefore decided to use Equation 6, including the first power as written.

All results were calculated on a Control Data Corp. 3600 computer.

Table I. Constants Used in Modified Debye-Hückel Calculation of Heat Capacities of Sea Water Solutions

T, °C.	A_j	C_p^*	$\overline{C_p}^\circ$	B'
0	7.498	1.00804	−0.76760	0.22811
5	8.136	1.00434	−0.61757	0.16929
10	8.737	1.00194	−0.51709	0.13140
15	9.309	1.00040	−0.44876	0.10679
20	9.862	0.99947	−0.40269	0.09112
25	10.405	0.99893	−0.37021	0.08057
30	10.945	0.99866	−0.34659	0.07305
35	11.492	0.99860	−0.32950	0.06751
40	12.055	0.99869	−0.31662	0.06287
45	12.643	0.99889	−0.30641	0.05844
50	13.264	0.99919	−0.29853	0.05403
55	13.927	0.99959	−0.29301	0.04961
60	14.640	1.00008	−0.28951	0.04501
65	15.414	1.00065	−0.28771	0.04001
70	16.255	1.00132	−0.28842	0.03496
75	17.175	1.00208	−0.29133	0.02966
80	18.180	1.00295	−0.29726	0.02445

RESULTS

Values of the computed constants, $\overline{C_p}^\circ$ and B', are given for every 5° from 0° to 80° C. in Table I.

Figure 1 compares the partial values of sea salts at infinite dilution, $\overline{C_p}^\circ$, with those obtained for sodium chloride by Criss and Cobble (*3*) and Eigen and Wicke (*4*). The results appear compatible.

At 25°, a value of $\overline{C_p}^\circ$, calculated from the tabulated individual ionic values of Criss and Cobble (*3*), gives −0.40 cal. per gram per °C. compared to our value of −0.37. Once again the values are not in serious disagreement. All values in these tables are in defined calories per gram per °C.

Values of the heat capacities of sea salt solutions, of the apparent heat capacities of the salts in sea salt solutions, of the partial heat capacities of water in sea salt solutions, and of the partial heat capacities of sea salts in sea salt solutions are available from the American Documentation Institute.

CONSISTENCY, ACCURACY, AND SIGNIFICANT FIGURES

Random values from these tables have been tested for consistency by use of Equations 1 through 4. The absolute accuracy in the heat capacity, compared to individual experimental values, is about 1 part per 1000. The partial values for water are in general somewhat better than this and the values for the salts somewhat poorer. The figures given have proved useful in calculating the effect of temperature changes on measured or calculated heats or vapor pressure. For such calculations the extra decimal places frequently appear to be significant.

EXAMPLE OF USE OF RESULTS

We have experimentally measured the heat of mixing of sea water with distilled water at 25° and 50° C. Let us calculate the value to be expected at 50° C. from the value measured at 25° C.

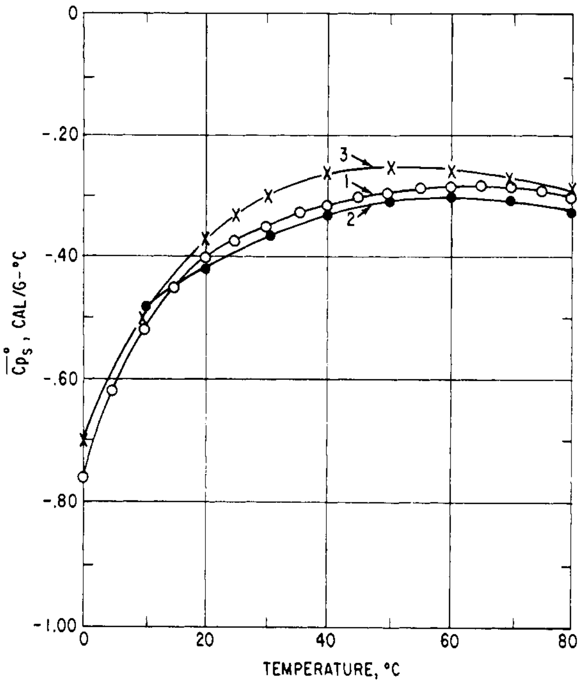

Figure 1. Partial heat capacities of the salts at infinite dilution for sea water and NaCl solutions

1. Sea water solutions, present work
2. NaCl solutions, Eigen and Wicke (*4*)
3. NaCl solutions, Criss and Cobble (*3*)

$\overline{C_p}^\circ$ on unit mass basis

At 25° C., 260 grams of sea water of 3.35% salinity + 4058 grams of distilled water = 4318 grams of dilute solution, with measured value $\Delta H = -5.8 \pm 1$ cal. (this corresponds to a temperature rise of the order of 0.001° C. only).

	Sea Water	Distilled Water	Solution	$\Delta(WC_p)$
C_p at 25° C.	0.95692	0.99893	0.99622	
WC_p at 25° C.	248.80	4053.66	4301.68	−0.78
30° C.				−0.73
35° C.				−0.75
40° C.				−0.75
45° C.				−0.77
50° C.				−0.76
		Weighted average		−0.754

$$\Delta H \text{ predicted at } 50^\circ\text{ C.} = -5.8 + (-0.754 \times 25) = 5.8 - 18.9 = -24.7 \text{ cal.}$$

$$\Delta H \text{ measured at } 50^\circ\text{ C.} = -25.6 \pm 2 \text{ cal.}$$

If the values of C_p for the dilute solution had all been smaller by only 0.00001, the predicted value at 50° C. would have been −25.8 cal. It thus appears that the fourth and possibly the fifth digit after the decimal point are significant for the heat capacities in this case.

NOMENCLATURE

A = Debye-Hückel constant (Table I)
B = extended Debye-Hückel equation constant (5, p. 642)
B' = see Equation 9 and Table I
C_p = heat capacity of solution, cal./g. ° C.
C_p^{*} = heat capacity of pure water
(ϕC_{p_2}) = apparent heat capacity of salts, cal./g. salts ° C.
$\overline{C}_{p_2}$ = partial heat capacity of salts in solution, cal./g. salts ° C.
$\overline{C}_{p_1}$ = partial heat capacity of water in solution, cal./g. water ° C.
$\overline{C}_{p_2}^{\circ}$ = partial heat capacity of salts at infinite dilution
I = ionic strength = $(\sum m_i Z_i^2/2)$
M_i = molecular weight of ion i
$\sum m_i$ = sum of the molality of all ions (and H_3BO_3)
$\sum m_+$ = sum of the molality of + ions
$\sum m_-$ = sum of the molality of − ions
R = gas constant
T = absolute temperature
W = weight of solution, g.
x = salinity in mass fraction
Z_i = charge on ion i
ΔH = heat of mixing, cal.
$(\sigma I^{1/2}/3)$ = $(1/I^{3/2})[1 + I^{1/2} - 1/(1 + I^{1/2}) - 2 \ln(1 + I^{1/2})]$

The following are numerical values for sea salt solutions used in the calculations. They were calculated from the composition of sea water given by Sverdrup (8, Table 35, p. 173).

$$\frac{\sum M_i Z_i^2}{\sum m_i M_i} = 0.03965$$

and

$$\frac{\sum m_i Z_i^2}{\sum m_i} = 1.2457$$

From these, one may calculate an apparent molecular weight for sea water salts (if one to one type):

$$\frac{2\sum m_i M_i}{\sum m_i} = 62.83$$

Although not used in the calculations,

$$\frac{4(\sum m_+)(\sum m_-)}{\sum m_i^2} = 0.998$$

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