and that the true K_1 of H_2CO_3 is

$$K_1 = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 1.7 \times 10^{-4}$$

Since the H_2CO_3 concentration in water is a function of the sparingly soluble CO_2 concentration (0.503 molal), a weaker acid will displace HCO_3^- from its salt at low pH values (by swamping the system with H_3O^+); however, at higher pH values and in the presence of a reserve buffer of CO_2, carbonic acid will displace the acid conjugate of a weaker acid. This effect is further enhanced, in the present investigation, by the ability of CO_2 to deplete further the free amine concentration in the benzene phase by forming carbamates.

NOMENCLATURE

H(DNNS), (DNNS) = Dinonylnaphthalenesulfonic acid and anion
H(ϕSt), (ϕSt) = phenylstearic acid and phenylstearate anion
ϕ—CH_2—NH_2 = benzylamine
(TIAA) = triisoamylamine
ΔG° = standard free energy change
[salt] = molal concentration of methylammonium (DNNS)
$[H_3O^-]$ = aqueous phase hydronium ion activity
K_{eq} = equilibrium constant due to either dissociation or metathesis
K_f = equilibrium constant of formation of salt from its corresponding acid and base
K_a K_b = acid and base dissociation constants
K_1 = first dissociation constant of a multiprotic acid

Subscripts

a = dissolved in aqueous phase
o = dissolved in organic phase
R = dinonylnaphthalene radical
R′ = organic radical bonded to a functional group

LITERATURE CITED

(1) Baker, H.R., Singleterry, C.R., *Ind. Eng. Chem.* **48**, 1190 (1956).
(2) Barrow, G.M., Yearger, E.A., *J. Am. Chem. Soc.* **76**, 5802 (1956).
(3) Everett, D.H., Wynn-Jones, W.F.K., *Proc. Roy. Soc. (London)* **177A**, 499 (1941).
(4) Fritz, J.S., "Acid-Base Titrations in Nonaqueous Solvents," G. Frederick Smith Chemical Co., Columbus, Ohio, 1952.
(5) Herz, W., Stanner, E., *Z. Physik. Chem.* **A128**, 399 (1927).
(6) Kaufman, S., Singleterry, C.R., *J. Colloid Sci.* **10**, 139 (1955).
(7) *Ibid.*, **12**, 465 (1957).
(8) McBain, J.W., Buckingham, R., *J. Chem. Soc.* **1927**, 2679.
(9) McBain, J.W., Eaton, M., *Ibid.*, **1928**, 2166.
(10) Meier, J., Schwartzenbach, G., *Helv. Chim. Acta* **40**, 907 (1957).
(11) Pearson, R.G., Vogelsgang, D.C., *J. Am. Chem. Soc.* **80**, 1038 (1958).
(12) Roughton, F.J.W., *Ibid.*, **63**, 2930 (1941).
(13) Scheiman, M.A., "Review of Monoethanolamine Chemistry," Naval Research Laboratory, Rept. **5746** (June 1, 1962).
(14) Scheuer, P.G., Brownell, R.M., Luvalle, J.E., *J. Phys. Chem.* **62**, 809 (1958).
(15) Singleterry, C.R., Naval Research Laboratory, Washington, D. C., private communication.
(16) Wissburn, K.F., French, D.M., Patterson, A., Jr., *J. Phys. Chem.*, **58**, 693 (1954).

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Relative Enthalpies of Sea Salt Solutions at 25° C.

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Heats of dilution and concentration of sea water have been measured at 25° C. These values have been correlated by use of extended Debye-Hückel theory. Values of the relative, apparent, and partial enthalpies of sea salts and water have been calculated. Although small, these values differ considerably from those for NaCl solutions.

IN most calculations relating to sea water conversion, the heat effects are assumed to be negligible in separating water from sea salt solutions. Sometimes the heat effects are assumed to be the same as those of sodium chloride solutions.

The purpose of this paper is to examine these approximations, to report experimental measurements of the heat effects at 25° C., and to present correlations and tabulated values based on extended Debye-Hückel theory applied to these data.

THEORY

At very dilute concentrations, enthalpies of solutions may be calculated from Debye-Hückel theory, but deviations from this theory may be very large at concentrations above about 0.01 molal. Extended Debye-Hückel theory as presented by Lewis *et al.* (*1*) was modified slightly and used to correlate the data. The sea salts were treated as a single component, as was done for heat capacity (*2*). The standard states of zero enthalpy chosen at 25° C. are pure water and sea salts at infinite dilution. The equations are consistent with those published.

The salt content is related to salinity. Salinity is strictly defined 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." For sea water, it is lower than the total disolved solids by about 4 p.p.t.

All quantities are expressed in defined calories per gram. Total enthalpies are related to the apparent and partial enthalpies as follows:

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

where H is the enthalpy of the solution, ϕL_s is the apparent enthalpy of the salts in solution; $\bar{L}_s$ is the partial enthalpy of the salts in solution; $\bar{L}_w$ is the partial enthalpy of the water in solution; x is approximately the mass fraction of salts in solution—exactly, it is 0.001 times the salinity in parts per thousand (0.01 times the salinity in per cent).

The quantity L_s, which is equal to $\partial H/\partial W_s$, represents the increase in enthalpy of solution per unit mass of salts added at constant composition. For unit mass;

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

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

and;

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

the doubly primed constants are related (for 1 to 1 salts) to those of Lewis *et al.* (*1*) by;

$$\frac{B''}{dB/dT} = \frac{C''}{dC/dT}\;2.303\,RT^2\;\frac{\Sigma m_i}{2\Sigma m_i M_i}\left[\frac{(4\Sigma m_-)(\Sigma m_+)}{(\Sigma m_i)^2}\right] \qquad (5)$$

B'' is also related to B' as used in heat capacity work (*2*);

$$\frac{B''}{dB/dT} = \frac{B'}{(2/T)(dB/dT) + (d^2B/dT^2)} \qquad (6)$$

The B'' and C'' are treated simply as constants to be evaluated from experimental data at any particular temperature, in this case, 25° C.

The exponent on $(\Sigma m_i)/2$ in the last terms involving C'' in Equations 2, 3, and 4 is n rather than 2 as given by Lewis *et al.* (*1*). It is arbitrary what form of series expansion is used to approximate the experimental values and since, as will be shown, the single term with n equal to $3/2$ is better than $n = 2$, this form appears justified.

EXPERIMENTAL

The equipment used in this study was a modification of that used in a previous study on heat capacity of sea water solutions (*3*). The stirred Dewar of about 4 liters' capacity was filled with one solution to be mixed. A rubber balloon was filled with about 250 cc. of the other solution to be mixed. After thermal equilibration had been established and no temperature drift observed (±0.0001° C.) in over 1 hour, the balloon was ruptured and the temperature and temperature change were measured to 10^{-4}° C. with a platinum resistance thermometer. Several precautions were taken to ensure accurate results. The balloons were especially manufactured from latex rubber to be only 1.5 mils thick, yet pin hole free. This was necessary to minimize heat effects. In general, the cooling due to rubber relaxation amounted to 0.0003° C. The Mueller bridge used to measure the temperatures of the platinum resistance thermometer was modified by thermally insulating it following the recommendation of Ross and Dixon (*4*). This reduced electrical noise considerably. Samples were measured by weight and analyzed by titration with silver nitrate. Since all sea water samples were taken from LaJolla, the author assumed that they were representative of typical sea water with the normal distribution of ions (*5*). The author estimated that the measured heat effects are accurate to ±1 cal. About half of this error is from temperature measurement and most of the rest from poor reproducibility of the balloons. For calculation of the constants B'' and C'', the procedure used was a modification of that outlined by Guggenheim and Prue (*6*).

Table I summarizes experimentally measured heats of mixing with calculated values based on the correlation. The value of n was $3/2$; the two constants B'' and C'' were 6.0993 and −2.2359, respectively.

The computer program was written to determine the resulting standard deviation of B'' for the value of C'' (the best value) chosen by the computer. The resulting standard deviation was ±0.0367 (Figure 1). Values of the standard

Table I. Experimental and Correlated Heats of Mixing of Sea Water Solutions at 25° C.

Salinity Balloon, ‰	Weight in Balloon, Grams	Salinity in Dewar, %	Weight in Dewar, Grams	Measured Heat, Calories	Correlated Heat, Calories
3.34	271.5	0.0	3989.2	−5.39	−5.84
3.34	269.8	0.212	3980.7	0.39	0.31
3.34	293.8	0.411	4002.2	1.86	2.52
3.34	280.4	0.611	4007.1	3.48	3.23
3.34	271.0	0.790	3967.7	2.46	3.36
3.34	292.0	1.112	4017.0	2.85	3.43
3.34	273.4	1.385	4011.2	1.93	2.77
3.34	294.3	1.511	4033.5	1.94	2.70
3.34	245.5	0.0	4002.7	−6.20	−5.69
3.34	251.2	0.193	4005.5	0.87	−0.09
3.34	256.0	0.0	3989.0	−5.87	−5.75
3.34	261.0	0.200	4016.3	0.91	0.07
3.34	275.6	0.387	4016.3	2.48	2.17
3.34	285.0	0.571	4027.9	3.27	3.17
3.34	279.0	0.752	4022.6	3.26	3.44
3.34	270.6	0.918	4032.1	4.25	3.36
3.34	277.2	1.067	4000.1	3.22	3.32
3.34	283.6	1.211	4014.5	3.13	3.19
3.34	283.2	1.365	4027.5	2.18	2.90
3.34	264.0	1.497	4018.1	2.55	2.46
0.30	253.0	0.0	4098.7	−1.45	−0.86
1.03	301.0	0.0	4009.5	−4.38	−3.94
10.02	262.0	0.0	4014.0	52.74	53.59
6.59	250.1	0.0	4126.5	12.85	10.75
2.39	240.0	0.0	4024.4	−6.63	−6.06
5.48	260.0	0.0	4037.0	3.24	3.09
10.62	268.0	0.0	4047.3	67.80	64.41
10.12	171.5	3.360	4142.3	25.48	26.77
0	272.2	9.980	4079.0	84.03	81.61
7.52	281.2	0.0	4055.5	23.08	23.24
10.75	242.5	3.360	4127.6	40.38	43.98
3.36	235.0	10.038	3994.3	31.66	31.59
0	277.6	3.340	4112.6	7.57	6.75

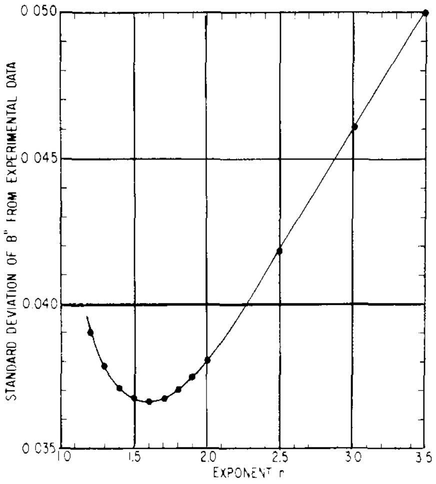

Figure 1. Standard deviation of B'' as a function of the exponent n

Table II. Sea Salt Solutions—Selected Values of Relative Enthalpies at 25° C. in Cal. per Gram

Sea Salt Concentration, %	Apparent ϕL_s of Sea Salts	Partial $\bar{L}_s$ of Sea Salts	Partial $\bar{L}_w$ of Water	Enthalpy H of Solution
0	0	0	0	0
0.001	0.126	0.187	0.0000	0.0000
0.002	0.177	0.262	0.0000	0.0000
0.003	0.215	0.319	0.0000	0.0000
0.004	0.247	0.366	0.0000	0.0000
0.005	0.275	0.407	0.0000	0.0000
0.01	0.38	0.56	0.0000	0.0000
0.02	0.53	0.77	−0.0000	0.0001
0.03	0.63	0.92	−0.0001	0.0002
0.04	0.72	1.04	−0.0001	0.0003
0.05	0.80	1.14	−0.0002	0.0004
0.1	1.07	1.50	−0.0004	0.0011
0.2	1.39	1.90	−0.0010	0.0028
0.3	1.61	2.14	−0.0016	0.0048
0.4	1.76	2.29	−0.0021	0.0070
0.5	1.89	2.40	−0.0026	0.0094
1	2.20	2.54	−0.0035	0.022
2	2.30	2.17	+0.0026	0.046
3	2.15	1.53	0.019	0.064
4	1.90	0.82	0.045	0.076
5	1.60	0.10	0.079	0.080
6	1.27	−0.59	0.119	0.076
7	0.94	−1.25	0.165	0.066
8	0.60	−1.86	0.214	0.048
9	0.27	−2.41	0.265	0.024
10	−0.05	−2.91	0.317	−0.005
11	−0.36	−3.3	0.37	−0.040
12	−0.66	−3.7	0.41	−0.079

deviation of B'' were also calculated using values for n ranging from 1.2 to 3.5.

Figure 1 is a plot of the standard deviation of B'' against the assumed exponent n. The minimum is not far from $n = 1.5$, hence, $N = 3/2$ was arbitrarily chosen. Although the deviation was higher with $n = 2$, the latter would still probably adequately represent the experimental data.

Table II summarized calculated values for the apparent, partial, and total enthalpies at 25°C. with $n = 3/2$. The values calculated with $n = 2.0$ in general do not differ by more than 1 in the next to the last digit given except at the highest concentration.

The apparent and partial enthalpies for the sea salts are below 4 cal. per gram of salt, but may be positive or negative depending on the concentration. The relative partial enthalpies of the water in these solutions is less than 0.5 cal. per gram.

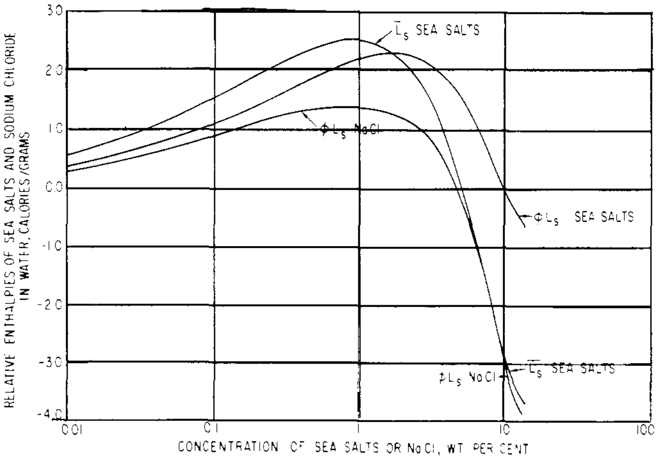

Figure 2. Relative apparent enthalpies of sea salts and NaCl solutions

Relative partial enthalpies of sea salt solutions

The relative enthalpies of the sea salt solutions, compared with pure water and salt at infinite dilution, in no case differ from zero by more than 0.08 cal. per gram of salt up to 12% salinity.

The heat effect in producing triply concentrated brine from 3.5% sea water would be calculated to be at 25° C.

1 kg. of sea water → 0.33 kg. of brine + 0.67 kg. of pure water
3.5% salt 10.5%

$\Delta H = -78$ cal./kg. of sea water

which would produce a temperature rise of less than 0.1° C. Hence, the usual engineering approximation that heat effects are negligible is justified even though it is not exact.

COMPARISON TO NaCl SOLUTIONS

Sea salts are frequently compared with sodium chloride solutions. The relative apparent enthalpies of NaCl in aqueous solutions at 25° are computed from the values given by Wagman *et al.* (7) and are plotted for comparison in Figure 2. Except that all values are small, NaCl values are not very similar to those for sea salts. The values for sea salts of ϕL_s become over 60% larger (positive) than those for NaCl. At infinite dilution the ratio is;

$$\operatorname{Lim}\left(\frac{\phi L_{s\,\text{sea salts}}}{\phi L_{s\,\text{NaCl}}}\right)_{x \to 0} = 1.16$$

as calculated from Debye-Hückel theory. This appears to be compatible with the experimental data.

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NOMENCLATURE

A_H = Debye-Hückel constant for enthalpy
B, B', B'' = constant

C, C'' = constant
H = enthalpy of the solution; cal. per gram of solution
I = ionic strength = $\Sigma(m_i z_i^2)/2$
$\bar{L}_s$ = partial enthalpy of salts in solution; cal. per gram of salt
$\bar{L}_w$ = partial enthalpy of water in solution; cal. per gram of water
m_i = molality of ion i
m_+ = molality of positive ion
m_- = molality of negative ion
M_i = molecular weight of i
n = exponent in Equations 2, 3, and 4
R = gas constant
T = absolute temperature
W_s = mass of salt
x = mass fraction of salts in solution; (more exactly 0.001 times salinity in parts per thousand) the term % salinity is 100 times x
Z_i = charge on ion i

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

ϕL_s = apparent relative enthalpy of the salts in solution; cal. per gram of salt

LITERATURE CITED

(1) Lewis, G.N., Randall, M., Pitzer, K.S., Brewer, L., "Thermodynamics," 2nd ed., McGraw-Hill, New York, 1961.
(2) Bromley, L.A., J. CHEM. ENG. DATA 13, 60 (1968).
(3) Bromley, L.A., deSaussure, V.A., Clipp, J.C., Wright, J.S., *Ibid.*, **12**, 202-6 (1967).
(4) Ross, G.S., Dixon, H.D., *J. Res. Natl. Bur. Std.* **64**, 271 (1960).
(5) Sverdrup, H.V., Johnson, M.W., Fleming, R.H., "The Oceans," p. 173, Prentice Hall, Englewood Cliffs, N.J., 1942.
(6) Guggenheim, E.A., Prue, J.E., *Trans. Faraday Soc.* **50**, 710 (1954).
(7) Wagman, D.D., Evans, W.H., Levine, S., Jaffey, I., *Natl. Bur. Std. (U.S.) Circ.* **500** (1952).

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Heat Capacities of 90% Hydrogen Peroxide and Commercial Anhydrous Hydrazine

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Heat capacities of commercial 90% by weight hydrogen peroxide solution and commercial anhydrous hydrazine (97% by weight) were measured by means of heat balances on a small tube-in-tube exchanger at temperatures to 191° C. Data in the range from ambient to 200° C. are represented by a set of linear relations. The accuracy of these heat capacity data is estimated to be better than ±2%.

HIGH STRENGTH hydrogen peroxide and "anhydrous" hydrazine have become popular rocket propellants and have served both as an oxidizer and fuel, respectively, and as monopropellants. Both materials have become important items of commerce because of their high activity as an oxidizing and reducing agent, respectively. In both instances, applications require detailed knowledge of various physical and thermodynamic properties.

Both materials are thermodynamically unstable with respect to one or more decomposition reactions. The kinetics of decomposition lead to only modest rates at low temperatures. However, rates are finite and lead to measurable heat release with increasing temperatures. This research was undertaken in an effort to measure the heat capacities of 90% hydrogen peroxide and common "anhydrous" hydrazine (about 97% by weight).

The primary objective was to measure the properties of the fluids in a defined chemical state. Since equilibrium constants are very large, only such data are meaningful and offer any possibility of reproducibility. Conventional static experiments were erratic and involved large corrections owing to chemical reactions. Consequently, measurements were undertaken in a flow system involving accurate heat balances around a small tube-in-tube heat exchanger. Small corrections owing to homo- and heterogeneous decomposition were required. These corrections were substantially smaller, by as much as an order of magnitude, than corrections for a conventional calorimeter experiment. Finally, the choice of a particular concentration for hydrogen peroxide was dictated by the degree of interest in various high strength solutions offered by several commercial sources.

PROCEDURE

A flow bench was constructed of seamless Type 321 stainless steel tubing, thoroughly cleaned and passivated to assure compatibility with the test fluid. Water, heated electrically, was used to heat the test fluid in a simple tube-in-tube exchanger. This technique was used to limit the temperature of surfaces in contact with the test fluids. Temperature control was provided by regulating power to the water heater by means of a variable autotransformer. A pressure relief device on the water heater was set to operate at 600 p.s.i.g., corresponding to a water temperature of 252° C. Water flow to the test fluid heater would terminate if this condition were reached. Figure 1 is a schematic diagram of the apparatus.

Heat exchangers and flow paths were designed to reclaim as much heat from the exit streams as possible to minimize heater capacity and power consumption. Cold inlet water, at a pressure of about 500 p.s.i.g., was preheated by heat exchange with the test fluid after it had passed through

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