Heat Capacities and Enthalpies of Sea Salt Solutions to 200° C.

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A pressure calorimeter has been designed, constructed, and used to measure the heat capacity of sea salt solutions from 80° to 200° C. and up to 12% salinity. C_p values calculated from experimental measurements are correlated by the use of extended Debye-Hückel theory. Heat capacity values at saturation, C_{sat}, and partial and apparent values for sea salts and water are included. The heat capacities, C_{sat} and C_p, are in general considered accurate to ± 0.001 cal. per gram per ° C. with a maximum error of ± 0.003. Values are smoothed to include previously measured heat capacities between 0° and 80° C. All values are in defined calories = 4.1840 absolute joules per gram per ° C. Enthalpies are given in calories per gram, referred to pure water and salts at infinite dilution as zero at 0° C.

IN THE DESIGN or evaluation of sea water conversion equipment it is necessary to calculate energy requirements. This can be done accurately only with a knowledge of the heat capacity of sea water solutions. Bromley *et al.* (*2*, *4*) have published values to 80° C. as measured in an atmospheric pressure calorimeter. These data agreed with the data of Cox and Smith (*5*). Jamieson *et al.* (*6*) recently measured values for a synthetic sea water with 1% accuracy to 180° C. and 15% salt concentration.

As a guide, for measurement of heat capacity above 80° C. many of the techniques employed were those used by Osborne *et al.* (*10*) in the measurement of the heat capacity of water.

Sea water solutions are rather corrosive and contain many ions, including bicarbonate. For this reason, and also because of the availability of new materials, a new calorimeter was designed. From the measured heat capacities the partial and apparent values as well as enthalpies were calculated.

CALORIMETER

Figure 1 shows the pressure calorimeter and containment vessel. The samples were contained in a hemispherically domed "bomb" of about 1400-cc. capacity placed inside a vacuum chamber whose temperature was controlled. Figure 2 is a diagram of the calorimeter. The details of this calorimeter and results obtained have been recorded by Wilkins (*13*).

The sample chamber was built of beryllium copper (alloy Berylco 10) appropriately heat-treated to give it high strength. This alloy was chosen, not only because of its high strength, but also because of its excellent thermal conductivity.

The vessel lid (bottom flange) was of brass for runs to 140° C. and of beryllium copper for high-temperature runs. It was sealed with an ethylene-propylene O-ring. A new ring was used for each high-temperature run. A Teflon-coated V seal was found to be satisfactory only when the surfaces were carefully machined. The vessel was designed with a safety factor of 3 and hydraulically tested to 500 p.s.i.

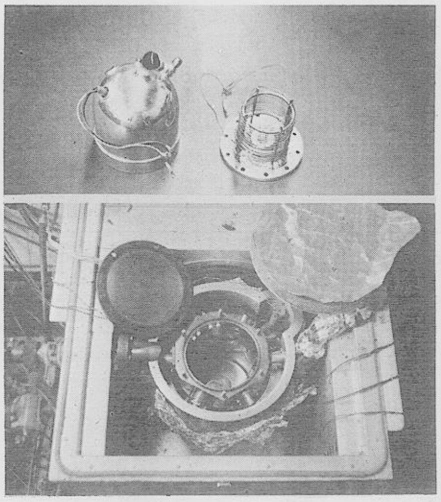

Figure 1. Pressure calorimeter (upper) and containment vessel (lower)

Gold plating was used outside the vessel to minimize radiant heat exchange with the surrounding vessel which was also gold-plated. The interior plate was an approximately 0.002-inch layer of 24-carat gold deposited from a bath, free of organic material, over a layer of nickel previously deposited on the beryllium copper. It was somewhat dull in appearance and has been tested in boiling 8*N* HNO_3. The exterior plate was bright.

During all measurements, the space between the sample chamber and surrounding vessel was evacuated to below 10^{-4} torr through a cold trap by means of an oil diffusion pump. The vacuum was used to minimize conduction and convection. The sample chamber was supported on three pointed stainless steel pins to reduce conduction heat transfer further.

The surrounding vessel, which had annular cavities within it, was kept at constant temperature by a bath held to ±0.01° C. by means of a Hallikainen Thermotrol unit. This vessel was in turn placed in a constant-temperature air-thermostated oven maintained to ±1° C.

The main heater located within the sample chamber was Nichrome-V wire of about 110-ohm resistance contained

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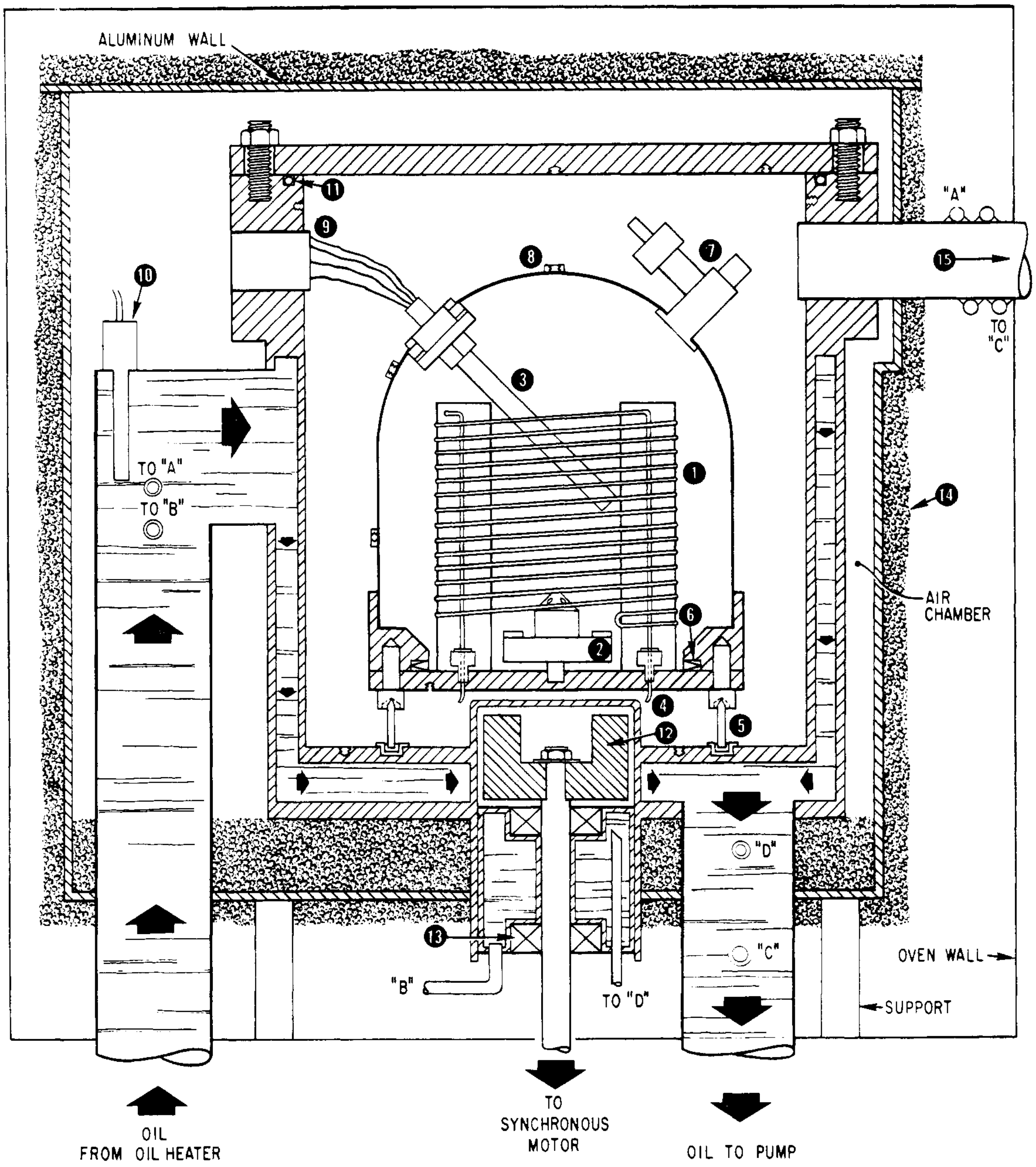

Figure 2. Pressure calorimeter assembly

1. Heater
2. Stirrer
3. Resistance thermometer
4. Heater lead
5. Chamber support

6, 11. O-rings
7. Valve
8. Thermocouple boss (typical)
9. Electrical receptacle
10. Bath resistance thermometer

12. Stirrer drive magnet
13. Ball bearing (typical)
14. Insulation
15. To vacuum diffusion pump

in an Inconel-w tube, but electrically insulated from it by compacted magnesium oxide insulation, helically wound on gold-plated copper bar supports. Other heaters which proved unsatisfactory included one of anodized aluminum, glass fiber-insulated wire in a copper tube, Teflon-insulated wire, and several other variations of these.

The energy input to the sample chamber was from a 60-cycle, 110-volt constant-voltage source. It was measured with a calibrated Sangamo rotating standard, J-5. Its absolute accuracy was ±0.17%, although its reproducibility, which is more important, was ±0.02%. This easily satisfied the desired accuracy and was simpler to use than the usual d.c. system employing accurate measurement of voltage and amperage as functions of time.

The stirrer consisted of a slave magnet in a gold-plated Monel can, supported vertically on a pointed shaft and aligned radially by a Teflon sleeve. The master magnet was driven by a synchronous motor at 300 r.p.m. The heat of stirring alone would cause about 0.1° C. per hour rise if the bomb were perfectly insulated.

Bomb temperature measurements were made using a platinum resistance thermometer calibrated by the National Bureau of Standards. A Leeds & Northrup Mueller bridge, sensitive null detector, and recorder were used to detect temperature changes to ±0.0002° C.

Most other temperatures were measured with iron-constantan thermocouples using a Leeds & Northrup K-5 potentiometer. A few temperatures were displayed directly on the console by means of indicating thermometers accurate to about 1° C.

PROCEDURE

The sea water used for all measurements was taken from the end of the pier at Scripps Institution of Oceanography, La Jolla, Calif., about midway between the free surface and the sand. It was filtered and acidified with concentrated H_2SO_4 to pH 4 as previously described (*4*). The amount of concentrated H_2SO_4 required was about 120 p.p.m.

For concentrations other than that of normal (La Jolla) sea water (about 3.34%), water was carefully removed by evaporation, or distilled water was added.

All samples were analyzed for chloride by titration with silver nitrate, using the Knudsen (*11*) method. The normal distribution of ions (*12*) was assumed. The sea salt content was finally expressed as per cent salinity—i.e., parts per hundred as opposed to parts per thousand, 0/00, as used in oceanography. This is approximately the percentage of total dissolved solids (1% salinity = 1.0046% total dissolved solids).

After weighing, filling, and reweighing the sample chamber, leaving space for expansion, the assembly was inverted and evacuated to remove air and carbon dioxide. The chamber was again weighed to 0.2 gram and the necessary air-buoyancy correction was made.

The entire calorimeter was assembled, and the vacuum chamber evacuated and heated to the desired temperature. A small linear increase in temperature with time was observed and allowed to stabilize.

A predetermined amount of heat (about 3000 cal.) was added in 2 minutes.

Temperatures were observed until the drift was again linear downward. A theoretical analysis is performed on the data to evaluate the hypothetical, instantaneous temperature rise, and, from it, the heat capacity at saturation.

THEORY

The procedure used to evaluate the hypothetical zero time and the temperature rise at that time is the same as that used previously (*4*).

The present calorimeter is essentially one of constant volume in which evaporation (or condensation) is expected to occur as the temperature rises. The procedure used is essentially that due to Osborne (*9*) and corrects for the heat of vaporization and the expansion of liquid water. The heat, δQ, required to raise the calorimeter and its contents an amount dT is given by

$$\delta Q = dH - VdP \tag{1}$$

If this is applied separately to the calorimeter and its contents and the results are added, one obtains

$$\delta Q = KdT + MC_{\text{sat}}dT + d\,\frac{(V - Mu)\,(h' - h)}{(u' - u)} - (V - Mu)dP \tag{2}$$

Since all quantities are known or can be estimated with reasonable accuracy, the values of C_{sat}, the heat capacity at thermal saturation for the liquid may be calculated. For these experiments the order of magnitude of the various quantities is

δQ = about 3000 cal.
K = about 300 cal./° C.
M = about 1200 grams
V = about 1400 cc.

The sum of the last two terms in Equation 2 which represents the evaporation (or condensation) correction and, hence, may be positive or negative has not been over 3 cal. per ° C.

Table I. Experimental Heat Capacities at Saturation, C_{sat}, from 80° to 200°C.

(Calories per gram degree centigrade. Salinities, *S*, in per cent)

	S							
T	1.02	2.00	3.34	5.00	6.75	8.50	10.24	12.00
80	0.9902	0.9781	0.9637	0.9444	0.9264	0.9095	0.8928	0.8760
	0.9906	0.9785	0.9642	0.9451	0.9266	0.9093	0.8925	0.8761
90	0.9923	0.9803	0.9658	0.9463	0.9280	0.9110	0.8936	0.8776
	0.9922	0.9811	0.9651	0.9466	0.9279	0.9106	0.8937	0.8774
100	0.9947	0.9832	0.9680	0.9477	0.9302	0.9124	0.8950	0.8792
	0.9948	0.9829	0.9678	0.9481	0.9303	0.9120	0.8953	0.8785
110	0.9979	0.9856	0.9703	0.9508	0.9321	0.9142	0.8969	0.8804
	0.9981	0.9858	0.9706	0.9501	0.9322	0.9134	0.8964	0.8804
120	1.0013	0.9886	0.9735	0.9528	0.9346	0.9162	0.8991	0.8823
	1.0011	0.9892	0.9736	0.9529	0.9342	0.9160	0.8982	0.8813
130	1.0044	0.9921	0.9767	0.9559	0.9367	0.9189	0.9004	0.8837
	1.0049	0.9926	0.9772	0.9562	0.9370	0.9182	0.9002	0.8834
140	1.0090	0.9969	0.9802	0.9597	0.9395	0.9212	0.9026	0.8854
	1.0092	0.9967	0.9812	0.9594	0.9399	0.9206	0.9023	0.8857
150	1.0137	1.0004	0.9830	0.9629	0.9430	0.9237	0.9048	0.8870
	1.0137	1.0008	0.9828	0.9632	0.9429	0.9242	0.9055	0.8866
160	1.0204	1.0052	0.9878	0.9673	0.9464	0.9272	0.9075	0.8893
	1.0200	1.0059	0.9874	0.9674	0.9468	0.9284	0.9076	0.8899
170	1.0263	1.0123	0.9932	0.9724	0.9509	0.9313	0.9108	0.8921
	1.0268	1.0115	0.9930	0.9721	0.9515	0.9308	0.9114	0.8931
180	1.0334	1.0194	0.9994	0.9781	0.9563	0.9347	0.9157	0.8959
	1.0338	1.0196	0.9998	0.9778	0.9563	0.9357	0.9153	0.8966
190	1.0421	1.0268	1.0063	0.9846	0.9617	0.9404	0.9202	0.9005
	1.0418	1.0268	1.0073	0.9850	0.9622	0.9404	0.9204	0.9006
200	1.0520	1.0359	1.0160	1.9919	0.9686	0.9454	0.9252	0.9055
	1.0513	1.0359	1.0154	0.9917	0.9689	0.9468	0.9251	0.9057

From the values of C_{sat} the values of the heat capacity at constant pressure may be calculated directly as

$$C_p = C_{\text{sat}} + T\left(\frac{\partial u}{\partial T}\right) P \left(\frac{\partial P}{\partial T}\right)_{\text{sat}} \tag{3}$$

Extended Debye-Hückel theory as used by Bromley (2) was used to correlate these data. Apparent and partial heat capacity are related to heat capacity at constant pressure, all per unit mass, as follows:

$$C_p = C^*_{p_w}\ (1-x) + x(\phi C_{p_s}) = \overline{C_{p_w}}\ (1-x) + x\overline{C_{p_s}} \tag{4}$$

For x, the salinity in mass fraction is used. By extended Debye-Hückel theory

$$(\phi C_{p_s}) = \overline{C_{p_s}}^{\circ} + \frac{A_j}{2}\left(\frac{\Sigma m_i Z_i^2}{\Sigma m_i M_i}\right) I^{1/2}\left(\frac{1}{1+I^{1/2}} - \frac{\sigma I^{1/2}}{3}\right) - B'\ \frac{\Sigma m_i}{2} + \cdots \tag{5}$$

and similar equations may be written for the partial quantities (2).

$$\overline{C_{p_w}} = C^*_{p_w} - \frac{A_j}{2}\left(\frac{\sigma I^{1/2}}{3}\right)\left(\frac{2I^{3/2}}{1000}\right) + \frac{B'}{1000}\left(\frac{2\Sigma m_i M_i}{\Sigma m_i}\right)\left(\frac{\Sigma m_i}{2}\right)^2 + \cdots \tag{6}$$

$$\overline{C_{p_s}} = \overline{C_{p_s}}^{\circ} + \frac{A_j}{2}\left(\frac{\Sigma m_i Z_i^2}{\Sigma m_i M_i}\right)\ \frac{I^{1/2}}{1+I^{1/2}} - 2B'\ \frac{\Sigma m_i}{2} + \cdots \tag{7}$$

$$B' = 2.303\ RT^2\left(\frac{\Sigma m_i}{2\Sigma m_i M_i}\right)\left[\frac{4(\Sigma m_-)(\Sigma m_-)}{\Sigma m_i^{\ 2}}\right]\left(\frac{2\,dB}{T\,dT} + \frac{d^2B}{dT^2}\right) \tag{8}$$

DATA AND ERRORS

Experimental data for C_{sat} are given in Table I. Two values (those considered the most reliable) are given at each temperature and salinity listed.

A careful error analysis has been made and indicates the following for any single measured value of C_{sat} at 140° F. and 6% salinity:

Maximum Error in C_{sat}

Distilled water value for C_{sat}	0.0005 cal./g. ° C.
Temperature rise	0.0007
Heat input	0.0005
Mass of solution	0.0003
Salinity	0.00004
Absolute temperature	0.00003
Other systematic errors	0.0001
Maximum probable error	0.0022

Table II. Heat Capacity of Sea Salt Solutions
(Defined calories per gram degree centigrade)

Temp., ° C.	Salinity, % 0	1	2	3	4	5	6	7	8	9	10	11	12
							At Constant Pressure						
0	1.0080	0.9911	0.9752	0.9601	0.9458	0.9323	0.9198	0.9081	0.8973	0.8874	0.8785	0.8706	0.8637
10	1.0019	0.9872	0.9731	0.9596	0.9467	0.9343	0.9225	0.9112	0.9006	0.8905	0.8810	0.8722	0.8640
20	0.9995	0.9860	0.9731	0.9606	0.9486	0.9369	0.9257	0.9148	0.9044	0.8944	0.8848	0.8757	0.8670
30	0.9987	0.9859	0.9737	0.9618	0.9503	0.9391	0.9282	0.9176	0.9074	0.8974	0.8879	0.8786	0.8697
40	0.9987	0.9863	0.9744	0.9629	0.9516	0.9406	0.9300	0.9195	0.9094	0.8995	0.8899	0.8806	0.8716
50	0.9992	0.9869	0.9752	0.9638	0.9527	0.9419	0.9313	0.9209	0.9108	0.9009	0.8913	0.8820	0.8729
60	1.0001	0.9879	0.9762	0.9648	0.9538	0.9430	0.9324	0.9221	0.9120	0.9021	0.8925	0.8831	0.8739
70	1.0013	0.9891	0.9774	0.9660	0.9550	0.9442	0.9336	0.9233	0.9132	0.9033	0.8936	0.8842	0.8750
80	1.0030	0.9907	0.9789	0.9676	0.9565	0.9456	0.9351	0.9247	0.9146	0.9047	0.8950	0.8855	0.8762
90	1.0051	0.9926	0.9808	0.9694	0.9582	0.9474	0.9367	0.9263	0.9162	0.9062	0.8964	0.8869	0.8776
100	1.0076	0.9950	0.9831	0.9715	0.9603	0.9494	0.9387	0.9282	0.9179	0.9079	0.8981	0.8885	0.8791
110	1.0107	0.9979	0.9858	0.9741	0.9628	0.9517	0.9408	0.9303	0.9199	0.9098	0.8998	0.8901	0.8806
120	1.0145	1.0014	0.9890	0.9771	0.9656	0.9543	0.9433	0.9326	0.9220	0.9117	0.9017	0.8918	0.8821
130	1.0189	1.0054	0.9928	0.9806	0.9688	0.9573	0.9461	0.9351	0.9244	0.9139	0.9036	0.8935	0.8837
140	1.0240	1.0101	0.9971	0.9846	0.9725	0.9607	0.9492	0.9380	0.9270	0.9163	0.9057	0.8954	0.8853
150	1.0300	1.0155	1.0021	0.9893	0.9768	0.9647	0.9529	0.9414	0.9301	0.9191	0.9083	0.8977	0.8873
160	1.0368	1.0218	1.0079	0.9947	0.9818	0.9694	0.9572	0.9454	0.9338	0.9225	0.9114	0.9005	0.8899
170	1.0446	1.0290	1.0146	1.0009	0.9876	0.9748	0.9623	0.9502	0.9383	0.9267	0.9153	0.9042	0.8933
180	1.0535	1.0372	1.0222	1.0081	0.9944	0.9812	0.9684	0.9559	0.9437	0.9318	0.9202	0.9088	0.8977
190	1.0635	1.0464	1.0309	1.0162	1.0022	0.9886	0.9754	0.9626	0.9501	0.9380	0.9261	0.9145	0.9032
200	1.0747	1.0567	1.0406	1.0254	1.0108	0.9969	0.9833	0.9702	0.9575	0.9450	0.9329	0.9211	0.9096
							At Thermal Saturation						
0	1.0080	0.9911	0.9752	0.9601	0.9458	0.9323	0.9198	0.9081	0.8973	0.8874	0.8785	0.8706	0.8637
10	1.0019	0.9872	0.9731	0.9596	0.9467	0.9343	0.9225	0.9112	0.9006	0.8905	0.8810	0.8722	0.8640
20	0.9995	0.9860	0.9731	0.9606	0.9486	0.9369	0.9257	0.9148	0.9044	0.8944	0.8848	0.8757	0.8670
30	0.9987	0.9859	0.9737	0.9618	0.9503	0.9391	0.9282	0.9176	0.9074	0.8974	0.8879	0.8786	0.8697
40	0.9987	0.9863	0.9744	0.9629	0.9516	0.9406	0.9300	0.9195	0.9094	0.8995	0.8899	0.8806	0.8716
50	0.9992	0.9869	0.9752	0.9638	0.9527	0.9419	0.9313	0.9209	0.9108	0.9009	0.8913	0.8820	0.8729
60	1.0000	0.9878	0.9761	0.9648	0.9537	0.9429	0.9324	0.9220	0.9119	0.9021	0.8924	0.8830	0.8739
70	1.0012	0.9890	0.9773	0.9660	0.9549	0.9441	0.9336	0.9232	0.9131	0.9032	0.8936	0.8841	0.8749
80	1.0029	0.9906	0.9788	0.9675	0.9564	0.9455	0.9350	0.9246	0.9145	0.9046	0.8949	0.8854	0.8761
90	1.0049	0.9925	0.9807	0.9693	0.9581	0.9473	0.9366	0.9262	0.9161	0.9061	0.8963	0.8868	0.8775
100	1.0074	0.9948	0.9829	0.9713	0.9601	0.9492	0.9385	0.9280	0.9177	0.9077	0.8979	0.8883	0.8789
110	1.0104	0.9976	0.9855	0.9738	0.9625	0.9514	0.9405	0.9300	0.9196	0.9095	0.8995	0.8898	0.8803
120	1.0139	1.0009	0.9885	0.9766	0.9651	0.9539	0.9429	0.9322	0.9216	0.9113	0.9013	0.8914	0.8817
130	1.0181	1.0047	0.9921	0.9799	0.9681	0.9567	0.9455	0.9345	0.9238	0.9133	0.9030	0.8930	0.8832
140	1.0230	1.0091	0.9961	0.9837	0.9716	0.9599	0.9484	0.9372	0.9262	0.9156	0.9050	0.8947	0.8846
150	1.0285	1.0142	1.0008	0.9881	0.9756	0.9635	0.9517	0.9403	0.9290	0.9181	0.9073	0.8968	0.8864
160	1.0349	1.0200	1.0061	0.9929	0.9801	0.9677	0.9556	0.9439	0.9324	0.9211	0.9101	0.8993	0.8887
170	1.0420	1.0265	1.0122	0.9986	0.9853	0.9726	0.9602	0.9482	0.9364	0.9249	0.9135	0.9025	0.8917
180	1.0500	1.0339	1.0190	1.0050	0.9914	0.9783	0.9656	0.9532	0.9412	0.9294	0.9179	0.9066	0.8956
190	1.0590	1.0420	1.0267	1.0122	0.9983	0.9848	0.9718	0.9592	0.9468	0.9348	0.9231	0.9116	0.9004
200	1.0689	1.0511	1.0352	1.0202	1.0058	0.9921	0.9787	0.9658	0.9533	0.9410	0.9290	0.9174	0.9060

A similar value for the highest temperature, 200° C., and maximum salinity, 12%, is 0.003.

RESULTS

From each value of C_{sat} measured, a value for C_p was calculated and in turn correlated by extended Debye-Hückel theory. The resulting smoothed C_p values are presented in Table II. The smoothed saturation heat capacity values, C_{sat}, also shown in Table II, were calculated from C_p values.

Table III. Constants used in Modified Debye-Hückel Calculation of Heat Capacities of Sea Water Solutions

Temp., °C.	$\overline{C_{p_s}}^\circ$	B'	A_j	$C^*_{p_w}$
0	−0.7519547	0.2207251	7.859	1.00804
5	−0.6286866	0.1730745	8.131	1.00434
10	−0.5326990	0.1384558	8.496	1.00194
15	−0.4591725	0.1131234	8.943	1.00040
20	−0.4039477	0.09444761	9.460	0.99947
25	−0.3634661	0.08057092	10.036	0.99893
30	−0.3347135	0.07017338	10.664	0.99866
35	−0.3151657	0.06231164	11.334	0.99860
40	−0.3027379	0.05630773	12.040	0.99869
45	−0.2957356	0.05167180	12.777	0.99889
50	−0.2928088	0.04804805	13.540	0.99919
55	−0.2929087	0.04517675	14.324	0.99959
60	−0.2952471	0.04286738	15.127	1.00008
65	−0.2992585	0.04097953	15.948	1.00065
70	−0.3045645	0.03940921	16.786	1.00132
75	−0.3109415	0.03807911	17.642	1.00208
80	−0.3182903	0.03693145	18.517	1.00299
90	−0.3359688	0.03502087	20.336	1.00506
100	−0.3583266	0.03344351	22.279	1.00762
110	−0.3866099	0.03206476	24.395	1.01074
120	−0.4220917	0.03080604	26.754	1.01448
130	−0.4657488	0.02962081	29.441	1.01888
140	−0.5181096	0.02848113	32.557	1.02403
150	−0.5792712	0.02737002	36.221	1.02998
160	−0.6490865	0.02627704	40.570	1.03683
170	−0.7275219	0.02519567	45.756	1.04463
180	−0.8151843	0.02412183	51.951	1.05349
190	−0.9140188	0.02305290	59.340	1.06347
200	−1.1028176	0.02198723	68.127	1.07467

The values from 0° to 80° C. previously reported (*4*) were included in the smoothing process.

In correlating the values, a power series in molality was used as suggested by Lewis *et al.* (*7*); however, as was found for the data below 80° C. (*2*), only the two constants $\overline{C_{p_s}}^\circ$ and B' were found to be necessary. The standard deviation was not reduced significantly as more constants were added.

Figure 3 is a graph of the partial heat capacity of the sea salts at infinite dilution, $\overline{C_{p_s}}^\circ$, as a function of temperature. The previously obtained curve to 80° C. (*2*) is included for comparison.

Table III is a set of tabular values of $\overline{C_{p_s}}^\circ$, B', A_j, and $C^*_{p_w}$.

The values for A_j, $\overline{C_{p_s}}^\circ$, and B' were calculated from Equations 9, 10, and 11, respectively.

$$A_j = 7.858661 + 0.04424799t + (0.2129136 \times 10^{-2})t^2 - (0.1837382 \times 10^{-4})t^3 + (0.7077757 \times 10^{-7})t^4 \quad (9)$$

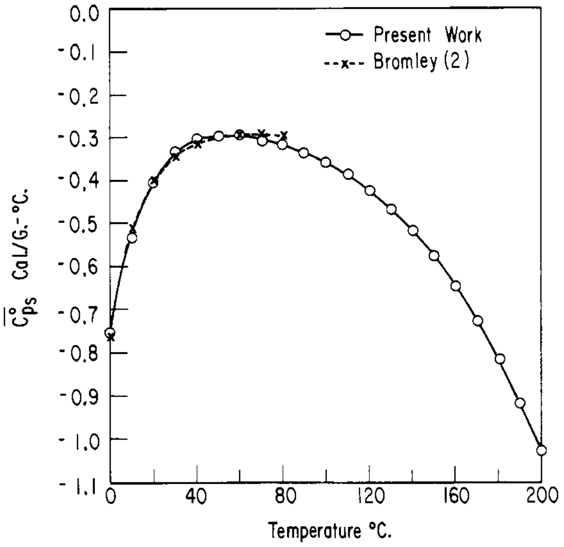

Figure 3. Partial heat capacities of sea salts at infinite dilution for sea water solutions

Table IV. Apparent Heat Capacity of Salts in Sea Salt Solutions

(Defined calories per gram degree centigrade)

Temp., °C.	Salinity, Wt. % 0	1	2	3	4	5	6	7	8	9	10	11	12
0	−0.752	−0.682	−0.635	−0.592	−0.549	−0.506	−0.463	−0.420	−0.376	−0.332	−0.287	−0.241	−0.195
10	−0.533	−0.473	−0.439	−0.409	−0.379	−0.351	−0.322	−0.294	−0.265	−0.236	−0.207	−0.178	−0.148
20	−0.404	−0.347	−0.319	−0.295	−0.273	−0.251	−0.230	−0.210	−0.189	−0.168	−0.147	−0.126	−0.105
30	−0.335	−0.276	−0.251	−0.230	−0.211	−0.193	−0.176	−0.159	−0.143	−0.126	−0.109	−0.093	−0.076
40	−0.303	−0.240	−0.215	−0.196	−0.178	−0.162	−0.147	−0.132	−0.118	−0.103	−0.089	−0.075	−0.060
50	−0.293	−0.225	−0.200	−0.180	−0.163	−0.148	−0.133	−0.119	−0.106	−0.092	−0.079	−0.066	−0.054
60	−0.295	−0.221	−0.195	−0.175	−0.157	−0.142	−0.128	−0.114	−0.101	−0.088	−0.076	−0.064	−0.051
70	−0.305	−0.224	−0.195	−0.175	−0.157	−0.141	−0.127	−0.113	−0.100	−0.088	−0.076	−0.064	−0.052
80	−0.318	−0.230	−0.200	−0.178	−0.160	−0.144	−0.129	−0.115	−0.102	−0.090	−0.077	−0.065	−0.054
90	−0.336	−0.240	−0.208	−0.185	−0.166	−0.149	−0.134	−0.120	−0.106	−0.093	−0.081	−0.069	−0.057
100	−0.358	−0.254	−0.220	−0.195	−0.175	−0.158	−0.142	−0.127	−0.113	−0.100	−0.088	−0.076	−0.064
110	−0.387	−0.273	−0.236	−0.210	−0.189	−0.171	−0.154	−0.139	−0.125	−0.111	−0.098	−0.086	−0.074
120	−0.422	−0.298	−0.259	−0.231	−0.208	−0.189	−0.172	−0.156	−0.141	−0.127	−0.114	−0.101	−0.088
130	−0.466	−0.330	−0.287	−0.257	−0.233	−0.213	−0.194	−0.178	−0.162	−0.148	−0.134	−0.121	−0.108
140	−0.518	−0.369	−0.322	−0.290	−0.264	−0.242	−0.222	−0.205	−0.189	−0.173	−0.159	−0.145	−0.132
150	−0.579	−0.414	−0.363	−0.327	−0.299	−0.275	−0.255	−0.236	−0.219	−0.202	−0.187	−0.173	−0.159
160	−0.649	−0.464	−0.408	−0.369	−0.338	−0.312	−0.290	−0.270	−0.251	−0.234	−0.218	−0.202	−0.188
170	−0.728	−0.520	−0.457	−0.414	−0.380	−0.352	−0.327	−0.305	−0.285	−0.266	−0.249	−0.232	−0.217
180	−0.815	−0.580	−0.509	−0.461	−0.423	−0.392	−0.365	−0.341	−0.319	−0.298	−0.280	−0.262	−0.245
190	−0.914	−0.646	−0.566	−0.512	−0.470	−0.435	−0.404	−0.378	−0.353	−0.331	−0.310	−0.291	−0.272
200	−1.028	−0.722	−0.630	−0.569	−0.521	−0.481	−0.448	−0.418	−0.391	−0.366	−0.343	−0.321	−0.301

$$\overline{C_{p,}}^{\circ} = -0.7519547 + 0.02773842t - (0.6551250 \times 10^{-3})t^2 + (0.7890734 \times 10^{-5})t^3 - (0.5240100 \times 10^{-7})t^4 + (0.1756529 \times 10^{-9})t^5 - (0.2361268 \times 10^{-12})t^6 \quad (10)$$

$$B' = -(272)(0.171253 \times 10^{39})T^{-17} - 0.072070739 + (1.05884208 \times 10^{-4})T \quad (11)$$

These equations were obtained by fitting individual values at each temperature by the method of least squares. The B' values did not fit a simple power function but did fit rather well the form of the equation chosen. Individual values below 80° C. differ somewhat from those given previously (*2*). Part of this resulted from the use of a simple power function to correlate values of A_j to 200° C. Values of $\overline{C_{p,}}^{\circ}$ and B' were found to be not completely independent. The values given are the best set found by the computer, including the 0° to 80° C. data given previously (*4*).

Values of the apparent and partial values for salts and water are calculated as had been done previously (*2*) and are presented in Tables IV and V.

Enthalpy. Values of the heat capacity, C_p, expressed in terms of the heat capacity of pure water, were used to evaluate enthalpies. The enthalpy values given by the National Engineering Laboratory Steam Tables (*8*) were considered correct, and deviations from these were calculated by use of heat capacity values contained herein. An estimate was made of the correction to be applied to the calculated enthalpy values due to the effect of pressure not allowed for in the evaluation of the enthalpy of water. This was a maximum at the highest temperature and salinity and was about 0.01 cal. per gram and, hence, was neglected. These were combined with values of the relative enthalpies at 25° C. (*3*) to give enthalpies. These were then corrected to refer to 0° C., with the values of water and the salts at infinite dilution being taken to be zero. Table VI is the resulting values in calories per gram. Values in B.t.u. per pound may be approximated by multiplying by 1.8. Since the B.t.u. is now defined (*1*) using the $\text{Calorie}_{\text{It}}$ = 4.1868 joules, then strictly to convert from defined calories per gram to B.t.u. per pound multiply by 1.8 × (4.1840/4.1868) = 1.8/1.0067.

Calcium Sulfate. The contents of the calorimeter were carefully examined after each high temperature run. No calcium sulfate or other solid was observed to have precipitated from the acidified sea water solutions for all salinities

Table V. Partial Heat Capacities of Salts and Water in Sea Salt Solutions

(Defined calories per gram degree centigrade)

Temp., °C.	Salinity, %												
	0	1	2	3	4	5	6	7	8	9	10	11	12
							Salts						
0	−0.752	−0.633	−0.548	−0.466	−0.385	−0.303	−0.221	−0.137	−0.053	0.034	0.122	0.211	0.303
10	−0.533	−0.436	−0.377	−0.322	−0.269	−0.216	−0.162	−0.108	−0.054	0.001	0.058	0.115	0.173
20	−0.404	−0.316	−0.270	−0.229	−0.189	−0.151	−0.113	−0.075	−0.036	0.003	0.042	0.082	0.123
30	−0.335	−0.247	−0.207	−0.173	−0.141	−0.110	−0.080	−0.050	−0.020	0.010	0.040	0.070	0.101
40	−0.303	−0.211	−0.173	−0.142	−0.114	−0.088	−0.062	−0.037	−0.011	0.014	0.039	0.064	0.090
50	−0.293	−0.194	−0.157	−0.128	−0.101	−0.077	−0.053	−0.030	−0.007	0.015	0.037	0.060	0.083
60	−0.295	−0.189	−0.151	−0.121	−0.096	−0.072	−0.049	−0.028	−0.006	0.015	0.036	0.056	0.077
70	−0.305	−0.189	−0.150	−0.120	−0.094	−0.070	−0.048	−0.027	−0.007	0.014	0.034	0.054	0.073
80	−0.318	−0.193	−0.152	−0.121	−0.095	−0.071	−0.049	−0.028	−0.008	0.012	0.032	0.051	0.070
90	−0.336	−0.200	−0.156	−0.124	−0.098	−0.074	−0.051	−0.030	−0.010	0.009	0.029	0.048	0.067
100	−0.358	−0.211	−0.165	−0.131	−0.104	−0.079	−0.057	−0.035	−0.015	0.005	0.024	0.043	0.061
110	−0.387	−0.227	−0.178	−0.143	−0.114	−0.089	−0.065	−0.044	−0.023	−0.004	0.016	0.035	0.053
120	−0.422	−0.248	−0.196	−0.159	−0.129	−0.102	−0.079	−0.057	−0.036	−0.016	0.004	0.023	0.041
130	−0.466	−0.276	−0.220	−0.180	−0.149	−0.121	−0.097	−0.074	−0.052	−0.032	−0.012	0.007	0.026
140	−0.518	−0.309	−0.249	−0.207	−0.173	−0.144	−0.119	−0.095	−0.073	−0.052	−0.032	−0.012	0.007
150	−0.579	−0.348	−0.282	−0.237	−0.201	−0.171	−0.144	−0.119	−0.096	−0.074	−0.053	−0.033	−0.014
160	−0.649	−0.392	−0.319	−0.270	−0.231	−0.199	−0.170	−0.144	−0.120	−0.097	−0.076	−0.055	−0.035
170	−0.728	−0.439	−0.358	−0.304	−0.262	−0.227	−0.196	−0.168	−0.143	−0.119	−0.096	−0.075	−0.054
180	−0.815	−0.489	−0.399	−0.339	−0.293	−0.254	−0.221	−0.191	−0.164	−0.138	−0.115	−0.092	−0.070
190	−0.914	−0.543	−0.442	−0.375	−0.323	−0.281	−0.244	−0.212	−0.182	−0.155	−0.130	−0.105	−0.082
200	−1.028	−0.604	−0.489	−0.413	−0.356	−0.309	−0.268	−0.233	−0.201	−0.171	−0.143	−0.118	−0.093
							Water						
0	1.0080	1.0075	1.0063	1.0042	1.0012	0.9974	0.9926	0.9868	0.9799	0.9719	0.9626	0.9521	0.9402
10	1.0019	1.0016	1.0007	0.9993	0.9973	0.9948	0.9917	0.9880	0.9835	0.9784	0.9725	0.9658	0.9582
20	0.9995	0.9992	0.9985	0.9974	0.9960	0.9942	0.9920	0.9893	0.9862	0.9826	0.9784	0.9738	0.9685
30	0.9987	0.9984	0.9978	0.9969	0.9957	0.9943	0.9925	0.9905	0.9880	0.9853	0.9821	0.9785	0.9745
40	0.9987	0.9984	0.9978	0.9970	0.9960	0.9948	0.9933	0.9915	0.9895	0.9871	0.9845	0.9815	0.9782
50	0.9992	0.9989	0.9983	0.9976	0.9966	0.9955	0.9941	0.9925	0.9907	0.9886	0.9862	0.9836	0.9806
60	1.0001	0.9998	0.9992	0.9984	0.9975	0.9964	0.9951	0.9936	0.9918	0.9899	0.9877	0.9853	0.9825
70	1.0013	1.0010	1.0004	0.9996	0.9987	0.9976	0.9963	0.9948	0.9932	0.9913	0.9892	0.9868	0.9843
80	1.0030	1.0026	1.0020	1.0012	1.0003	0.9992	0.9979	0.9964	0.9948	0.9929	0.9909	0.9886	0.9861
90	1.0051	1.0047	1.0040	1.0032	1.0022	1.0011	0.9998	0.9983	0.9967	0.9949	0.9929	0.9906	0.9882
100	1.0076	1.0072	1.0065	1.0057	1.0046	1.0035	1.0022	1.0007	0.9991	0.9972	0.9952	0.9930	0.9906
110	1.0107	1.0103	1.0095	1.0087	0.0076	1.0064	1.0051	1.0036	1.0019	1.0001	0.9981	0.9958	0.9934
120	1.0145	1.0140	1.0132	1.0123	1.0112	1.0099	1.0086	1.0070	1.0053	1.0035	1.0014	0.9992	0.9968
130	1.0189	1.0183	1.0175	1.0165	1.0154	1.0141	1.0126	1.0111	1.0093	1.0074	1.0054	1.0031	1.0007
140	1.0240	1.0234	1.0225	1.0215	1.0202	1.0189	1.0174	1.0158	1.0140	1.0120	1.0099	1.0076	1.0051
150	1.0300	1.0293	1.0283	1.0272	1.0259	1.0245	1.0229	1.0212	1.0193	1.0173	1.0151	1.0128	1.0102
160	1.0368	1.0361	1.0350	1.0338	1.0324	1.0308	1.0292	1.0274	1.0254	1.0233	1.0210	1.0186	1.0160
170	1.0446	1.0438	1.0426	1.0412	1.0397	1.0381	1.0363	1.0343	1.0323	1.0301	1.0277	1.0252	1.0225
180	1.0535	1.0526	1.0512	1.0497	1.0480	0.0462	1.0443	1.0422	1.0400	1.0377	1.0352	1.0325	1.0297
190	1.0635	1.0624	1.0609	1.0592	1.0574	1.0554	1.0533	1.0510	1.0486	1.0461	1.0434	1.0406	1.0376
200	1.0747	1.0735	1.0718	1.0699	1.0678	1.0656	1.0632	1.0608	1.0582	1.0554	1.0525	1.0495	1.0463

Table VI. Enthalpy of Sea Salt Solutions at Thermal Saturation

(Defined calories per gram)

Temp., °C.	Salinity, Wt. %												
	0	1	2	3	4	5	6	7	8	9	10	11	12
0	0	0.007	0.001	−0.029	−0.076	−0.145	−0.235	−0.345	−0.477	−0.630	−0.805	−0.996	−1.209
5	5.032	4.958	4.874	4.771	4.654	4.520	4.368	4.200	4.014	3.811	3.591	3.358	3.109
10	10.050	9.900	9.744	9.572	9.389	9.191	8.979	8.754	8.515	8.261	7.994	7.718	7.429
15	15.056	14.834	14.610	14.371	14.125	13.866	13.596	13.315	13.023	12.719	12.404	12.084	11.753
20	20.056	19.765	19.475	19.173	18.866	18.548	18.221	17.885	17.541	17.187	16.824	16.458	16.084
25	25.055	24.698	24.344	23.981	23.614	23.239	22.856	22.466	22.070	21.666	21.255	20.843	20.425
30	30.051	29.629	29.214	28.791	28.365	27.934	27.496	27.053	26.605	26.151	25.693	25.235	24.773
35	35.044	34.559	34.083	33.601	33.118	32.631	32.139	31.644	31.145	30.642	30.135	29.631	29.124
40	40.038	39.491	38.955	38.415	37.876	37.333	36.788	36.240	35.691	35.138	34.583	34.032	33.480
45	45.034	44.425	43.830	43.232	42.637	42.040	41.441	40.842	40.241	39.639	39.037	38.439	37.842
50	50.033	49.363	48.709	48.054	47.403	46.752	46.100	45.448	44.797	44.146	43.495	42.851	42.208
55	55.03	54.30	53.59	52.87	52.17	51.46	50.76	50.06	49.35	48.65	47.95	47.26	46.58
60	60.03	59.24	58.47	57.70	56.94	56.18	55.42	54.67	53.91	53.16	52.42	51.68	50.94
65	65.03	64.18	63.35	62.53	61.71	60.90	60.09	59.28	58.48	57.68	56.88	56.10	55.32
70	70.04	69.13	68.24	67.36	66.49	65.62	64.76	63.90	63.04	62.19	61.35	60.52	59.69
75	75.05	74.08	73.13	72.19	71.26	70.34	69.43	68.52	67.61	66.71	65.82	64.94	64.07
80	80.07	79.03	78.03	77.03	76.05	75.07	74.10	73.14	72.19	71.24	70.30	69.37	68.45
85	85.09	83.99	82.93	81.87	80.84	79.80	78.78	77.77	76.76	75.77	74.78	73.80	72.84
90	90.12	88.95	87.83	86.72	85.63	84.54	83.47	82.40	81.35	80.30	79.26	78.24	77.23
95	95.15	93.92	92.74	91.57	90.43	89.29	88.16	87.04	85.93	84.84	83.75	82.68	81.62
100	100.23	98.94	97.70	96.48	95.27	94.08	92.89	91.72	90.57	89.42	88.28	87.16	86.06
105	105.23	103.88	102.58	101.30	100.03	98.79	97.55	96.33	95.12	93.92	92.74	91.57	90.42
110	110.29	108.87	107.51	106.17	104.85	103.55	102.26	100.98	99.72	98.47	97.24	96.02	94.82
115	115.35	113.87	112.45	111.05	109.67	108.31	106.97	105.64	104.33	103.03	101.74	100.48	99.23
120	120.42	118.87	117.39	115.93	114.50	113.08	111.68	110.30	108.93	107.58	106.25	104.94	103.64
125	125.51	123.90	122.35	120.83	119.34	117.87	116.42	114.98	113.56	112.16	110.77	109.41	108.07
130	130.60	128.92	127.31	125.74	124.18	122.66	121.14	119.66	118.18	116.73	115.29	113.88	112.49
135	135.72	133.97	132.30	130.66	129.05	127.46	125.89	124.35	122.82	121.31	119.83	118.36	116.92
140	140.83	139.02	137.28	135.58	133.91	132.26	130.64	129.04	127.46	125.89	124.35	122.84	121.35
145	145.97	144.09	142.28	140.52	138.79	137.08	135.40	133.74	132.11	130.49	128.90	127.33	125.79
150	151.13	149.18	147.31	145.48	143.69	141.92	140.18	138.46	136.77	135.10	133.45	131.83	130.24
155	156.30	154.27	152.33	150.44	148.58	146.76	144.95	143.18	141.43	139.70	138.00	136.33	134.68
160	161.48	159.38	157.37	155.41	153.49	151.61	149.75	147.91	146.11	144.32	142.57	140.84	139.14
165	166.70	164.52	162.44	160.41	158.43	156.48	154.56	152.66	150.80	148.96	147.14	145.36	143.61
170	171.91	169.65	167.50	165.41	163.36	161.34	159.36	157.40	155.48	153.58	151.71	149.88	148.07
175	177.17	174.83	172.61	170.44	168.33	166.25	164.20	162.19	160.20	158.24	156.32	154.43	152.56
180	182.43	180.01	177.71	175.48	173.29	171.15	169.04	166.96	164.91	162.90	160.91	158.97	157.05
185	187.73	185.23	182.86	180.56	178.30	176.09	173.91	171.77	169.67	167.59	165.55	163.54	161.57
190	193.04	190.45	188.01	185.63	183.30	181.02	178.78	176.58	174.41	172.28	170.17	168.11	166.08
195	193.39	195.72	193.20	190.74	188.35	186.00	183.69	181.43	179.19	177.00	174.83	172.71	170.62
200	203.77	201.01	198.41	195.88	193.41	190.99	188.62	186.28	183.99	181.73	179.51	177.32	175.18

up to and including 5%. Some precipitation may have occurred at high temperatures and then redissolved on cooling. For salinities of 6.75% and above, calcium sulfate was observed ranging up to about 1 gram per kg. of solution. No attempt was made to correct the observed heat capacities for this effect. The pH changed from about 4 to 7.5. This may have been due to some small corrosion of the calorimeter.

CONCLUSIONS

Experimental and correlated values for heat capacity and enthalpies of sea salt solutions have been presented. A new high temperature calorimeter designed for use with sea water was used and will be used in the future with other aqueous ionic solutions.

With the aid of thermodynamics, measurements on heats of mixing and of boiling point elevation for sea salt solutions will be used to confirm the values reported.

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NOMENCLATURE

A_j = Debye-Hückel constant
B = extended Debye-Hückel equation constant (7)
B' = see Equation 8 and Table IV
C_p = heat capacity of solution at constant pressure, cal./g. °C.
C_{sat} = heat capacity of solution at saturation, cal./g. °C.
(ϕC_{p_s}) = apparent heat capacity of salts, cal./g. salts °C.
$\overline{C_{p_s}}$ = partial heat capacity of salts in solution, cal./g. salts °C.
$\overline{C_{p_s}}^{\circ}$ = partial heat capacity of salts at infinite dilution, cal./g. salts °C.
$C^*_{p_w}$ = heat capacity of pure water at constant pressure, cal./g. °C.
$\overline{C_{p_w}}$ = partial heat capacity of water in solution, cal./g. water °C.
H = enthalpy, cal.
h = specific enthalpy of saturated liquid, cal./g.
h' = specific enthalpy of saturated vapor, cal./g.
I = ionic strength = $\Sigma m_i Z_i^2/2$
K = heat capacity of calorimeter, cal./° C.
M = mass of solution in calorimeter, g.
M_i = molecular weight of ion i
Σm_i = sum of molality of all ions
Σm_+ = sum of molality of + ions
Σm_- = sum of molality of − ions
P = pressure

Q = electrical heat input, cal.
S = salinity in weight per cent. Approximately per cent total solids (see Procedure section for discussion)
T = temperature, ° K.
t = temperature, ° C.
u = specific volume of saturated liquid, cm.^{3}/g.
u' = specific volume of saturated vapor, cm.^{3}/g.
V = internal volume of calorimeter, cm.^{3}
x = mass fraction of liquid in calorimeter
Z_i = charge on ion i
$\sigma I^{1/2}/3$ = $(1/I^{3/2})\,[1 + I^{1/2} - 1/(1 + I^{1/2}) - 2\ln(1 + I^{1/2})]$
σ = standard deviation

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Vapor-Liquid Equilibria in the Ethane–*n*-Hexane System

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Vapor and liquid equilibrium phase compositions were determined in the ethane–*n*-hexane system at 150°, 250°, and 350° F. at pressures from approximately 60 p.s.i.a. to near the critical. Phase envelopes were extrapolated to yield critical composition and pressure at each temperature. Equilibrium ratios ($K = y/x$) from the experimental data are compared with those from the most recent revision of the NGPSA *K*-charts. As previous studies of the ethane–*n*-hexane binary are not found in the literature, no comparison with other experimental work is possible.

THE MIXTURES of ethane and *n*-hexane were confined over mercury in a 35-ml. windowed stainless steel cell. The equilibrium cell was immersed in a controlled-temperature oil bath. By means of a magnetic pump, vapor from the top of the cell was recirculated through the bottom of the cell for 2 to 4 hours, after which from 3 to 6 hours were allowed for complete phase separation. Sampling was carried out under constant pressure conditions by simultaneously injecting mercury into the bottom of the cell while the sample was being withdrawn. No single-phase samples were taken; however, in a number of instances, insufficient amount of one of the equilibrium phases precluded its being sampled.

The equilibrium temperature was determined from the average indication of four iron-constantan thermocouples at separate locations near the cell. The thermocouple-potentiometer combination was calibrated against mercury-in-glass thermometers which had been calibrated by the National Bureau of Standards. The accuracy of any indicated temperature is estimated to be 0.1° F., and deviations of the average cell temperature from the nominal temperature of each isotherm did not exceed 0.25° F.

Pressure measurements were made with 1000- and 5000-p.s.i.g. Bourdon tube pressure gages with sensitivities of 0.1% of full scale. These gages were calibrated against a dead-weight pressure gage with calibration traceable to NBS standards. Uncertainties in the reported experimental pressures are believed not to exceed 2 p.s.i. below 1000 p.s.i.g. but may be as great as 7.5 p.s.i. for pressures greater than 1000 p.s.i.g.

Further details of the apparatus and experimental procedures have been given by Roberts *et al.* (*3*) and Poston and McKetta (*2*). Recent modifications were described by Zais (*5*).

ANALYTICAL

The vapor and liquid phase samples were analyzed by means of a Beckman Model GC-2A gas chromatograph equipped with a 6-foot silicone column (Beckman No. 17449). Chromatograms were interpreted by the peak height