crystals (item 51) that gave two long spacings, one for the A form (10 orders) and the other for the B form (4 orders), but the short-spacing pattern differed from the A pattern only by an additional strong spacing at 3.74 Å. Therefore, a strong short spacing at 3.74 Å can be taken as characteristic of the B form.

A review of the long-spacing data based on the X-ray powder-diffraction data of Kurokawa (*11*), five values, and those calculated ($c \sin \beta$) from the single-crystal data of Turner and Lingafelter (*12*), six values, and of Sakurai (*9*), three values, indicates that the A modification has been the only form observed for even-carbon amides up to myristamide. When plotted against n, these data were satisfied by eq 3 with an average deviation

$$L = 1.755n + 3.263 \qquad (3)$$

of 0.16 Å. The calculated angle of tilt is therefore $\sin^{-1} 1.755/2.54 = 43° 42'$.

Because only limited X-ray data were published on four long-chain methyl ketones reported in a previous publication (*13*), these four compounds (2-tridecanone, 2-pentadecanone, 2-heptadecanone, and 2-nonadecanone) are listed in Table I with complete X-ray data. When the long spacings of these compounds are plotted vs. number of carbons, the three longer compounds fall squarely on a straight line (the C_{13} compound is slightly off the line) represented by eq 4. The calculated angle

$$L = 2.40n + 6.60 \qquad (4)$$

of tilt of these long-chain methyl ketones is therefore $\sin^{-1} 2.40/2.54 = 70° 53'$.

Item 21 in Table I, prepared by melting an equimolar mixture of morpholine stearate and cyclohexylamine palmitate and allowing it to crystallize from the melt, gave a long spacing characteristic of cyclohexylamine stearate (item 16) and none for the other combination possible from the four ions present. Mod et al. (*14*) have studied the ternary reciprocal salt pair system involving the cyclohexylamine and morpholine salts of stearic and palmitic acids and prepared a freezing-point diagram for this system. A study of this diagram indicates that the first crystals to form from the melt of a 50:50 mixture would be cyclohexylamine stearate. The first crystals would tend to grow and be larger and better formed than those coming out later when components of eutectic mixtures were crystallizing. It is therefore not surprising that the long spacing for only cyclohexylamine stearate was observed in the X-ray data for the mixture.

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Densities of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ Aqueous Solutions at 1 atm from 0 to 50 °C and from 0.001 to 1.5 *m*

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The relative densities ($d - d_0$) of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions have been determined at 1 atm with a vibrating flow densimeter from 0.001 to 1.5 *m* and from 0 to 35 °C. The data have been combined with our earlier measurements at temperatures up to 55 °C and fitted to equations of the following form (precisions better than 15×10^{-6} g cm^{-3}): $d - d_0 = Am + Bm^{3/2} + Cm^2 + Dm^{5/2}$, where d and d_0 are the densities of solution and pure water, respectively, m is the molality, and A, B, C, and D are temperature-dependent parameters. The equations agree well with the results of other workers.

Introduction

The basic pressure-volume-temperature-concentration properties of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions are of prime importance for various thermodynamic calculations in solution chemistry, geochemistry, and oceanography. They are also important in the engineering calculations such as those concerning the process of converting salty water to potable water and the process of assessing salty water intrusion in the freshwater aquifers. A survey of the literature (*14*) reveals the scarcity of reliable experimental 1-atm density data for these solutions at temperatures other than 25 °C. The present paper provides precise 1-atm density data from 0 to 55 °C and from 0 to 1.5 *m* for the major sea salts. The results have been fitted to equations that are simple polynomial functions of t (°C) and $m^{1/2}$ (molality).

Experimental Section

Densities of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions have been measured at various temperatures and concentrations on a high-precision digital readout flow densimeter

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Table I. Relative Density of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ Aqueous Solutions

m	1000Δ*d*
NaCl, 0 °C	
0.01029	0.470
0.04120	1.864
0.16630	7.429
0.50190	21.845
0.99920	42.290
NaCl, 5 °C	
0.01029	0.455
0.04120	1.819
0.09485	4.154
0.16630	7.257
0.19849	8.631
0.50120	21.347
0.50190	21.360
0.72467	30.469
0.99920	41.420
1.00120	41.512
1.49986	60.719
NaCl, 15 °C	
0.01029	0.437
0.04120	1.751
0.09485	4.004
0.16630	6.986
0.19849	8.312
0.50120	20.610
0.50190	20.634
0.72467	29.457
0.99920	40.087
1.00120	40.168
1.49986	58.848
NaCl, 25 °C	
0.00992	0.414
0.01011	0.420
0.01029	0.426
0.04120	1.696
0.05002	2.068
0.05003	2.066
0.09485	3.894
0.09989	4.101
0.10039	4.129
0.19849	8.096
0.20009	8.162
0.29972	12.145
0.40009	16.116
0.49946	20.012
0.50120	20.097
0.50190	20.113
0.59971	23.907
0.69917	27.740
0.72467	28.740
0.79957	31.578
0.90125	35.435
0.99920	39.126
1.00010	39.156
1.00120	39.215
1.49986	57.520
NaCl, 35 °C	
0.04120	1.670
0.09485	3.817
0.16630	6.673
0.50190	19.740
0.99920	38.413
$MgCl_2$, 0 °C	
0.00469	0.391
0.00469	0.397
0.00978	0.822
0.01972	1.645
0.04137	3.423
0.04851	4.018
0.07890	6.478
0.09627	7.909
0.19500	15.811
0.19525	15.856
0.28278	22.731
0.37485	29.875
0.40811	32.434
0.55193	43.342
0.63404	49.489
0.79758	61.551
0.97410	74.252
$MgCl_2$, 5 °C	
0.00469	0.384
0.00978	0.816
0.01972	1.615
0.04137	3.381
0.04851	3.967
0.07890	6.388
0.09627	7.805
0.19500	15.624
0.19525	15.624
0.28278	22.428
0.37485	29.484
0.40811	32.016
0.55193	42.831
0.63404	48.895
$MgCl_2$, 15 °C	
0.00469	0.377
0.00978	0.790
0.01972	1.593
0.04137	3.319
0.04851	3.886
0.07890	6.275
0.09627	7.665
0.19525	15.334
0.37485	28.994
0.40811	31.464
0.55193	42.109
0.63404	48.105
0.97410	72.309
$MgCl_2$, 25 °C	
0.00469	0.372
0.00978	0.785
0.00989	0.797
0.00989	0.802
0.01972	1.576
0.04851	3.854
0.05038	3.994
0.05038	3.999
0.07890	6.212
0.09970	7.845
0.09970	7.850
0.19500	15.185
0.19525	15.172
0.19893	15.476
0.19893	15.475
0.28278	21.818
0.37485	28.701
0.49487	37.572
0.49487	37.575
0.55193	41.719
0.63404	47.644
0.71531	53.503
0.79758	59.328
0.99097	72.852
0.99097	72.850
1.47531	105.418
1.47531	105.422
$MgCl_2$, 35 °C	
0.00469	0.362
0.04851	3.805
0.09627	7.547
0.28278	21.689
0.37485	28.558
0.40811	30.988
0.55193	41.473
Na_2SO_4, 0 °C	
0.00340	0.481
0.01055	1.464
0.01399	1.954
0.03178	4.381
0.05050	6.918
0.05553	7.610
0.10019	13.584
0.16373	21.944
0.19951	26.583
0.50208	64.261
0.56760	72.106
0.70189	87.887
Na_2SO_4, 5 °C	
0.00340	0.468
0.01055	1.438
0.01399	1.905
0.03178	4.302
0.05050	6.780
0.05553	7.446
0.16373	21.547
0.19951	26.097
0.30182	38.931
0.50208	63.252
0.56760	71.015
0.70189	86.634
Na_2SO_4, 15 °C	
0.00340	0.458
0.01055	1.388
0.01399	1.850
0.01399	1.859
0.03178	4.171
0.05050	6.583
0.05553	7.234
0.10019	12.941
0.16373	20.922
0.19951	25.387
0.30182	37.908
0.33307	41.680
0.40356	50.095
0.50208	61.705
0.56760	69.311
0.70189	84.640
Na_2SO_4, 25 °C	
0.00259	0.335
0.00340	0.436
0.00504	0.651
0.01055	1.361
0.01270	1.591
0.01682	2.162
0.03022	3.867
0.03581	4.575
0.04293	5.477
0.05050	6.437
0.05553	7.075
0.05958	7.569
0.07698	9.753
0.08861	11.205
0.09850	12.443
0.10019	12.652
0.11256	14.185
0.13651	17.137
0.16801	20.993
0.19951	24.841
0.24072	29.799
0.30182	37.131
0.33307	40.842
0.35894	43.890
0.40356	49.122
0.50061	60.360
0.50208	60.537
0.56760	68.027
0.70189	83.141
0.72018	85.166
Na_2SO_4, 35 °C	
0.00340	0.443
0.01055	1.339
0.05050	6.331
0.05553	6.961
0.10019	12.461
0.16373	20.184
0.30182	36.603
0.33307	40.251
0.40356	48.438
0.50208	59.687
0.56760	67.098
$MgSO_4$, 0 °C	
0.00099	0.129
0.00549	0.730
0.01177	1.538
0.02786	3.584
0.03855	4.944
0.07019	8.908
0.11669	14.678
$MgSO_4$, 5 °C	
0.00099	0.131
0.00549	0.717
0.01177	1.515
0.02231	2.851
0.02786	3.551
0.03855	4.883
0.07019	8.797
0.11669	14.503
0.12010	14.905
0.21211	26.013
0.23758	29.092
1.48251	166.290
$MgSO_4$, 15 °C	
0.00099	0.133
0.00549	0.698
0.01177	1.488
0.02231	2.792
0.02786	3.486
0.03855	4.793
0.07019	8.629
0.11669	14.242
0.12010	14.641
0.21211	25.561
0.23758	28.575
0.39375	46.690
0.64325	74.884
0.88167	101.076
1.23320	138.504
$MgSO_4$, 25 °C	
0.00099	0.128
0.00549	0.688
0.01177	1.458
0.02231	2.742
0.02786	3.426
0.03855	4.726
0.03855	4.727
0.07019	8.526
0.07019	8.528
0.11669	14.048
0.12010	14.459
0.12010	14.463
0.21211	25.246
0.21211	25.253
0.23758	28.188
0.39375	46.132
0.39375	46.138
0.64325	74.089
0.88167	100.043
0.88167	100.049
1.23320	137.220
1.23320	137.223
1.35795	150.078
1.35795	150.082
1.42400	156.831
1.42400	156.843
1.48251	162.740
1.48251	162.748
$MgSO_4$, 35 °C	
0.00099	0.115
0.00549	0.675
0.01177	1.444
0.02231	2.718
0.02786	3.399
0.03855	4.704
0.07019	8.452
0.11669	13.960
0.12010	14.321
0.23758	27.997
0.39375	45.770
0.64325	73.548
0.88167	99.331
1.23320	136.281
1.35795	149.108
1.42400	155.833
1.48251	161.662

(*10*, *13*). The data have been combined with the results of our earlier measurements (*15*–*17*) to give reliable equations of state for the four major sea salts at 1 atm over the total range 0–55 °C and 0–1.5 *m*.

All of the solutions have been made by weight with reagent-grade (Baker Analyzed) chemicals (without further purification) and ion-exchanged water (Millipore Super Q System). The concentrations of NaCl and Na_2SO_4 stock solutions have been analyzed by heating to dryness, whereas the concentration of the $MgCl_2$ stock solution has been analyzed for Cl^- by titration with $AgNO_3$; the concentration of the $MgSO_4$ stock solution has been analyzed for SO_4^{2-} by titration with $BaCl_2$.

The vibrating flow densimeter used to make the density measurements is described in detail elsewhere (*1*, *10*, *13*). The instrument applies the principle of the vibrating tube. By measuring the resonance frequency of a hollow metallic tube filled with the solution, one can readily determine the density of the solution. In this study, only relative densities (Δd) are desired

$$\Delta d = d - d_0 = k(\tau^2 - \tau_0^2) \qquad (1)$$

where d and d_0 are respectively the densities of the unknown and reference fluids, k is a constant (at a given T and P), and τ and τ_0 are the periods of the natural frequency of the oscillator containing the unknown and reference fluids, respectively. The instrument constant, k, is determined by measuring the τ in pure water (ion-exchanged, Millipore Super Q System) and N_2. The densities of pure water are taken from Kell (*9*), and the densities of nitrogen are obtained from the van der Waals equation (*8*). The temperature of the densimeter has been controlled to ±0.001 °C. The temperature has been set to ±0.002 °C with

Table II. Coefficients for Eq 2[a]

variables	NaCl	$MgCl_2$	Na_2SO_4	$MgSO_4$
m	45.872	84.223	140.89	131.174
mt	−0.243	−0.290	−0.608	−0.3261
mt^2	4.05E-3	8.36E-3	7.88E-3	1.88E-3
mt^3	−4.39E-5	−1.48E-4	−3.67E-5	8.43E-5
mt^4	2.91E-7	1.34E-6	6.70E-8	−1.12E-6
$m^{3/2}$	−2.766	−6.215	−15.710	−17.615
$m^{3/2}t$	0.0534	0.0816	0.272	0.1629
$m^{3/2}t^2$	−6.02E-4	−1.38E-3	−3.11E-3	−1.96E-3
m^2	−0.793	−1.909	−3.598	5.395
m^2t				−1.35E-2
$m^{5/2}$				−2.665
validity range	0–1.5 *m*, 0–55 °C	0–1 *m*, 0–50 °C	0–1 *m*, 0–50 °C	0–1.5 *m*, 0–50 °C
std dev (10^{-6} g cm^{-3})	11.6	10.0	8.9	15.2

[a] The terms E-*a*, given for each variable, mean the coefficient is times 10^{-a}.

a platinum resistance thermometer and a G-2 Mueller bridge (IPTS 1968 temperature scale).

Results

The relative densities of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions have been measured over the range 0.001–1.5 *m* and 0–35 °C. The results are tabulated in Table I. The values given in Table I are combined with the magnetic float data obtained earlier in this laboratory (*15–17*) and fitted into equations of the form (g cm^{-3})

$$10^3\Delta d = 10^3(d - d_0) = Am + Bm^{3/2} + Cm^2 + Dm^{5/2} \quad (2)$$

where *A*, *B*, *C*, and *D*, the temperature dependent parameters, are given in Table II along with the standard deviations of the fit and *m* is the molality.

In order to calculate the density of the solutions, one needs the densities of pure water. We have thus refitted the pure water density equation given by Kell (*9*) to a polynomial equation which is precise to 0.044 × 10^{-6} g cm^{-3} (one standard deviation) over the range 0–55 °C (*3*)

$$d_0\ (\mathrm{g\ cm^{-3}}) = 0.9998395 + 6.7914 \times 10^{-5}t - 9.0894 \times 10^{-6}t^2 + 1.0171 \times 10^{-7}t^3 - 1.2846 \times 10^{-9}t^4 + 1.1592 \times 10^{-11}t^5 - 5.0125 \times 10^{-14}t^6 \quad (3)$$

Discussion and Conclusion

The relative densities of NaCl aqueous solutions ($d - d_0$) calculated from eq 2 at various concentrations and temperatures are compared with the data of Dunn (*5*, *6*), Lee (*11*), and Desnoyers and co-workers (*7*, *12*) in Figure 1 over the temperature range 0.05–45 °C and the concentration range 0–0.85 *m*. The data of Dunn are precise to 20 × 10^{-6} g cm^{-3} (duplicate measurements) and ours to 12 × 10^{-6} g cm^{-3} (one standard deviation of the fit). The agreement is within the combined precision of 32 × 10^{-6} g cm^{-3} over most of the concentration and temperature ranges.

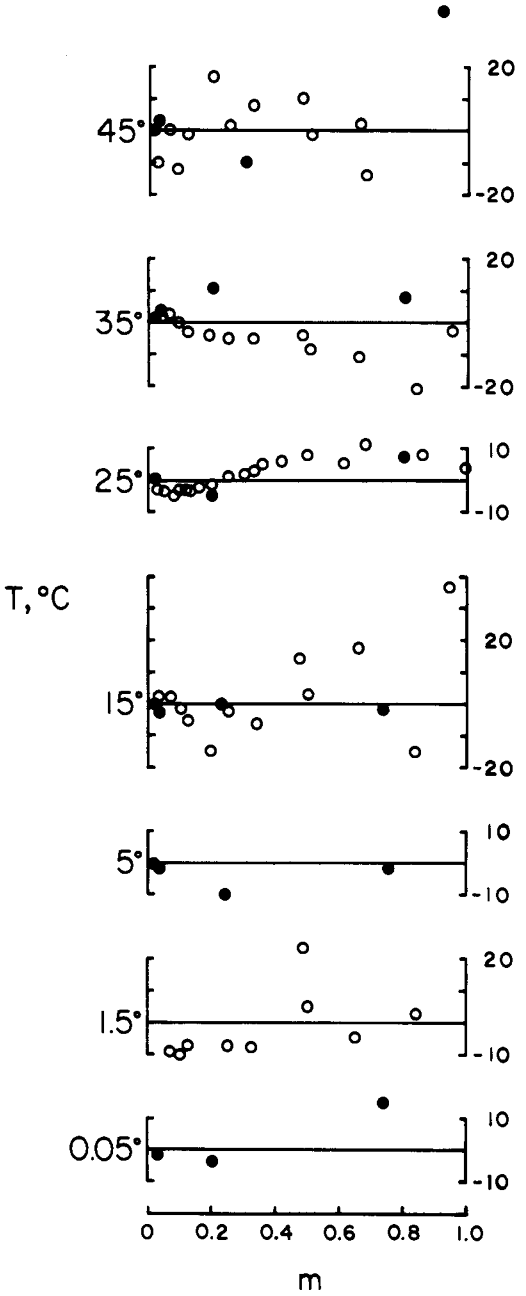

Figure 1. Comparisons of the relative densities ($d - d_0$ in 10^{-6} g cm^{-3}) of NaCl aqueous solutions with the data of Dunn (*5*, *6*) (solid circles) and Fortier et al. (*7*) and Perron et al. (*12*) (open circles) at various temperatures.

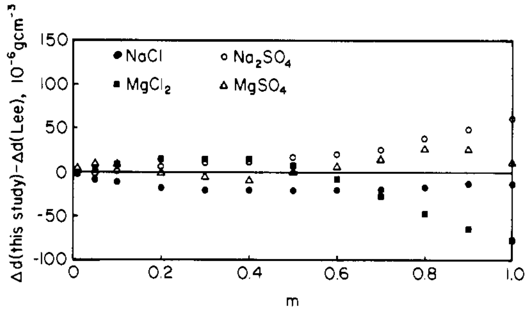

Figure 2. Comparisons of the relative densities ($d - d_0$ in 10^{-6} g cm^{-3}) of NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions with the data of Lee (*11*) at 25 °C.

Little, if any, density data with precisions better than 100 × 10^{-6} g cm^{-3} at 1 *m* are available in the literature for $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions at temperatures other than 25 °C. Therefore, it is only attempted to compare our density results for $MgCl_2$, Na_2SO_4, and $MgSO_4$ solutions with the data of other workers at 25 °C. The data of Lee (*11*) were chosen for comparisons because they cover wide concentration ranges and have good precisions (concentrations up to 3.4, 1.3, 1.3, and 1.0 *m* for NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions, respectively, with standard deviations of 13 × 10^{-6}, 6 × 10^{-6}, 12 × 10^{-6}, and 12 × 10^{-6} g cm^{-3}). It is shown in Figure 2 that our NaCl relative densities agree with the data of Lee to within ±20 × 10^{-6} g cm^{-3} from 0 to 1 *m*. Our $MgCl_2$ density agrees with the data of Lee to within ±15 × 10^{-6} g cm^{-3} up to 0.6 *m* and is 76 × 10^{-6} g cm^{-3} lower than the data of Lee at 1 *m*. The densities of Na_2SO_4 agree to within $\pm 20 \times 10^{-6}$ g cm^{-3} from 0 to 0.6 *m*. Our value is higher than the data of Lee by 60×10^{-6} g cm^{-3} at 1 *m*. The measured densities of $MgSO_4$ agree with the data of Lee to within 25×10^{-6} g cm^{-3}.

The 1-atm density equations obtained in this study have been combined with the high-pressure sound speeds (*2*) to derive high-pressure equations of state for NaCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ aqueous solutions. The results will be presented in a future publication (*4*).

Acknowledgment

A. Lo Surdo and P. Chetirkin performed the sulfate and chloride analysis.

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Thermodynamic Properties of Magnesium Potassium Orthophosphate Hexahydrate

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The low-temperature heat capacity of magnesium potassium orthophosphate hexahydrate, $MgKPO_4 \cdot 6H_2O$, was measured by adiabatic calorimetry over the temperature range 10–316 K. The standard enthalpy of formation at 298.15 K was determined with a solution calorimeter. Related thermodynamic properties and the solubility product constant were derived.

Introduction

Magnesium potassium orthophosphate hexahydrate, $MgKPO_4 \cdot 6H_2O$, may occur as a soil-fertilizer reaction product (*3*) or as a precipitate in liquid fertilizers containing potassium and prepared from wet-process phosphoric acid (*1*). It also is an excellent source of potassium and phosphorus for plants (*8*). Presented here are measurements of the heat capacity of magnesium potassium orthophosphate hexahydrate from 10 to 316 K, entropies and enthalpies at 298.15 K derived therefrom, and the enthalpy of formation at 298.15 K. The entropy and enthalpy of formation are combined with other values from the literature in the calculation of the solubility product constant, which is compared with the value derived from the direct measurements of solubilities.

Materials. Magnesium potassium orthophosphate hexahydrate was prepared by the method of Lehr et al. (*2*). Chemical analyses showed it to contain 17.4% K_2O, 15.2% MgO, and 26.8% P_2O_5 (stoichiometric: 17.68% K_2O, 15.13% MgO, and 26.63% P_2O_5); microscopic examination showed it to comprise an essentially homogeneous phase of $MgKPO_4 \cdot 6H_2O$.

Monopotassium orthophosphate was prepared by recrystallizing the reagent-grade salt from distilled water and drying it by vacuum desiccation over $MgClO_4$. It contained 34.6% K_2O and 52.1% P_2O_5 (stoichiometric: 34.61% K_2O and 52.15% P_2O_5). The magnesium chloride solution was prepared by dissolving the reagent-grade salt in distilled water. It contained 14.6% MgO and 25.2% Cl ($MgCl_2 \cdot 10.05H_2O$, based on the MgO analysis).

Low-Temperature Heat Capacity. The adiabatic calorimeter and the method of operation have been described previously (*10*), and the overall accuracy of our technique has been reported (*5*). The defined calorie was taken as 4.1840 absolute J and the ice point as 273.15 K.

The calorimeter was charged with 35.8460 g or 0.134 518 mol. The weight was corrected for bouyancy in air on the basis of a density of 1.83 g cm^{-3} (*2*), and the gram formula weight was taken as 266.4774. The air in the calorimeter was replaced with helium by evacuating to a pressure of 100 torr and then relieving to atmospheric pressure with helium. This cycle was repeated twice, and then the pressure was adjusted to give the same mass of helium as was used in the measurements on the empty calorimeter. The final observed weight of the calorimeter was 5 mg greater than the summation of the masses in each step of the preparation, evacuation, and sealing of the calorimeter. This difference (+0.01% based on the sample weight) was considered sufficiently small to assure that no appreciable alteration of the sample occurred during evacuation and sealing of the calorimeter. The heat capacity of the sample ranged from 28% of the total at 10 K to 49% at 300 K.

The measured heat capacities were corrected for curvature and for small differences in the amount of eutectic solder relative to the empty calorimeter. Because small temperature differences were important, temperatures were measured to four decimal places; but these were rounded to two decimal places in the final tabulation. The heat capacities below 10 K were read from a large-scale plot of C_P/T against T^2 that extrapolated smoothly to 0 K. Observed molal heat capacities are shown in Table I. Heat capacity and derived functions at round values