$\Delta\mu$ = salt effect defined by Equation 5
ν = number of moles of both ions dissociated from 1 mole of salt, mol

Subscripts

0 = no salt
1 = THF
2 = water
3 = salt

Superscripts

$'$ = vapor phase
$^{\circ}$ = pure component

Literature Cited

(1) Cigna, R., Sebastiani, E., *Ann. Chim. (Rome)*, **54**, 1048 (1964).
(2) Fukala, E., Kopechy, F., *Khim. Prom.*, **16** (41), 22 (1966).
(3) Johnson, A. I., Furter, W. F., *Can. J. Chem. Eng.*, **38**, 78 (1960).
(4) Matous, J., Hrncirik, J., Novak, J. P., Sobr, J., *Coll. Czeck. Chem. Commun.*, **35**, 1904 (1970).
(5) Matous, J., Novak, J. P., Sobr, J., Pick, J., *ibid.*, **37**, 2653 (1972).
(6) Miyahara, K., MS thesis, Nagoya University, Nagoya, Japan, 1974.
(7) Riddick, J. A., Bunger, W. B., "Organic Solvents," in "Techniques of Organic Chemistry," Weissberger, Ed., 3rd ed., pp 66, 220, Wiley-Interscience, New York, N.Y., 1970.
(8) Sada, E., Morisue, T., *J. Chem. Eng. Jpn.*, **6**, 385 (1973).
(9) Shnitko, A. V., Kogan, V. B., *Zh. Prikl. Khim.*, **41**, 1305 (1968).
(10) Signa, R., Arm, H., Daenicker, H., *Helv. Chim. Acta*, **52**, 2349 (1969).
(11) Yoshioka, T., Taniyama, M., Sakata, I., *Kogyo Kagaku Zasshi*, **58**, 294 (1955).

Received for review September 9, 1974. Accepted January 15, 1975.

Heats of Dilution of Aqueous Electrolytes: Temperature Dependence

Harriet P. Snipes, Charles Manly, and Dale D. Ensor[1]
Department of Chemistry, University of North Carolina at Greensboro, Greensboro, N.C. 27412

The heats of dilution of KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ were measured over a concentration range of 0.005–2.0m at temperatures between 40–80°C. The data were extrapolated to infinite dilution by use of the Debye-Hückel limiting law to obtain relative apparent molal heat contents (ϕ_L). The heats of dilution of $MgCl_2$ and $MgSO_4$ were measured at 25°C and combined with the low concentration work of Lange and Streeck to yield values of ϕ_L. The relative partial molal heat content of solvent and solute was calculated from the experimental values. The heat content data were then used to calculate activity and osmotic coefficients in the temperature range 40–80°C.

The thermodynamic properties of aqueous electrolytes have been under investigation for many years. Extensive data exist for a wide variety of aqueous electrolytes at or near 25°C. A need for thermodynamic data at temperatures above 25°C has developed in recent years, owing mainly to the interest in desalination processes. Several electrolytes have been studied by different investigators (*3, 9, 15*) at temperatures between 100–300°C. However, very few precise data exist for aqueous electrolytes above 25° and below 100°C.

Ensor and Anderson (*2*) have shown that the measurement of heats of dilution as a function of temperature and concentration is an efficient way of obtaining accurate heat content data. These data were then used to extend existing thermodynamic data at 25°C to the experimental temperature range 40–80°C. The activity and osmotic coefficients of NaCl derived by Ensor and Anderson were in excellent agreement with existing data. The purpose of the present research was to extend this treatment to other electrolytes important in seawater (KCl, $MgCl_2$, $MgSO_4$, and Na_2SO_4).

[1] To whom correspondence should be addressed.

Experimental

Solutions. Near saturated stock solutions of Baker analyzed reagent Na_2SO_4, $MgCl_2$, and KCl and Fisher certified $MgSO_4$ were prepared using distilled deionized water and stored in polyethylene bottles. The molalities of the KCl and $MgCl_2$ stock solutions were determined by AgCl gravimetric analysis. The $MgSO_4$ stock solution was analyzed by EDTA titration. $BaSO_4$ gravimetric analysis was used to determine the molality of the Na_2SO_4 stock solution. All less concentrated solutions were made by diluting a known weight of stock solution with a known weight of deionized water.

Table I. Extrapolation Coefficients for Equation 2

Temp, °C	B	C	SD, cal/mol
	KCl		
40	−782.99	1378.78	2.1
60	−158.55	−353.71	1.7
80	−1006.82	2094.86	2.3
	$MgCl_2$		
40	−377.80	633.22	5.4
50	−231.76	326.67	4.4
60	621.17	−1263.68	4.4
70	1738.3	−4575.8	5.5
80	679.29	−1949.08	5.1
	$MgSO_4$		
40	2125.02	−2988.20	9.6
60	19594.8	−43115.7	6.8
80	7307.60	−11066.9	10.5
	Na_2SO_4		
40	−402.38	−1177.90	2.2
60	611.79	−2849.73	3.2
80	7789.30	−20777.09	5.1

Calorimeter. The heats of dilution of the salts were measured with a previously described 250-ml dewar calorimeter (*1*) with microdegree sensitivity. The vessel was submerged in a water bath whose temperature was regulated to better than ±0.005°C with a Hallikainen thermotrol. The amount of heat evolved when a known amount of salt solution was diluted in a known amount of deionized water was monitored as a resistance change using a 10-Kohm thermistor incorporated in a Wheatstone bridge. The resistance change was calculated using the expression:

$$\Delta r = \ln r_1/r_2 \tag{1}$$

This chemical heat was converted into calories (Q) by matching it with the resistance change caused by adding (to the system) a known amount of calories provided by a calibrated electrical heating circuit. The electrical calibration was performed after each experiment.

Extrapolation procedure. The heat of dilution from an initial concentration to infinite dilution, which is equal to but of opposite sign of the relative apparent molal heat content, ϕ_L, is not a directly measurable quantity. The experimental heat measured was a $_\Delta\phi_L$, the heat evolved going from an initial concentration to a finite final concentration. The extended Debye-Hückel limiting law was used to extrapolate the data to infinite dilution. The Debye-Hückel equation takes the form

$$\phi_L = \frac{\nu}{2} A_H |Z^+Z^-| I^{1/2}\left[(1 + I^{1/2})^{-1} - \frac{\sigma(I^{1/2})}{3}\right] + BI + CI^{3/2} \tag{2}$$

Jongenburger and Wood (*4*) have established the validity of the above equation for 1-1 electrolytes with a ϕ_L greater than −36 cal/mol at 0.1*m*. The 2-1 electrolytes with ϕ_L greater than 360 cal/mol at 0.1*m* obey Equation 2 at concentrations less than 0.1*m*. With a ϕ_L greater than 140 cal/mol, 1-2 electrolytes obeyed Equation 2 at concentrations less than 0.05*m*.

The extrapolation of 2-2 salts to infinite dilution using Equation 2 has never been shown to be valid (*5*). Robinson and Wallace (*14*) have indicated that agreement may be found if measurements are made in the very dilute region (below 0.05*m*). The extrapolation of $MgSO_4$ to infinite dilution was done using Equation 2 because it represented the best approximation presently available. The uncertainty present in the $MgSO_4$ data is larger for this reason.

The calorimeter used in this research was not capable of measuring the heat of dilution of salts below 0.1*m* with sufficient accuracy to be used in the extrapolation to infinite dilution. This necessitated the use of a multiple pipet sequence. This technique used three differently sized pipets at the same

Table II. Apparent Molal Heat Content, Cal/Mol

40°		50°		60°		70°		80°	
m	ϕ_L	*m*	ϕ_L	*m*	ϕ_L	*m*	ϕ_L	*m*	ϕ_L
				KCl					
0.1203	120.6			0.1268	175.0			0.1397	251.4
0.1917	129.0			0.5206	243.0			0.5514	372.0
0.4186	135.7			1.024	257.0			1.343	445.0
0.5809	128.7			1.213	269.0			1.975	474.5
0.8143	115.5			1.512	262.0			3.054	494.6
1.024	99.0			2.039	253.0			4.109	529.3
1.993	20.4			2.813	234.0				
2.965	−49.0			4.388	199.5				
4.388	−126.0								
				$MgCl_2$					
0.0723	573.6	0.0673	662.0	0.0673	780.0	0.0706	899.0	0.0652	986.0
0.1433	735.4	0.1380	850.0	0.1393	984.0	0.1398	1112.	0.1347	1241.
0.2811	932.0	0.2811	858.0	0.2811	1246.	0.3714	1578.	0.3433	1705.
0.4184	1083.	0.4096	1262.	0.4100	1466.	0.5706	1855.	0.5471	2034.
0.5551	1212.	0.5438	1428.	0.5459	1631.	0.6508	1945.	0.6914	2213.
0.6852	1325.	0.6749	1524.	0.6743	1785.	1.029	2384.	1.016	2595.
1.017	1669.	0.9604	1821.	0.9987	2130.	1.316	2688.	1.302	2940.
1.312	1856.	1.317	2135.	1.315	2452.	1.992	3363.	1.992	3682.
1.992	2336.	2.053	2683.	2.053	3059.				
				$MgSO_4$					
0.0991	1113.			0.1004	1730.			0.1027	2215.
0.3873	1387.			0.3996	2366.			0.4106	2771.
0.7980	1622.			0.6908	2711.			0.7751	3231.
1.002	1726.			0.9768	2917.			0.9768	3436.
1.493	1902.			1.654	3289.			1.953	4188.
1.968	2066.								
				Na_2SO_4					
0.1015	477.3								
0.1963	482.0			0.0736	722.5			0.0988	1226.
0.3830	407.0			0.1003	785.6			0.3703	1682.
0.5744	293.3			0.4360	993.0			0.7074	1887.
0.8000	167.7			0.6105	1003.			1.076	2027.
0.9451	76.3			0.9483	973.			1.595	2080.
1.003	50.5			1.601	909.8				
1.208	42.1								
1.504	173.5								

initial concentration. Three different $\Delta\phi_L$'s are obtained for the initial concentration going to different final concentrations. The $\Delta\phi_L$ from one final concentration to another final concentration can be obtained from the differences in the corresponding experimental $\Delta\phi_L$. This procedure was used by Ensor and Anderson. For all the salts under investigation, at least two multiple pipet sequences were done, generally at 0.2 and 0.6*m* which yielded extrapolation data from 0.06 to 0.005*m*.

The extrapolation of KCl and $MgCl_2$ was done using $\Delta\phi_L$ data derived from the multiple pipet sequence and experimental points at 0.1*m* or below. The extrapolation of Na_2SO_4 and $MgSO_4$ was done using $\Delta\phi_L$ data at 0.05*m* or less. The $\Delta\phi_L$ data along with the appropriate Debye-Hückel slope taken from Lewis and Randall (*8*) were substituted into Equation 2, and a least-squares computer program was used to obtain the best values of *B* and *C*. These values and the standard deviation of the extrapolation are contained in Table I. The ϕ_L of all experimental final concentrations was evaluated using the appropriate values of *B* and *C* in Equation 2. This value added to the experimentally determined $\Delta\phi_L$ yielded a ϕ_L for that particular initial concentration.

Results

The ϕ_L for $MgCl_2$ was measured at 40°, 50°, 60°, 70°, and 80°C over the concentration range 0.1–2.0*m*. A careful study of the $MgCl_2$ data and NaCl data previously done at this lab showed that the accuracy of the derived data was not significantly different using only ϕ_L at three temperatures (40°, 60°, and 80°C). Therefore, the ϕ_L of KCl, Na_2SO_4, and $MgSO_4$ were measured at 40°, 60°, and 80° over the concentration ranges 0.1–4.0*m*, 0.1–1.5*m*, and 0.1–2.0*m*, respectively. All experimentally measured ϕ_L's are found in Table II.

The accuracy of this present research depends on availability of very precise 25° data for each salt. Parker (*11*) has published accurate values of ϕ_L for KCl and Thompson et al. (*16*) have published ϕ_L values for Na_2SO_4 at 25°C. ϕ_L values available for $MgSO_4$ and $MgCl_2$ are not very satisfactory. Lange and Streeck (*6, 7*) have published ϕ_L for both salts up to 0.1*m*. Values in the more concentrated range available in NBS Circular 500 (*10*) were, in many cases, of questionable accuracy. A $\Delta\phi_L$ for $MgSO_4$ and for $MgCl_2$ was measured at 25°C in the concentration range 0.1–2.0*m* (Table III). These measurements were combined with the low concentration work of Lange and Streeck to obtain ϕ_L values.

A comparison of the NBS data and the data from this work was possible using a general equation developed by Wood (*17*) to describe the relationship between free energies of the cross-mixings in a reciprocal salt pair and the excess free energies of the component salts. This equation, when converted to heats of mixing and the corresponding excess heat content, takes the form

$$\Delta H_m\ (\mathrm{NaCl} - \mathrm{MgSO_4},\ E,\ y = 1/2) + E/2\ \mathrm{mol\ NaCl}\ [\phi_L\ (\mathrm{NaCl},\ m = E)] + E/4\ \mathrm{mol\ MgSO_4}\ [\phi_L (\mathrm{MgSO_4},\ m = E/2)] = \Delta H_m\ (\mathrm{MgCl_2} - \mathrm{Na_2SO_4},\ E,\ y = 1/2) + E/4\ \mathrm{mol}\ [\phi_L\ (\mathrm{MgCl_2})\ m = E/2] + E/4\ [\phi_L\ (\mathrm{Na_2SO_4})\ m = E/2] \quad (3)$$

where *E* is defined as the concentration in equivalents per kg of solvent. The difference (Δ) between the right and the left sides of Equation 3, when literature values for ΔH_{mix} and ϕ_L are substituted into it, is a measure of the consistency of the values. By use of the NBS values for the ϕ_L of $MgCl_2$ and $MgSO_4$, the Δ at $E = 1$ is 40.3 cal/mol and at $E = 3$, $\Delta =$ 197.0 cal/mol. By use of the ϕ_L data from this research, the Δ at $E = 1$ is 2.5 cal/mol and at $E = 3$ $\Delta = 3.0$ cal/mol. This

Table III. Heat of Dilution at 25°C

m_i	m_f	Q, cal	$\Delta\phi_L$, cal/mol	ϕ_{L_f}, cal/mol	ϕ_{L_i}, cal/mol
		$MgSO_4$			
0.1023	0.002323	0.3810	623.3	232.	855.3
0.1023	0.002341	0.3811	619.4	234.	853.4
				Average	854.4
0.3997	0.009036	1.512	635.8	521.	1157.
0.3997	0.008873	1.4823	636.2	517.	1153.
				Average	1155.
0.6908	0.01631	2.650	617.4	614.	1231.
0.6908	0.01673	2.704	613.5	619.	1233.
				Average	1232.
1.002	0.02424	3.870	606.4	695.	1301.
1.002	0.02339	3.769	612.4	690.	1302.
				Average	1302.
1.946	0.04526	8.351	701.1	798.	1499.
1.946	0.04468	8.228	700.2	796.	1496.
				Average	1498.
		$MgCl_2$			
0.06930	0.003295	0.2830	325.9	122.9	448.8
0.06930	0.003241	0.2794	327.4	121.8	449.2
0.06930	0.003211	0.2780	328.9	121.2	450.1
				Average	449.4
0.2763	0.006123	0.9050	562.7	163.2	725.9
0.2763	0.006305	0.9310	562.2	165.7	727.9
				Average	726.9
0.5635	0.01250	2.416	735.7	217.6	953.3
0.5635	0.01257	2.428	734.8	218.0	952.8
				Average	953.1
0.7128	0.01614	3.418	805.4	240.3	1046.
0.7128	0.01620	3.451	810.4	240.6	1051.
				Average	1049.
1.379	0.03282	9.921	1148.	321.3	1469.
1.379	0.03265	9.852	1146.	320.6	1467.
				Average	1468.
1.992	0.03216	13.090	1556.	319.	1875
1.992	0.04190	16.587	1514.	356.	1870
				Average	1873

Table IV. Apparent Molal Heat Content (Cal/Mol) Coefficients for $\phi_L = a + bm^{1/2} + cm + dm^{3/2}$

Temp, °C	*a*	*b*	*c*	*d*	*e*
		KCl (concn range 0.1–4.0*m*)			
40	37.952	358.01	−373.35	78.860	...
60	47.839	453.72	−292.28	52.607	...
80	45.167	684.23	−387.81	82.752	...
		$MgCl_2$ (0.1–2.0*m*)			
25	108.98	1486.3	−842.51	478.21	...
40	356.58	869.10	379.17	...	...
50	348.37	1264.1	253.93	...	...
60	394.17	1481.4	264.90	...	...
70	529.36	1418.3	414.08	...	...
80	641.21	1521.9	441.88	...	...
		$MgSO_4$ (0.1–2.0*m*)			
25	242.02	2645.4	−2453.1	861.78	...
40	824.61	921.67	−27.743	...	...
60	971.55	2594.2	−618.19	...	...
80	1641.3	1758.9	47.814	...	...
		Na_2SO_4 (0.1–2.0*m*)			
25	−11.507	2098.4	−5023.7	2680.6	−470.40
40	−378.64	4752.2	−7736.4	3439.4	...
60	194.82	2624.9	−2699.2	846.60	...
80	591.90	2315.3	−901.15	...	...

Table V. Activity Coefficients

M	25° (13)	40°	50°	60°	70°	80°
			KCl			
0.1	0.770	0.767	0.764	0.760	0.756	0.752
0.2	0.718	0.715	0.712	0.708	0.704	0.699
0.3	0.688	0.685	0.682	0.679	0.674	0.669
0.4	0.666	0.664	0.661	0.658	0.653	0.648
0.5	0.649	0.648	0.645	0.642	0.637	0.632
0.6	0.637	0.636	0.634	0.630	0.626	0.620
0.7	0.626	0.626	0.624	0.621	0.616	0.610
0.8	0.618	0.619	0.617	0.614	0.609	0.604
0.9	0.610	0.611	0.610	0.606	0.602	0.596
1.0	0.604	0.606	0.604	0.601	0.597	0.592
1.2	0.593	0.596	0.595	0.592	0.588	0.583
1.4	0.586	0.590	0.590	0.587	0.583	0.577
1.6	0.580	0.585	0.585	0.583	0.579	0.573
1.8	0.576	0.582	0.582	0.580	0.576	0.571
2.0	0.573	0.580	0.581	0.579	0.575	0.570
2.5	0.569	0.578	0.579	0.578	0.575	0.569
3.0	0.569	0.580	0.582	0.581	0.577	0.572
3.5	0.572	0.584	0.587	0.586	0.582	0.577
4.0	0.577	0.590	0.593	0.593	0.589	0.582
			$MgSO_4$			
	(12)					
0.1	0.161	0.153	0.148	0.142	0.135	0.129
0.2	0.116	0.109	0.105	0.0995	0.0943	0.0891
0.3	0.0945	0.0885	0.0841	0.0796	0.0750	0.0703
0.4	0.0817	0.0767	0.0727	0.0685	0.0643	0.0601
0.5	0.0730	0.0686	0.0650	0.0612	0.0573	0.0535
0.6	0.0666	0.0622	0.0587	0.0549	0.0511	0.0474
0.8	0.0579	0.0539	0.0506	0.0472	0.0436	0.0402
1.0	0.0524	0.0486	0.0455	0.0422	0.0389	0.0357
1.2	0.0490	0.0453	0.0423	0.0391	0.0359	0.0328
1.4	0.0469	0.0432	0.0403	0.0372	0.0340	0.0309
1.6	0.0457	0.0413	0.0384	0.0354	0.0324	0.0294
1.8	0.0451	0.0411	0.0382	0.0352	0.0320	0.0289
2.0	0.0451	0.0409	0.0380	0.0349	0.0318	0.0285
			$MgCl_2$			
	(13)					
0.1	0.528	0.517	0.509	0.500	0.492	0.483
0.2	0.488	0.475	0.466	0.456	0.446	0.435
0.3	0.476	0.461	0.450	0.439	0.427	0.415
0.4	0.474	0.457	0.445	0.432	0.419	0.406
0.5	0.480	0.461	0.448	0.433	0.419	0.404
0.6	0.490	0.469	0.454	0.438	0.422	0.406
0.7	0.505	0.482	0.465	0.448	0.430	0.412
0.8	0.521	0.495	0.477	0.458	0.438	0.419
0.9	0.543	0.514	0.494	0.473	0.452	0.431
1.0	0.569	0.537	0.515	0.492	0.468	0.445
1.2	0.630	0.591	0.563	0.535	0.507	0.480
1.4	0.708	0.659	0.626	0.592	0.559	0.526
1.6	0.802	0.740	0.700	0.659	0.619	0.579
1.8	0.914	0.839	0.789	0.740	0.693	0.646
2.0	1.051	0.957	0.897	0.838	0.781	0.725
			Na_2SO_4			
	(13)					
0.1	0.445	0.441	0.436	0.430	0.423	0.415
0.2	0.365	0.363	0.360	0.355	0.348	0.341
0.3	0.320	0.320	0.318	0.313	0.307	0.300
0.4	0.289	0.291	0.289	0.286	0.280	0.273
0.5	0.266	0.269	0.268	0.264	0.259	0.253
0.6	0.248	0.252	0.251	0.248	0.244	0.237
0.7	0.233	0.238	0.238	0.235	0.231	0.225
0.8	0.221	0.226	0.226	0.224	0.220	0.214
0.9	0.210	0.215	0.216	0.213	0.210	0.204
1.0	0.201	0.207	0.208	0.206	0.202	0.197
1.2	0.186	0.192	0.194	0.192	0.189	0.184
1.4	0.175	0.182	0.183	0.182	0.179	0.175
1.6	0.165	0.172	0.173	0.173	0.170	0.166

Table VI. Osmotic Coefficients

M	25° (13)	40°	50°	60°	70°	80°
			KCl			
0.1	0.927	0.926	0.925	0.924	0.924	0.923
0.2	0.913	0.913	0.912	0.911	0.910	0.908
0.3	0.906	0.906	0.906	0.905	0.904	0.902
0.4	0.902	0.903	0.903	0.902	0.901	0.899
0.5	0.899	0.901	0.901	0.900	0.899	0.898
0.6	0.898	0.900	0.901	0.900	0.899	0.897
0.7	0.897	0.900	0.900	0.900	0.899	0.898
0.8	0.897	0.900	0.901	0.901	0.900	0.899
0.9	0.897	0.901	0.902	0.902	0.901	0.900
1.0	0.897	0.902	0.903	0.903	0.902	0.901
1.2	0.899	0.905	0.906	0.907	0.906	0.905
1.4	0.901	0.908	0.910	0.911	0.911	0.910
1.6	0.904	0.911	0.914	0.915	0.915	0.914
1.8	0.908	0.916	0.919	0.920	0.920	0.920
2.0	0.912	0.921	0.924	0.926	0.926	0.925
2.5	0.924	0.934	0.938	0.940	0.941	0.940
3.0	0.937	0.948	0.953	0.955	0.955	0.955
3.5	0.950	0.962	0.966	0.969	0.969	0.968
4.0	0.965	0.977	0.981	0.984	0.984	0.982
			Na_2SO_4			
0.1	0.793	0.793	0.792	0.790	0.787	0.783
0.2	0.753	0.757	0.756	0.755	0.752	0.748
0.3	0.725	0.732	0.732	0.731	0.730	0.726
0.4	0.705	0.715	0.718	0.718	0.716	0.712
0.5	0.690	0.702	0.706	0.707	0.705	0.701
0.6	0.678	0.693	0.698	0.700	0.699	0.695
0.7	0.667	0.684	0.690	0.692	0.691	0.688
0.8	0.658	0.675	0.682	0.685	0.684	0.681
0.9	0.650	0.668	0.673	0.676	0.675	0.672
1.0	0.642	0.659	0.664	0.665	0.664	0.661
1.2	0.631	0.651	0.659	0.662	0.663	0.661
1.4	0.625	0.646	0.655	0.660	0.662	0.659
			$MgSO_4$			
0.1	0.606	0.596	0.589	0.583	0.576	0.570
0.2	0.562	0.552	0.543	0.534	0.525	0.516
0.3	0.540	0.530	0.521	0.511	0.500	0.490
0.4	0.529	0.519	0.509	0.498	0.486	0.474
0.5	0.522	0.512	0.501	0.489	0.476	0.462
0.6	0.518	0.508	0.497	0.484	0.470	0.455
0.7	0.517	0.506	0.495	0.481	0.466	0.451
0.8	0.518	0.507	0.496	0.482	0.466	0.450
0.9	0.520	0.509	0.497	0.483	0.466	0.449
1.0	0.525	0.513	0.501	0.486	0.470	0.452
1.2	0.542	0.529	0.517	0.502	0.484	0.465
1.4	0.567	0.552	0.540	0.525	0.508	0.486
1.6	0.597	0.580	0.568	0.553	0.535	0.513
1.8	0.630	0.610	0.598	0.583	0.566	0.543
2.0	0.666	0.641	0.624	0.605	0.584	0.559
			$MgCl_2$			
0.1	0.861	0.856	0.853	0.849	0.845	0.841
0.2	0.877	0.870	0.865	0.860	0.854	0.848
0.3	0.895	0.887	0.880	0.873	0.866	0.858
0.4	0.919	0.909	0.901	0.893	0.884	0.875
0.5	0.947	0.936	0.927	0.917	0.907	0.897
0.6	0.976	0.963	0.953	0.942	0.931	0.920
0.7	1.004	0.989	0.978	0.967	0.954	0.942
0.8	1.036	1.020	1.008	0.995	0.982	0.968
0.9	1.071	1.054	1.040	1.026	1.012	0.997
1.0	1.108	1.089	1.075	1.060	1.044	1.028
1.2	1.184	1.162	1.146	1.129	1.111	1.093
1.4	1.264	1.238	1.220	1.202	1.182	1.162
1.6	1.347	1.318	1.298	1.278	1.257	1.234
1.8	1.434	1.401	1.379	1.357	1.335	1.310
2.0	1.523	1.486	1.463	1.439	1.415	1.389

Table VII. Experimental Uncertainties in ϕ_L, Cal/Mol

	$MgCl_2$	KCl	Na_2SO_4	$MgSO_4$
40°	±10	±3	±5	±16
50°	±8			
60°	±8	±3	±6	±16
70°	±9			
80°	±10	±3	±10	±17

	Derived activity coeff[a]	Derived osmotic coeff[a]
$MgCl_2$	±0.002	±0.002
KCl	±0.001	±0.001
Na_2SO_4	±0.002	±0.002
$MgSO_4$	±0.0009	±0.003

[a] Does not take into account uncertainties present in 25° data.

would indicate that the data from this research were more reliable.

Data treatment. The ϕ_L for all salts at each temperature was fitted to a polynomial equation of the type

$$\phi_L = a + bm^{1/2} + cm + dm^{3/2} \ldots \quad (4)$$

This was accomplished using a FORTRAN computer program (*2*). The coefficients of the above fits can be found in Table IV.

The relative partial molal heat content of the solvent and solute, $\bar{L}_1$, $\bar{L}_2$, were calculated from ϕ_L values using Equations 5 and 6.

$$\bar{L}_2 = \phi_L + \frac{m}{2}^{1/2}(\partial\phi_L/\partial m^{1/2}) \quad (5)$$

$$\bar{L}_1 = -MW_1 m^{3/2}/2000(\partial\phi_L/\partial m^{1/2}) \quad (6)$$

The partial molal heat contents were then fitted as a function of temperature at even molalities using polynomial equations of the type

$$\bar{L}_2 = f + qT + hT^2 \ldots \quad (7)$$

$$\bar{L}_1 = M + NT + PT^2 \quad (8)$$

The mean activity coefficient for any salt can be related to $\bar{L}_2$ using the following equation:

$$\int d \ln \gamma = \int -\bar{L}_2/\nu RT^2 dT \quad (9)$$

When Equation 7 is substituted into Equation 9 and integrated from a reference temperature (25°C in this research) to any desired temperature, the following equation is obtained:

$$\ln \gamma(m) = \ln \gamma(m)^{T_R} - \frac{1}{\nu R}\left[f\left(\frac{1}{T_R} - \frac{1}{T}\right) + q\left(\ln \frac{T}{T_R}\right) + h\,(T - T_R)\right] \quad (10)$$

The mean activity coefficients for all salts under investigation were calculated using Equation 10 and are contained in Table V. The 25°C data were from Pitzer (*12*) and Robinson and Stokes (*13*).

The osmotic coefficients were derived in a similar manner.

$$\int d\phi = \int 1000\,\bar{L}_1/MW_1RT^2\nu m dT \quad (11)$$

$$\phi = \phi^{T_R} + \frac{-1000}{MW_1R\nu m}\left[M\left(\frac{1}{T_R} - \frac{1}{T}\right) + N\left(\ln \frac{T}{T_R}\right) + P\,(T - T_R)\right] \quad (12)$$

The integrated form (Equation 12) of Equation 11 was derived using Equation 8. A list of osmotic coefficients for each salt calculated in this manner is found in Table VI. The 25°C data were taken from ref. *12*.

The reliability of the values published from this research can only be estimated from uncertainties present in experimental data and inherent in the treatment of data. The uncertainty in the ϕ_L for each salt can be calculated by combining the uncertainty in the extrapolation with the uncertainty present in the experimental measurement. Uncertainties for each salt are found in Table VII. With the above uncertainties and taking into account the average magnitude of the correction terms in Equations 10 and 12, the uncertainties of the osmotic and activity coefficients can be calculated. These uncertainties are contained in Table VII.

Acknowledgment

The authors thank John R. Jezorek and Robert H. Wood for helpful suggestions and discussion concerning the completion of this work.

Nomenclature

A_H = Debye-Hückel limiting slope
I = ionic strength
ϕ_L = relative apparent molal heat content
$\bar{L}_1$, $\bar{L}_2$ = relative partial molal heat contents of the solvent, solute
m = molality (concentration in mol/1000 grams of solvent)
n = number of moles
MW_1 = molecular weight of H_2O
Q = experimental heat in calories
R = universal gas constant
r = resistance
T = absolute temperature
T_R = reference temperature
ν^{+-} = total number of ions
ϕ = osmotic coefficient
γ = activity coefficient
$\sigma(I^{1/2}) = 3(I^{1/2})^{-3}\,[1 + I^{1/2} - 2\ln(1 + I^{1/2} - 1/1 + I^{1/2})]$
Z^+Z^- = valence of ion indicated
y = mole fraction

Literature Cited

(1) Anderson, H. L., Petree, L. A., *J. Phys. Chem.*, **74**, 1455 (1970).
(2) Ensor, D. D., Anderson, H. L., *J. Chem. Eng. Data*, **18**, 205 (1973).
(3) Gardner, E. R., *Trans. Faraday Soc.*, **65**, 91 (1969).
(4) Jongenburger, H. S., Wood, R. H., *J. Phys. Chem.*, **69**, 4231 (1965).
(5) Lange, E., "The Structure of Electrolyte Solutions," W. J. Hamer, Ed., Chap. 9, Wiley, New York, NY, 1959.
(6) Lange, E., Streeck, H., *Z. Phys. Chem.*, **152A**, 1 (1931).
(7) Lange, E., Streeck, H., *ibid.*, **157A**, 1 (1931).
(8) Lewis, G. N., Randall, M., Rev. by Pitzer, K. S., Brewer, L., "Thermodynamics," 2nd ed., McGraw-Hill, New York, NY, 1961.
(9) Lindsay, W. T., Lui, C.-T., *J. Phys. Chem.*, **75**, 3723 (1971).
(10) NBS "Selected Values of Chemical Thermodynamic Properties," *Nat. Bur. Stand. Circ.*, No. 500 (1952).
(11) Parker, V. B., National Standard Reference Data System–National Bureau of Standards NBRDS-NBS **2**, 10 (1965).
(12) Pitzer, K. S., *J. Chem. Soc.* (*Faraday II*), **68**, 101 (1972).
(13) Robinson, R. A., Stokes, R. H., "Electrolyte Solutions," 2nd rev. ed., Butterworths, London, England, 1965.
(14) Robinson, A. L., Wallace, W. E., *J. Am. Chem. Soc.*, **63**, 1582 (1941).
(15) Soldano, B., Bien, P., *J. Chem. Soc. A*, **12**, 1825 (1966).
(16) Thompson, P. T., Smith, D. E., Wood, R. H., *J. Chem. Eng. Data*, **19**, 386 (1974).
(17) Wood, R. H., University of Delaware, Newark, Del., private communications, 1974.

Received for review September 26, 1974. Accepted February 24, 1975. Support of this work by the Office of Saline Water, U.S. Department of the Interior, and the Research Council, the University of North Carolina at Greensboro, is gratefully acknowledged.