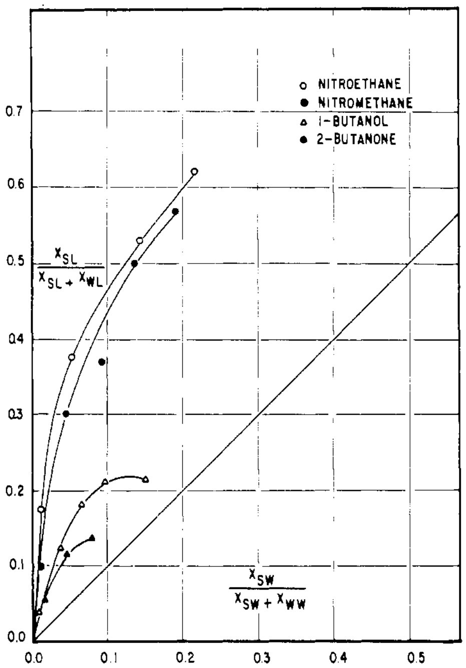

Figure 4. Selectivity curve for acrylamide at 25°C

Nomenclature

B = selectivity = $S_{SL} \cdot X_{WW}/X_{SW} \cdot X_{WL}$ = $(X_{WW}/X_{WL}) \cdot K$
K = distribution coefficient = X_{SL}/X_{SW}
X = concentration of a component in solution in weight fraction

Subscripts

L = liquid
S = solute, acrylamide
SL = solute S in solvent-rich phase L
SW = solute S in water-rich phase W
W = water
WL = water W in solvent-rich phase L
WW = water W in water-rich phase W

Literature Cited

(1) American Cyanamid Co, N.J., technical bulletin on the chemistry of acrylamide, 1965.
(2) Critchfield, F. E., Funk, G. L., Johnson, J. B., *Anal. Chem.* **28**, 76 (1956).
(3) Norris, M. V., "Encyclopedia of Industrial Chemical Analysis," Vol. 4, pp 160-8, Wiley, New York, N.Y., 1967.
(4) Treybal, R. E., "Liquid Extraction," 2nd ed., pp 14-155, McGraw-Hill, New York, N.Y., 1963.

Received for review August 31, 1972. Accepted December 16, 1972.

Heats of Dilution of NaCl: Temperature Dependence

Dale D. Ensor[1] **and Henry L. Anderson**[2]
Department of Chemistry, University of North Carolina at Greensboro, Greensboro, N.C. 27412

The heats of dilution of aqueous NaCl were measured over a concentration range of 0.1–6.0*m* at 40°, 50°, 60°, 70°, and 80°C. The relative partial molal heat contents of solute and solvent were calculated from the experimental heats of dilution. These values were used to extend by calculation existing activity and osmotic coefficients to higher temperatures. These calculated values were found to be in excellent agreement with existing data. It is concluded that the use of heat of dilution data to correct existing values of thermodynamic quantities to higher temperatures is an efficient and very precise technique.

The thermodynamic properties of aqueous electrolyte solutions have been under investigation for many years. The subject of many of these investigations was to prove the validity of the Debye-Hückel limiting law; therefore, it is not surprising that extensive data exist for 1–1 electrolytes at 25°C *(7, 14)*. In recent years aqueous electrolyte solutions have received much attention due to the interest in obtaining potable water from sea water. Most methods now under investigation for desalination of sea water involve high temperature processes. The thermodynamic behavior of aqueous electrolyte solutions must be well characterized at temperatures above 25°C in order for such processes to be both economical and efficient. However, very few precise data exist at such temperatures.

This lack of high temperature thermodynamic data is understandable in view of the experimental difficulties encountered in the direct measurement of thermodynamic parameters such as electromotive force, vapor pressure lowering, and boiling point elevation. The logical choice for obtaining high temperature data is to extend by calculation the existing thermodynamic properties at some reference temperature to the desired temperature using heat capacity data. However, this procedure is also limited. Eigen and Wicke *(4)* have measured heat capacities of a number of 1–1 aqueous electrolytes over a large temperature range. Ackermann *(1)*, using the data of the above study, published apparent molal heat capacity as a function of temperature. Unfortunately, the experimental method used by Eigen and Wicke and Ackermann did not allow them to make measurements below 0.4*m* or above 2.0*m*. Therefore, the attempt to obtain the partial molal heat capacity of the solute at infinite dilution, $C\bar{p}_2°$, by extrapolation of the ΦCp data was not accurate. Criss and Cobble *(3)* have published an extensive list of $C\bar{p}_2°$ values over a wide temperature range obtained using the integral heat method. However, this provides only the limiting values and does not yield thermodynamic data in real concentration ranges.

The present investigation was based upon the proposition that the measurement of heats of dilution as a function of temperature and concentration is an efficient way of obtaining the desired heat capacity data. The relative apparent heat content, ΦL, which is equal to and of opposite sign to that of heat of dilution, can be related to heat capacity functions in the following manner:

---

[1] To whom correspondence should be addressed.
[2] Deceased.

$$\bar{L}_2 = \Phi L + \frac{\sqrt{m}}{2} \, \partial \Phi L / \partial \sqrt{m} \quad (1)$$

$$\bar{J}_2 = \partial \bar{L}_2 / \partial \mathrm{T} \quad (2)$$

$$C\bar{p}_2 - C\bar{p}_2{}^\circ = \bar{J}_2 \quad (3)$$

It should then be possible to extend existing osmotic and activity coefficients at 25°C to higher temperatures by calculations using the heat content data derived from experimental measurements.

The decision to use NaCl as the 1-1 electrolyte in this study was based upon several factors. The most important was that an adequate amount of high temperature data was available to check the consistency of the values derived in this research. Secondly, NaCl is used as a standard 1-1 electrolyte in many comparative thermodynamic studies.

Experimental

Solutions. A near-saturated stock solution of doubly recrystallized Baker analyzed reagent NaCl was prepared and stored in polyethylene bottles. All other solutions were made by diluting a known weight of stock solution with a known weight of deionized water. The molality of the stock solution was checked every 2 months and was found to vary no more than 0.02% over a 6-month period.

Calorimeter. The heats of dilution of NaCl were measured using only one side of a previously described double calorimeter with microdegree sensitivity *(2, 13)*. The amount of heat evolved when a known amount of NaCl solution was diluted in a known amount of deionized water was monitored as resistance change using a 10-kohm thermistor incorporated in a Wheatstone bridge. This chemical heat was converted into calories *(Q)* by matching it with the resistance change caused by adding a known amount of heat to the system provided by a calibrated heat circuit. The $\Delta\Phi L$ for each experiment was then calculated using the following relationship *(2, 13)*.

$$\Delta\Phi L = Q/n, \text{ cal/mol} \quad (4)$$

The calorimeter was not capable of measuring the heats of dilution below $0.1m$ with sufficient accuracy for use in extrapolating the data to infinite dilution. This necessitated the use of a so called "multiple pipet sequence" to secure the data necessary for a precise extrapolation to infinite dilution. Three different sized Pyrex pipets (6, 10, 18 cc) were used, similar to the one described by Anderson and Petree *(2)*. The heats of opening of the pipets were checked at each operating temperature. These heats varied between 0.000 and 0.004 cal according to the pipet used and the temperature at which the measurements were made.

The use of the three pipets resulted in three different $\Delta\Phi L$ values for the dilution of the same initial concentration to three different final concentrations. Therefore, a $\Delta\Phi L$ value for one final concentration to another final concentration could be obtained from the differences in the experimental $\Delta\Phi L$. Table I contains the data from an actual multiple pipet sequence obtained in this study. To generate a descriptive extrapolation curve, it was necessary to use the multiple pipet sequence at 0.2 and $0.8m$ in conjunction with two experimental measurements at $0.1m$. This procedure yielded an extrapolation curve of at least 26 data points covering the concentration range 0.1 to $0.004m$.

Calculations

Extrapolation Procedure. The heat of dilution from an initial concentration to the reference state of infinite dilution is not a measurable quantity, so what is actually measured is the heat evolved in going from an initial to a final finite concentration, $\Delta\Phi L$. The extended Debye-Hückel equation for 1-1 electrolytes was used to calculate the ΦL of the finite final concentration going to infinite dilution.

$$\Phi L = A_H m^{1/2}[1/(1 + Am^{1/2}) - \sigma(Am^{1/2})/3] + Bm + Cm^{3/2} \quad (5)$$

Guggenheim and Prue *(5)* and Owen and Brinkley *(11)* have shown the equation without the C parameter to be valid for NaCl up to $0.1m$. More recently, Jongenburger and Wood *(9)* have established that the equation is valid for 1-1 electrolytes with a heat of dilution greater than −36 cal/mol at $0.1m$.

The $\Delta\Phi L$ data derived from multiple pipet sequences at 0.2 and $0.8m$ had initial concentrations of less than $0.1m$. These data plus experimental data using an initial concentration of $0.1m$ were substituted into Equation 5 and a least squares computer program was used to obtain the best values of B and C. The results of the extrapolation fit for each experimental temperature are given in Table II. This method is similar to that previously used by Jongenburger and Wood. The ΦL of all experimental final

TABLE I. Multiple Pipet Sequence Technique Used for Extrapolation

m_i	m_f	$\Delta\Phi L$, cal/mol
	Experimental Data	
0.1997	0.01484	107.57
0.1997	0.01486	108.02
0.1997	0.008596	122.47
0.1997	0.008160	125.13
0.1997	0.004873	141.34
0.1997	0.004764	140.27
	Derived Data Used in Extrapolation	
0.01484	0.008596	14.9
0.01484	0.008160	17.56
0.01484	0.004873	33.77
0.01484	0.004764	32.7
0.01486	0.008596	14.45
0.01486	0.008160	17.11
0.01486	0.004873	33.32
0.01486	0.004764	32.25
0.008596	0.004873	18.87
0.008596	0.004764	17.80
0.008160	0.004873	16.21
0.008160	0.004764	15.14

TABLE II. Coefficients from Least-Squares Fit of $\Delta\Phi L$ for Debye-Hückel Extrapolation Equation

Temp., °C	Debye-Hückel limiting slope	B	C	Std. dev.	No. of data points
40	856.0	−639.77	1221.10	1.75	46
50	982.0	377.98	−2137.69	1.41	29
60	1122.0	−603.38	1140.31	1.74	30
70	1277.0	−2043.11	5779.84	1.75	26
80	1450.0	−281.23	484.35	1.53	26

concentrations was evaluated by substitution of the B and C values obtained from the computer fit of the extrapolation data into Equation 5. This value, added to the experimentally determined $\Delta\Phi L$, yielded the ΦL for that particular initial concentration.

Data Treatment and Results

The ΦL of NaCl was measured at 40°, 50°, 60°, 70°, and 80°C over the concentration range 0.1-6.0m (Table III). The reliability of the thermodynamic quantities which can be derived from the experimental data, $\bar{L}_2$, $\bar{J}_2$, activity coefficients (γ), and osmotic coefficients (ϕ), depends largely upon the accuracy with which the slope of ΦL vs. $m^{1/2}$ curves ($\partial\Phi L/\partial m^{1/2}$) can be determined. A previous method used by Gulbransen and Robinson to evaluate the slope of experimental ΦL vs. $m^{1/2}$ curves utilized large scale plots *(6)*. A more recent technique is the chord-area method developed by Young and co-workers *(17, 18)*. Both of these methods were unsuitable for the present study, since the method of data collection necessitated the drawing of smoothed curves through large chords or widely spaced data points. Therefore, it was decided to fit the ΦL data to a polynomial equation of the type

$$\Phi L = a + bm^{1/2} + cm + dm^{3/2} \cdots \qquad (6)$$

TABLE III. Heat of Dilution of NaCl

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
		At 40°C			
0.07390	0.005390	0.10215	75.39	36.08	111.47
0.07390	0.00550	0.1035	74.65	37.08	111.73
0.07390	0.00300	0.06265	82.87	28.31	111.18
0.07390	0.00303	0.06066	79.51	29.44	108.95
0.07390	∞			Av.	110.83
0.1086	0.008206	0.1706	82.50	44.08	126.58
0.1086	0.008124	0.1650	80.64	43.89	124.54
0.1086	0.004574	0.10662	92.23	34.19	126.42
0.1086	0.004573	0.10436	90.32	34.19	124.51
0.1086	0.002727	0.06644	96.58	27.11	123.69
0.1086	0.002731	0.06480	94.03	27.13	121.16
0.1086	∞			Av.	124.48
0.2005	0.004877	0.14128	99.2	34.70	133.90
0.2005	0.004840	0.13594	100.35	34.59	134.94
0.2005	0.008314	0.19472	92.77	43.59	136.36
0.2005	0.008239	0.19172	92.21	43.43	135.64
0.2005	0.01458	0.28971	79.09	54.88	133.97
0.2005	0.01475	0.30030	80.95	55.14	136.09
0.2005	∞			Av.	135.2
0.3995	0.01660	0.39171	91.07	57.80	148.87
0.3995	0.01641	0.3732	90.05	57.54	147.59
0.3995	0.01627	0.35465	86.41	57.34	143.76
0.3995	∞			Av.	146.7
0.5982	0.02429	0.4583	74.12	67.08	141.20
0.5982	0.02470	0.4498	72.05	67.52	139.57
0.5982	0.02326	0.4422	75.51	65.97	141.48
0.5982	∞			Av.	140.8
0.8000	0.05803	0.51579	35.38	93.63	129.01
0.8000	0.05820	0.52570	35.94	93.74	129.68
0.8000	0.03181	0.42774	53.35	74.39	127.74
0.8000	0.03217	0.44399	54.75	74.71	129.46
0.8000	0.01896	0.32513	68.06	60.91	128.97
0.8000	0.01952	0.33966	69.00	61.61	130.61
0.8000	∞			Av.	129.2
0.9503	0.02284	0.29362	51.01	65.50	116.51
0.9503	0.02238	0.28649	50.82	64.99	115.81
0.9503	∞			Av.	116.2
1.505	0.03681	−0.02622	−2.82	78.65	75.83
1.505	0.03532	−0.02399	−2.70	77.42	74.72
1.505	∞			Av.	75.3
2.193	0.05066	−0.81822	−64.14	88.84	24.70
2.193	0.04907	−0.7855	−63.61	87.76	24.15
2.193	∞			Av.	24.4
2.948	0.06815	−1.9756	−120.15	99.76	−20.39
2.948	0.06871	−2.0995	−121.31	100.09	−21.22
2.948	∞			Av.	−20.8
4.081	0.09355	−4.2605	−180.89	113.80	−67.09
4.081	0.09151	−4.0993	−178.01	112.71	−65.30
4.081	∞			Av.	−74.0
		At 40°C			
5.010	0.1161	−5.8175	−198.92	125.53	−73.39
5.010	0.1116	−5.5245	−197.74	123.20	−74.54
5.010	∞			Av.	−74.00
6.078	0.1231	−5.9043	−190.96	129.13	−61.83
6.078	0.1302	−6.3082	−192.67	133.02	−59.65
6.078	∞			Av.	−60.7
		At 50°C			
0.09979	0.004030	0.09679	95.62	40.64	136.26
0.09979	0.004023	0.09405	93.09	40.61	133.70
0.09979	0.007446	0.16474	88.62	54.40	143.12
0.09979	∞			Av.	137.69
0.1997	0.008596	0.26551	122.47	58.30	180.77
0.1997	0.008160	0.25657	125.13	56.90	182.03
0.1997	0.001484	0.39832	107.57	74.85	182.42
0.1997	0.001486	0.40063	108.02	74.89	182.91
0.1997	0.004873	0.17298	141.34	44.54	185.88
0.1997	0.004764	0.16774	140.27	44.04	184.31
0.1997	∞			Av.	183.05
0.5964	0.01372	0.4932	143.34	72.26	215.60
0.5964	0.01362	0.4961	145.28	72.03	217.31
0.5964	∞			Av.	216.45
0.8025	0.05916	1.3594	91.75	126.49	218.24
0.8025	0.05792	1.3560	93.63	125.77	219.40
0.8025	0.03233	0.9393	115.71	103.63	219.34
0.8025	0.03208	0.93368	115.91	103.31	219.22
0.8025	0.01923	0.64319	133.22	83.85	217.07
0.8025	0.01881	0.64459	136.59	83.06	219.65
0.8025	∞			Av.	218.82
1.125	0.02499	0.79217	126.49	93.59	220.08
1.125	0.02713	0.8116	119.17	96.76	215.93
1.125	∞			Av.	218.00
1.503	0.03615	0.88484	97.49	108.02	205.51
1.503	0.03615	0.88428	97.43	108.02	205.45
1.503	∞			Av.	205.48
1.995	0.04732	0.73554	61.94	118.48	180.42
1.995	0.04564	0.71396	62.39	117.11	179.50
1.995	∞			Av.	179.96
2.996	0.07035	0.41559	23.55	131.81	155.36
2.996	0.06515	0.38921	23.85	129.58	153.43
2.996	∞			Av.	154.40
4.226	0.09209	0.01781	−0.77	137.29	136.52
4.226	0.09131	0.02038	−0.89	137.19	136.30
4.226	∞			Av.	136.41
5.012	0.1126	0.04360	−1.54	137.80	136.26
5.012	0.1114	0.03088	−1.11	137.88	136.77
5.012	∞			Av.	136.51
5.718	0.1237	0.29673	9.61	136.50	146.11
5.718	0.1264	0.39839	12.57	136.04	148.61
5.718	∞			Av.	147.36

(Continued on page 208)

TABLE III. ***Continued***

m_i	m_f	Q	$\Delta\Phi L$	ΦL^f	ΦL^i
		At 60°C			
0.1023	0.007562	0.2107	111.22	57.25	168.47
0.1023	0.007519	0.2086	110.77	57.10	167.87
0.1023	∞			Av.	168.17
0.2041	0.01510	0.5223	138.11	77.19	215.30
0.2041	0.01458	0.5099	139.98	76.06	216.04
0.2041	0.008312	0.3233	154.85	59.68	214.53
0.2041	0.008327	0.3246	155.25	59.73	214.98
0.2041	0.004717	0.2043	172.71	46.35	219.06
0.2041	0.004791	0.2065	171.81	46.69	218.50
0.2041	∞			Av.	216.40
0.4005	0.01643	0.7028	170.24	80.00	250.24
0.4005	0.01575	0.6749	170.73	78.59	249.32
0.4005	∞			Av.	249.78
0.6035	0.01475	0.7295	196.97	76.44	273.41
0.6035	0.01464	0.7236	196.76	76.19	272.95
0.6035	∞			Av.	273.19
0.8014	0.05926	2.1918	147.63	134.92	282.55
0.8014	0.05812	2.1684	149.15	133.87	283.02
0.8014	0.03234	1.4537	178.96	105.76	284.72
0.8014	0.03233	1.4544	179.09	105.75	284.84
0.8014	0.01956	0.9494	193.28	86.05	279.33
0.8014	0.01789	0.9068	202.24	82.90	285.14
0.8014	∞			Av.	283.27
0.9885	0.02365	1.1836	202.72	93.08	295.80
0.9885	0.02336	1.1806	201.40	92.61	294.01
0.9885	∞			Av.	294.91
1.497	0.03359	1.6439	194.07	107.40	301.47
1.497	0.03607	1.7355	191.63	110.52	302.16
1.497	∞			Av.	301.81
1.998	0.04482	2.0050	178.49	120.61	299.10
1.998	0.04540	2.0299	178.35	121.24	299.59
1.998	∞			Av.	299.34
2.991	0.06920	2.7686	159.51	143.66	303.17
2.991	0.06710	2.7597	162.24	141.83	304.07
2.991	∞			Av.	303.61
3.957	0.09099	3.4475	151.09	160.84	311.93
3.957	0.08601	3.3187	154.07	157.09	311.16
3.957	∞			Av.	311.54
4.873	0.1061	4.6661	175.64	171.73	347.37
4.873	0.1099	4.7190	171.36	174.43	345.79
4.873	∞			Av.	346.57
5.718	0.1222	6.454	210.98	182.77	393.75
5.718	0.1291	6.5376	202.10	187.38	389.48
5.718	∞			Av.	391.62
		At 70°C			
0.1002	0.007347	0.25390	138.63	57.21	195.84
0.1002	0.007458	0.25659	137.85	57.54	195.39
0.1002	∞			Av.	195.61
0.1957	0.007944	0.38430	192.59	58.99	251.58
0.1957	0.004676	0.23850	204.03	47.67	251.70
0.1957	0.004707	0.23955	203.56	47.77	251.33
0.1957	0.007824	0.37849	192.69	58.65	251.34
0.1957	0.01424	0.6165	173.77	74.01	247.78
0.1957	0.01415	0.6075	172.39	73.83	246.22
0.1957	∞			Av.	250.00
0.4005	0.01594	0.88225	220.45	77.30	297.75
0.4005	0.01607	0.88530	219.38	77.54	296.92
0.4005	∞			Av.	297.33
0.6035	0.02388	1.4096	236.27	90.51	326.78
0.6035	0.02362	1.3976	236.94	90.12	327.06
0.6035	∞			Av.	326.92
0.7998	0.01884	1.2143	257.92	82.46	340.38
0.7998	0.01847	1.1958	259.27	81.83	341.10
0.7998	0.05843	2.9735	204.19	136.37	340.56
0.7998	0.03187	1.9478	243.54	111.93	345.45
0.7998	0.03282	1.9721	239.10	103.22	343.32
0.7998	0.05815	2.9756	205.40	136.74	342.14
0.7998	∞			Av.	341.99
0.9997	0.02398	1.6156	269.58	90.67	360.25
0.9997	0.02457	1.6603	240.25	91.55	361.80
0.9997	∞			Av.	361.03
1.432	0.03385	2.2547	269.22	104.61	373.83
1.432	0.03447	2.2987	267.86	105.44	373.30
1.432	∞			Av.	373.57
2.003	0.04876	3.4531	284.32	124.11	408.43
2.003	0.04828	3.3901	282.05	123.49	405.54
2.003	0.04863	3.4567	285.34	123.94	409.28
2.003	∞			Av.	407.75
2.966	0.06896	4.8725	284.16	150.9	435.06
2.966	0.06801	4.9873	295.10	149.60	444.70
2.966	0.06536	4.6671	284.38	146.00	433.38
2.966	∞			Av.	437.68
5.023	0.05548	5.5183	404.86	132.87	537.73
5.023	0.05977	5.9370	404.23	138.52	542.75
5.023	∞			Av.	540.24
5.718	0.06582	7.0894	438.16	146.62	584.78
5.718	0.06269	6.8516	444.62	142.41	587.03
5.718	∞			Av.	585.91
		At 80°C			
0.1002	0.007467	0.3092	166.51	76.67	243.18
0.1002	0.007486	0.3084	165.74	76.74	242.48
0.1002	∞			Av.	242.83
0.2017	0.004953	0.3009	243.91	63.39	307.29
0.2017	0.005053	0.3065	243.42	63.99	307.41
0.2017	0.01489	0.7385	199.64	104.81	304.45
0.2017	0.01503	0.7508	200.01	105.24	305.25
0.2017	0.008100	0.4448	224.22	79.58	303.80
0.2017	0.008252	0.4535	221.46	80.26	301.72
0.2017	∞			Av.	304.99
0.4005	0.01630	1.0261	252.66	109.10	361.75
0.4005	0.01662	1.1218	250.69	110.15	360.74
0.4005	∞			Av.	361.25
0.6035	0.02497	1.7165	275.89	131.56	407.45
0.6035	0.02499	1.7155	276.45	131.60	408.05
0.6035	∞			Av.	407.75
0.7991	0.05803	3.7815	262.73	190.00	450.72
0.7991	0.05920	3.8490	266.73	189.56	451.29
0.7991	0.01908	1.5828	333.29	116.97	450.26
0.7991	0.01962	1.6261	332.67	118.42	451.08
0.7991	0.03293	2.4672	301.58	148.19	449.77
0.7991	0.02952	2.2316	306.15	141.41	447.56
0.7991	∞			Av.	450.11
0.9997	0.02488	2.1577	347.99	131.35	479.34
0.9997	0.02444	2.1355	350.55	130.33	481.18
0.9997	∞			Av.	480.26
1.432	0.03510	3.0776	352.01	152.27	504.28
1.432	0.03402	2.9240	345.32	150.26	495.58
1.432	∞			Av.	499.93
2.010	0.04442	3.9890	362.90	168.20	531.09
2.010	0.04505	2.9814	357.05	169.19	526.24
2.010	∞			Av.	528.67
3.965	0.05176	6.1695	486.17	179.29	665.46
5.023	0.04319	6.2309	591.11	166.22	757.33
5.023	0.04273	6.0262	577.82	165.48	743.30
5.023	∞			Av.	750.31
5.718	0.04052	6.3207	640.07	161.82	801.89
5.718	0.03470	5.4889	649.78	151.53	801.31
5.718	∞			Av.	801.60

This was accomplished using a Fortran computer program *(8)* which generated successive polynomials of increasing degree until no reduction in the residual sum-of-the-squares was encountered. The polynomial linear regression program, POLYR, was standardized using the 25°C ΦL vs. $m^{1/2}$ data published by Parker *(12)*. Good agreement was found between POLYR predicted slopes and the slopes Parker obtained using the chord-area method.

At each experimental temperature the data points were fitted to a polynomial equation using the POLYR program. Values of ΦL obtained from these computer fits are contained in Table IV. The apparent consistency of the equation was checked by comparing the POLYR-predicted ΦL with ΦL interpolated from hand-plotted graphs. At 40° and 60°C the NaCl ΦL vs. $m^{1/2}$ curves were adaptable to a single polynomial; however, at the other three experimental temperatures a single polynomial could not describe the curve with the desired accuracy. At these three temperatures it was necessary to use two polynomial equations to describe the experimental data, each describing a different portion of the curve. These could then be pieced together, such that a whole ΦL vs. $m^{1/2}$ curve was defined. An area in which the two equations overlapped provided a means of checking that a smooth curve was generated. The slopes obtained for these regions of overlap are slightly less precise than those for other portions of the curve.

Derived Thermodynamic Quantities

The relative partial molal heat content of the solute, $\bar{L}_2$, was derived from ΦL data using Equation 1. At each experimental temperature $\bar{L}_2$ values were calculated for the concentration range 0.1 to 6.0*m* (Table V). As per Equation 6, the POLYR program was then used to fit $\bar{L}_2$ data to a polynomial equation of the type

$$\bar{L}_2 = d + eT + fT^2 \cdots \qquad (7)$$

This procedure was performed at 0.1*m* increments from 0.1 to 6.0*m*.

The mean activity coefficients for NaCl at the temperature range investigated were calculated using Equations 8 and 9.

$$\int d \ln \gamma = \int -\bar{L}_2/\nu RT^2 \, dT \qquad (8)$$

$$\ln \gamma(m) = \ln \gamma(m)^{Tr} - \frac{1}{\nu R}\left[d\left(\frac{1}{Tr} - \frac{1}{T}\right) + e \ln \frac{T}{Tr} + f(T - Tr)\right] \qquad (9)$$

Equation 9 is derived by substituting Equation 7 into Equation 8 and integrating from a reference temperature to the desired higher temperature. In this research, 25°C was used as a reference temperature because accurate data were available. A large number of γ values for NaCl were calculated using Robinson and Stokes *(14)* γ data at 25°C and $\bar{L}_2$ data from this investigation (Table VI). The Robinson and Stokes γ data were used because they have given considerable attention to the best method for treating γ over the entire concentration range.

The reliability of the γ values derived in this study was checked using values published by Harned and Owen *(7)*, obtained from a combination of e.m.f. measurents and boiling point elevation studies. The comparison values were taken from a smoothed curve, since experimental difficulties inherent in the procedures caused consider-

TABLE IV. Smoothed ΦL (cal/mol) at Even Molality

m	40°	50°	60°	70°	80°
0.1	120	151	167	199	243
0.2	138	181	210	246	299
0.3	144	199	235	276	338
0.4	146	209	253	297	368
0.5	144	215	265	313	393
0.6	140	218	274	326	413
0.7	135	219	281	336	431
0.8	128	219	286	345	446
0.9	121	218	290	353	459
1.0	114	217	293	360	472
1.5	76	203	299	381	506
2.0	38	185	299	399	529
2.5	4	168	299	420	561
3.0	−24	154	301	443	595
3.5	−47	143	307	467	631
4.0	−62	136	317	492	668
4.5	−72	134	332	518	706
5.0	−75	137	352	543	746
5.5	−72	143	378	570	786
6.0	−62	156	408	597	827

TABLE V. Partial Molal Heat Content of the Solute

m	25° *(12)*	40°	50°	60°	70°	80°
0.1	97	148	194	225	262	314
0.2	78	159	225	273	318	390
0.3	50	154	236	297	349	440
0.4	17	143	239	311	370	476
0.5	−16	128	237	318	384	504
0.6	−50	111	231	321	394	526
0.7	−85	94	224	322	402	543
0.8	−119	76	216	322	408	557
0.9	−152	58	207	320	414	568
1.0	−185	40	198	317	418	576
1.2	−247	5	179	311	427	587
1.4	−305	−26	161	306	435	591
1.5	−333	−41	151	303	440	585
1.6	−360	−56	143	301	444	591
1.8	−410	−83	127	297	460	620
2.0	−455	−106	113	296	481	649
2.2	−497	−127	101	296	501	679
2.4	−534	−144	92	299	522	709
2.5	−551	−151	88	303	532	725
2.6	−567	−158	84	305	542	740
2.8	−621	−169	79	313	563	772
3.0	−621	−176	77	324	584	804
3.2	−642	−180	76	337	605	836
3.4	−659	−181	79	353	627	869
3.5	−666	−180	81	362	638	886
3.6	−673	−178	83	372	649	902
3.8	−682	−173	91	394	671	936
4.0	−688	−164	100	418	693	970
4.2	−691	−152	112	445	715	1004
4.4	−690	−137	127	474	738	1038
4.6	−685	−119	144	506	760	1073
4.8	−677	−98	163	541	783	1108
5.0	−665	−74	184	579	806	1143
5.2	−650	−48	208	619	829	1178
5.4	−632	−18	234	662	852	1214
5.6	−611	14	263	707	875	1249
5.8	−586	49	294	755	898	1285
6.0	−558	87	327	805	922	1321

able uncertainty in the data of the temperature range of 35-70°C. Good agreement was found (Table VII).

The relative partial molal heat content of the solvent, $\bar{L}_1$, was derived from the ΦL data using Equation 10.

$$\bar{L}_1 = -MW_1m^{3/2}/2000\ \partial\Phi L/\partial m^{1/2} \tag{10}$$

The values of $\bar{L}_1$ are contained in Table VIII. Equations describing $\bar{L}_1$ as a function of temperature were derived in the same manner as the $\bar{L}_2$ data. The osmotic coefficients, ϕ, were then calculated using Equations 11 and 12.

TABLE VI. Activity Coefficients

m	25° *(14)*	40°	50°	60°	70°	80°
0.1	0.778	0.774	0.771	0.767	0.763	0.758
0.2	0.735	0.731	0.727	0.723	0.718	0.713
0.3	0.710	0.705	0.702	0.697	0.692	0.687
0.4	0.693	0.691	0.688	0.683	0.678	0.672
0.5	0.681	0.680	0.677	0.672	0.667	0.661
0.6	0.673	0.672	0.669	0.665	0.660	0.654
0.7	0.667	0.667	0.665	0.660	0.655	0.649
0.8	0.662	0.663	0.661	0.656	0.651	0.645
0.9	0.659	0.660	0.658	0.654	0.649	0.642
1.0	0.627	0.659	0.657	0.654	0.648	0.641
1.2	0.654	0.653	0.648	0.642	0.634	0.624
1.4	0.655	0.660	0.660	0.657	0.652	0.645
1.6	0.657	0.662	0.662	0.658	0.653	0.646
1.8	0.662	0.668	0.667	0.664	0.658	0.651
2.0	0.668	0.675	0.675	0.671	0.665	0.658
2.2	0.675	0.683	0.683	0.680	0.674	0.666
2.4	0.683	0.693	0.693	0.690	0.684	0.675
2.6	0.692	0.703	0.704	0.701	0.694	0.684
2.8	0.702	0.713	0.713	0.710	0.704	0.694
3.0	0.714	0.731	0.732	0.728	0.721	0.711
3.2	0.726	0.738	0.739	0.736	0.728	0.715
3.4	0.737	0.752	0.753	0.749	0.741	0.730
3.6	0.753	0.766	0.767	0.763	0.755	0.743
3.8	0.768	0.782	0.783	0.778	0.769	0.756
4.0	0.783	0.797	0.798	0.793	0.783	0.770
4.2	0.800	0.814	0.815	0.809	0.799	0.785
4.4	0.817	0.831	0.831	0.825	0.814	0.799
4.6	0.835	0.848	0.848	0.841	0.829	0.813
4.8	0.854	0.868	0.868	0.860	0.848	0.831
5.0	0.874	0.888	0.887	0.879	0.865	0.848
5.2	0.895	0.908	0.906	0.898	0.884	0.865
5.4	0.916	0.929	0.926	0.917	0.901	0.882
5.6	0.939	0.951	0.948	0.937	0.921	0.900
5.8	0.962	0.973	0.969	0.958	0.940	0.919
6.0	0.986	0.996	0.991	0.978	0.959	0.937

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

$$\phi = \phi^{Tr} + \frac{-1000}{MW_1R\nu m}\left[f\left(\frac{1}{Tr} - \frac{1}{T}\right) + g\ln\frac{T}{Tr} + h\,(T - Tr)\right] \tag{12}$$

The integrated form (Equation 12 of Equation 11) was obtained using 25°C as a reference temperature and the appropriate polynomial equation describing $\bar{L}_1$ as a function of temperature. A list of ϕ values calculated in this manner is contained in Table IX. As with the γ data, the 25°C ϕ data used were taken from Robinson and Stokes *(14)*.

Osmotic coefficients from the literature were then used to check the consistency of the extended data from this investigation. Smith *(15)* and Smith and Hirtle *(16)*, using the boiling point elevation technique, published ϕ for NaCl at 60°, 70°, and 80°C. Liu and Lindsay *(10)*, using the vapor pressure lowering method, published ϕ values for NaCl at 75°C. The agreement was excellent in all cases (Table X). The consistency of the derived ϕ values is remarkable, since previous investigations measured solvent properties directly while this study obtained solute properties and calculated the solvent properties. The good agreement found in the comparison of ϕ values indicates that the procedure for determination of the slope of ΦL vs. $m^{1/2}$ curve was accurate, since $\bar{L}_1$ is directly proportional to the slope (see Equation 10).

The reliability of $\bar{L}_2$ and $\bar{L}_1$ values determined in this study can be estimated by using published values of γ and ϕ and attributing all uncertainty to $\bar{L}_1$ and $\bar{L}_2$. Using the average deviation from this study, the values taken from the literature and the average magnitude of the correction term from Equations 9 and 12, the maximum uncertainty in $\bar{L}_1$ is 4% and in $\bar{L}_2$, 3%. A second estimation of the reliability of the activity and osmotic coefficients is possible considering the experimental uncertainty present in the data gathered in this investigation. Taking into account the average magnitude of the correction terms in Equations 9 and 12, the error present is no more than 0.2 to 0.3%. Thus, the activity and osmotic coefficients re-

TABLE VII. Comparison of Activity Coefficients

	40°		50°		60°		70°		80°	
m	Present[a] research	*(7)*	Present[a] research	*(7)*	Present[a] research	*(7)*	Present[a] research	*(7)*	Present[a] research	*(7)*
0.1	0.774	0.774	0.771	0.770	0.767	0.766	0.763	0.762	0.758	0.757
0.2	0.729	0.728	0.725	0.725	0.721	0.721	0.716	0.717	0.711	0.711
0.5	0.677	0.678	0.675	0.675	0.670	0.671	0.665	0.667	0.659	0.660
1.0	0.658	0.657	0.656	0.656	0.652	0.654	0.646	0.648	0.640	0.641
1.5	0.660	0.661	0.660	0.662	0.656	0.659	0.651	0.655	0.644	0.646
2.0	0.678	0.678	0.678	0.678	0.674	0.676	0.669	0.672	0.661	0.663
2.5	0.701	0.698	0.702	0.699	0.698	0.696	0.692	0.692	0.683	0.685
3.0	0.731	0.728	0.732	0.728	0.728	0.726	0.721	0.721	0.711	0.712
3.5	0.756	0.761	0.766	0.762	0.762	0.760	0.754	0.758	0.742	0.742
4.0	0.816	0.802	0.824	0.802	0.827	0.799	0.824	0.791	0.817	0.777

[a] Values calculated using Equation 9 and Harned and Owen's (7) activity coefficient data at 25° as a reference.

TABLE VIII. Partial Molal Heat Content of Solvent

m	25° (*12*)	40°	50°	60°	70°	80°
0.1	−0.013	−0.051	−0.075	−0.11	−0.11	−0.13
0.2	0.039	−0.076	−0.16	−0.23	−0.26	−0.33
0.3	0.17	−0.54	−0.21	−0.34	−0.40	−0.55
0.4	0.37	0.018	−0.22	−0.42	−0.53	−0.78
0.5	0.65	0.14	−0.20	−0.48	−0.64	−1.01
0.6	0.99	0.30	−0.15	−0.51	−0.74	−1.22
0.7	1.40	0.51	−0.067	−0.52	−0.83	−1.42
0.8	1.85	0.75	0.046	−0.51	−0.92	−1.61
0.9	2.37	1.03	0.19	−0.49	−1.00	−1.77
1.0	2.92	1.33	0.35	−0.44	−1.07	−1.92
1.2	4.16	2.02	0.73	−0.33	−1.24	−2.12
1.4	5.52	2.78	1.17	−0.19	−1.45	−2.21
1.5	6.24	3.18	1.41	−0.12	−1.58	−2.34
1.6	6.99	3.58	1.65	−0.058	−1.72	−2.47
1.8	8.52	4.40	2.13	0.046	−2.15	−3.32
2.0	10.1	5.21	2.60	0.097	−2.88	−4.31
2.2	11.6	5.99	3.04	0.071	−3.75	−5.43
2.4	13.2	6.70	3.43	−0.056	−4.59	−6.69
2.5	13.9	7.02	3.61	−0.16	−5.04	−7.37
2.6	14.7	7.32	3.67	−0.31	−5.51	−8.09
2.8	16.0	7.83	4.01	−0.70	−6.53	−9.62
3.0	17.4	8.21	4.14	−1.26	−7.63	−11.3
3.2	18.6	8.43	4.15	−2.01	−8.83	−13.1
3.4	19.6	8.48	4.01	−2.97	−10.1	−15.1
3.5	20.0	8.43	3.88	−3.53	−10.8	−16.1
3.6	20.4	8.32	3.71	−4.15	−11.5	−17.2
3.8	21.1	7.95	3.24	−5.58	−12.9	−19.4
4.0	21.5	7.33	2.56	−7.28	−14.5	−21.8
4.2	21.7	6.46	1.67	−9.27	−16.2	−24.3
4.4	21.6	5.30	0.55	−11.6	−17.9	−27.0
4.6	21.2	3.85	−0.81	−14.2	−19.7	−29.8
4.8	20.5	2.07	−2.44	−17.1	−21.7	−32.7
5.0	19.5	−0.034	−4.34	−20.4	−23.7	−35.8
5.2	18.1	−2.50	−6.54	−24.1	−25.8	−39.1
5.4	16.4	−5.33	−9.04	−28.2	−28.0	−42.4
5.6	14.3	−8.55	−11.9	−32.7	−30.3	−46.0
5.8	11.7	−12.18	−15.0	−37.6	−32.7	−49.7
6.0	8.77	−16.2	−18.5	−43.0	−35.1	−53.5

TABLE IX. Osmotic Coefficients

m	25° (*14*)	40°	50°	60°	70°	80°
0.1	0.932	0.932	0.931	0.930	0.928	0.927
0.2	0.925	0.924	0.924	0.922	0.921	0.919
0.3	0.922	0.922	0.921	0.920	0.918	0.917
0.4	0.920	0.921	0.921	0.920	0.919	0.917
0.5	0.921	0.923	0.923	0.922	0.920	0.918
0.6	0.923	0.925	0.926	0.925	0.924	0.922
0.7	0.926	0.929	0.929	0.929	0.927	0.926
0.8	0.929	0.932	0.933	0.933	0.932	0.930
0.9	0.932	0.936	0.937	0.937	0.936	0.934
1.0	0.936	0.940	0.941	0.941	0.940	0.939
1.2	0.943	0.949	0.950	0.950	0.950	0.948
1.4	0.951	0.958	0.960	0.960	0.960	0.958
1.5	0.959	0.966	0.968	0.969	0.968	0.967
1.6	0.962	0.969	0.971	0.972	0.971	0.970
1.8	0.972	0.980	0.983	0.984	0.983	0.981
2.0	0.983	0.992	0.995	0.995	0.995	0.993
2.2	0.995	1.004	1.007	1.008	1.007	1.004
2.4	1.007	1.016	1.019	1.020	1.019	1.016
2.5	1.017	1.027	1.030	1.030	1.029	1.026
2.6	1.019	1.029	1.032	1.032	1.031	1.028
2.8	1.032	1.042	1.045	1.045	1.044	1.041
3.0	1.045	1.055	1.058	1.058	1.057	1.053
3.2	1.059	1.068	1.071	1.071	1.069	1.066
3.4	1.073	1.082	1.085	1.085	1.082	1.078
3.5	1.085	1.094	1.097	1.097	1.094	1.070
3.6	1.087	1.096	1.098	1.098	1.095	1.091
3.8	1.101	1.110	1.112	1.111	1.108	1.103
4.0	1.116	1.124	1.125	1.125	1.122	1.117
4.2	1.131	1.139	1.140	1.138	1.135	1.129
4.4	1.146	1.153	1.154	1.152	1.148	1.142
4.6	1.161	1.167	1.168	1.166	1.161	1.154
4.8	1.176	1.182	1.182	1.179	1.174	1.167
5.0	1.192	1.196	1.196	1.192	1.187	1.180
5.2	1.207	1.211	1.210	1.206	1.199	1.197
5.4	1.223	1.226	1.224	1.219	1.212	1.204
5.6	1.239	1.241	1.238	1.232	1.225	1.216
5.8	1.255	1.255	1.252	1.245	1.237	1.228
6.0	1.271	1.270	1.265	1.258	1.250	1.240

TABLE X. Comparison of Osmotic Coefficients

	60°		70°		75°		80°	
m	(*15, 16*)	Present research	(*15, 16*)	Present work	(*10*)	Present[a] work	(*15, 16*)	Present work
0.1	0.9291	0.930	0.9273	0.928	0.926	0.928	0.9263	0.927
0.2	0.9210	0.922	0.9190	0.921	0.918	0.920	0.9178	0.919
0.4	0.9207	0.920	0.9186	0.919	0.918	0.918	0.9170	0.917
0.6	0.9267	0.925	0.9246	0.924	0.924	0.923	0.9228	0.922
0.8	0.9350	0.933	0.9339	0.932	0.934	0.931	0.9310	0.930
1.0	0.9442	0.941	0.9424	0.940	0.940	0.940	0.9402	0.939
1.5	0.968	0.969	0.968	0.968	0.967	0.968	0.966	0.967
2.0	0.999	0.995	0.998	0.995	0.996	0.994	0.995	0.993
2.5	1.031	1.030	1.029	1.029	1.026	1.026	1.026	1.026
3.0	1.061	1.058	1.059	1.057	1.056	1.055	1.057	1.053
3.5	1.092	1.097	1.090	1.094	1.087	1.092	1.086	1.090
4.0	1.130	1.125	1.127	1.122	1.119	1.119	1.120	1.117
5.0	—	—	—	—	1.182	1.184	—	—
6.0	—	—	—	—	1.247	1.245	—	—

[a] Interpolated from values contained in Table IX.

TABLE XI. Relative Partial Molal Heat Capacity of NaCl ($\bar{J}_2$), Cal/Mol °C

m	25°	40°	50°	60°	70°	80°
0.1	3.4	3.7	3.8	4.0	4.2	4.4
0.2	5.6	5.6	5.6	5.6	5.6	5.6
0.3	6.9	6.9	6.9	6.9	6.9	6.9
0.4	8.1	8.1	8.1	8.1	8.1	8.1
0.5	9.8	9.5	9.3	9.1	8.9	8.6
0.6	11	11	10	10	9.7	9.4
0.7	12	12	11	11	11	10
0.8	13	13	12	12	11	11
0.9	14	14	13	12	12	11
1.0	15	14	14	13	12	12
1.5	21	19	17	15	14	12
2.0	24	22	20	19	18	16
2.5	27	25	24	22	21	19
3.0	30	28	24	25	22	22
3.5	32	30	28	27	26	24
4.0	34	32	30	28	27	26
4.5	36	33	32	30	29	27
5.0	37	35	33	31	29	27
5.5	39	36	34	31	29	27
6.0	41	37	34	31	28	26

ported in this study should be good to ±0.001 unit, provided the values at 25°C are that precise.

The relative partial molal heat capacity of the solute, $\bar{J}_2$, was calculated for NaCl from the temperature dependence of $\bar{L}_2$ using the relationship

$$\bar{J}_2 = \partial\bar{L}_2/\partial T \qquad (13)$$

These values are contained in Table XI and represent the first calorimetric determination of such values. An attempt was made to check the consistency of $\bar{J}_2$ using Relationship 14.

$$\bar{J}_2 = C\bar{p}_2 - C\bar{p}_2^{\circ} \qquad (14)$$

Ackermann's *(1)* published data allowed the calculation of $C\bar{p}_2$ and Criss and Cobble *(3)* have published $C\bar{p}_2^{\circ}$ values. These data were substituted into Equation 14 and the results were compared with the $\bar{J}_2$ values derived from this study. Unfortunately, the results were inconclusive and the reliability of the derived $\bar{J}_2$ values could not be evaluated.

A rough estimate of the internal consistency can be made using the average deviation of $\bar{L}_2$ values calculated from the POLYR program used to fit $\bar{L}_2$ data as a function of temperature. The present $\bar{J}_2$ values have an uncertainty of ±0.5 cal/mol °C at concentrations of 2.0*m* or less, with a slightly higher uncertainty as concentration increases to near the saturation point.

Acknowledgment

It is with great sorrow that we report that Henry L. Anderson was killed in an automobile accident shortly before this work was completed. Major credit for its inception and results should be given to him. His loss is felt deeply, both scientifically and personally.

Dale Ensor thanks John R. Jezorek and Robert H. Wood for helpful suggestions and discussions concerning the preparation of this manuscript.

Nomenclature

A_H = Debye-Hückel limiting slope
A = distance of closest approach parameter (NaCl, A = 1.0)
$C\bar{p}_2$ = partial molal heat capacity of solute
$C\bar{p}_2^{\circ}$ = partial molal heat capacity of solute at infinite dilution
$\bar{J}_2$ = relative partial molal heat capacity of solute
$\bar{L}_1$, $\bar{L}_2$ = relative partial molal heat content of solvent, solute
m = molality (concentration in moles per 1000 grams of solvent)
n = number of moles
MW_1 = molecular weight of H_2O
Q = experiment heat, cal
R = gas constant, cal/mol deg
T = absolute temperature
Tr = reference temperature (298K in this research)
ν^{+-} = total number of ions
ϕ = osmotic coefficient
ΦCp = apparent molal heat capacity
ΦL = relative apparent molal heat content, cal/mol
γ = activity coefficient
$\sigma(m^{1/2}) = 3(m^{1/2})^{-3}\,[1 + m^{1/2} - 2\ln(1 + m^{1/2} - 1/1 + m^{1/2})]$
∞ = infinite dilution

Literature Cited

(1) Ackermann, Th., *Z. Elektrochem.*, **62,** 411 (1958).
(2) Anderson, H. L., Petree, L. A., *J. Phys. Chem.*, **74,** 1455 (1970).
(3) Criss, C. M., Cobble, J. W., *J. Amer. Chem. Soc.*, **83,** 3223 (1961).
(4) Eigen, M., Wicke, E., *Z. Elektrochem.*, **55,** 354 (1951).
(5) Guggenheim, E. A., Prue, J. E., *Trans. Faraday Soc.*, **50,** 710, (1954).
(6) Gulbransen, E. A., Robinson, A. L., *J. Amer. Chem. Soc.*, **56,** 2637 (1934).
(7) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolyte Solutions," 3rd ed., Reinhold, New York, N.Y., 1958.
(8) IBM Applications Program No. GH20-0205-4, 6th ed., p. 408, International Business Machines, White Plains, N.Y., 1970.
(9) Jongenburger, H. S., Wood, R. H., *J. Phys. Chem.*, **69,** 4231 (1965).
(10) Liu, Chia-tsum, Lindsay, W. T., Final Report, Office of Saline Water, March 1971.
(11) Owen, B. B., Brinkley, S. R., *Ann. N.Y. Acad. Sci.*, **51,** 753 (1949).
(12) Parker, V. B., National Standard Reference Data System-National Bureau of Standards NBRDS-NBS **2,** 10 (1965).
(13) Petree, L. A., M.S. thesis, Univ. of North Carolina at Greensboro, 1970.
(14) Robinson, R. A., Stokes, R. H., "Electrolyte Solutions," 2nd rev. ed., Butterworths, London, 1965.
(15) Smith, R. P., *J. Amer. Chem. Soc.*, **61,** 417 (1939).
(16) Smith, R. P., Hirtle, D. S., *ibid.*, **61,** 1123 (1939).
(17) Young, T. F., Groenier, W. J., *ibid.*, **58,** 187 (1936).
(18) Young, T. F., Vogel, O. G., *ibid.*, **54,** 3030 (1932).

Received for review September 5, 1972. Accepted December 20, 1972. Study supported by a grant from the Office of Saline Water, U.S. Department of Interior, Washington, D.C.