Liquid-Vapor Equilibrium of Aqueous Sodium Chloride, from 298 to 373K and from 1 to 6 mol kg^{-1}, and Related Properties

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Vapor pressures of 1.0–6.1 mol kg^{-1} aqueous sodium chloride were measured from 298 to 373K. The apparatus for measuring vapor pressures was modified to increase the convenience and the precision so that it could be operated by a single observer; the precision of measurement was ±0.002K or ±0.005 torr, whichever was larger. From these measurements, other vapor-pressure and freezing-point measurements, and calorimetric enthalpies and heat capacities at 298K, 20 parameters of the modified Debye-Hückel-power-series-in-the-molality equation were determined for aqueous sodium chloride. The equation was compared with measurements of the vapor pressure, the electromotive force of concentration cells, and thermal properties. The agreement was usually excellent.

Previous static measurements of liquid-vapor equilibrium (*33–35*) indicated that the method is capable of even greater precision. Therefore, we reconstructed the cell and most of the auxiliary apparatus (*9, 10*). The changes which are of general interest were the replacement of the membrane null manometer by a liquid mercury manometer and the replacement of the air thermostat by an oil thermostat. The quantities to be measured were the equilibrium temperature and pressure, the total amount of each component, and the volume of the vapor phase.

Experimental

Apparatus. The core of the apparatus is shown in Figure 1. The thermostat box has three compartments. The third, not shown, is behind the right-hand compartment and contains the lighting system for the small manometer. Each side is vigorously stirred by a rotary propeller inside a cylindrical sleeve. To avoid vibration, the stirring motors are mounted directly on the floor with no connection to the thermostat or table. The thermostat contains a light motor oil on the cell side and Conoco white mineral oil on the manometer side.

The cell, which is almost identical with that previously described (*33*), contains the thermopile well W and a soft iron annular stirrer S in a glass ring. It has two tubes, one with a mercury-sealed ground glass stopper G, and the other leading to the vapor side of the small manometer. The small manometer, like the large one (*29, 31*), is made of 19-mm i.d. glass tubing, carefully chosen for uniformity of bore. It has the same type of diffuse lighting, and it is read with the same cathetometer and scale.

When the mercury in U is lowered, the cell may be connected to the degassing and vapor-transfer manifold through S_4 or to the vacuum pump and manostat through S_3. The helium side of the null manometer may be connected to the pump through S_1 or to the main manometer and the manostat through S_2.

The manometer side of the thermostat is kept 0.5K hotter than the cell side to prevent condensation and is regulated to ±0.01K. The cell side is controlled to ±0.001K with a platinum-resistance thermometer, reflecting galvanometer, cadmium photocell, and thyratron circuit. The temperature of the cell is measured with a 20-junction copper to constantan thermopile. The thermopile is calibrated in situ by measuring the vapor pressure of water and determining the temperature by interpolation from a table giving at 0.01K intervals from 273.15 to 373.15K the vapor pressure computed from the equation of Keyes (*16*).

The stirrer is raised and lowered every 6 sec. Twice in each cycle the stirrer breaks the surface, and most of the liquid is forced through narrow gaps between the stirrer and the thermopile well and the stirrer and the cell wall.

Pressures less than 25 torr, that is, at 298K and below for water, are measured on the small manometer alone. (Throughout this paper, torr = (101.325/760) kpA, cal = 4.184 J.) Higher pressures are measured on the large manometer, and the small one is used only as a null instrument. We believe that the accuracy of the temperature is ±0.002K, and that of the pressure is ±0.005 torr. At 298.15K, 0.002K corresponds to 0.003 torr for water so that the two limits have about the same effect, but at 373.15K, 0.002K corresponds to 0.054 torr.

Materials. Conductivity water was twice distilled and then boiled for several minutes. It was then degassed continuously until used in an apparatus similar to that of Taylor (*38*). Mallinckrodt analytic reagent-grade sodium chloride was precipitated from a nearly saturated solution by passing in hydrogen chloride gas. The precipitate was packed in a glass funnel and washed with a small amount of doubly distilled water. The washed precipitate was fused in a platinum crucible, then cooled, and ground to a fine powder in an agate mortar. It was stored in a drying oven at 403K.

Procedure. Helium is bled into the cell until the pressure is atmospheric. Then seal G is opened, and the salt is added through a long-stemmed funnel. To degas the salt and the cell, they are pumped on at room temperature overnight; then the temperature is raised to 378K for about 6 hr. The pumping is interrupted five or six times,

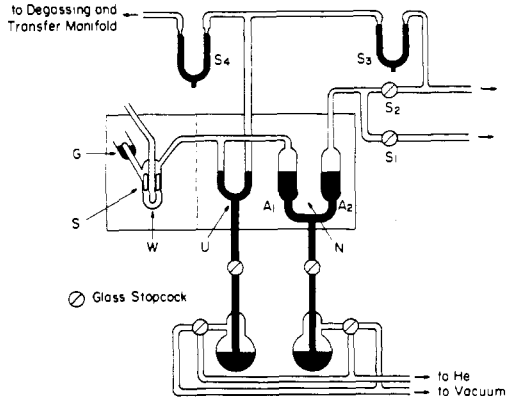

Figure 1. Apparatus
W, thermopile well; G, ground glass stopper; S, stirrer; U, seal; A_1, A_2, arms of null manometer N; S_1, S_2, stopcocks; S_3, S_4, mercury float valves

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and the cell is filled to a pressure of about 20 torr of water vapor for a few minutes to displace adsorbed gases by water. Then the cell is slowly cooled to room temperature. The salt is dissolved by distilling 6 cm^3 of water from the reservoir with the cell cooled to about 263K. The solution is degassed by expanding water vapor into the manifold frequently with the cell stirrer operating continuously. The permanent gas pressure is measured after each expansion in a MacLeod gauge after condensing the water vapor. The pressure is usually less than 10^{-2} torr at the start, and the degassing is continued until it is 10^{-4} torr or less. Then the water vapor is expanded off once more immediately before the first measurement.

The first measurement is made at 298K, with the right-hand side of the manometer evacuated. Pressure measurements begin after the thermopile potential has been constant (±0.001 mV) for 30 min. First, the left-arm reading is compared with the scale, then the right, and a thermopile reading is made after each scale reading. A difference of more than 0.001 mV is cause for rejection and repetition of the measurement.

Then the temperature is changed to the next higher value. The right-hand side of the manometer is connected to the thermostated 90-dm^3 manostat and the large manometer through stopcock 2. Mercury seal 3 is also opened. The helium pressure is adjusted until finally the difference between the heights of the two menisci of the null manometer is less than 10 μm, which is read without reference to the scale. The constancy of temperature criterion is the same as at 298K.

When equilibrium has been reached, stopcock 2 is closed and the pressure in the manostat is read while the temperature of the cell is changed to the next value. The pressures are corrected for the capillary depressions of the menisci in both manometers, for the static heads of water vapor and of helium, and for thermal expansion and ruling errors of the scale. After the measurement at the highest temperature is completed, the cell is cooled slowly to 298K, and that measurement is repeated.

The permanent gas pressure is determined as the difference in the pressure at 298K before and after heating. This pressure is seldom more than 0.02 torr and never twice that large. It is assumed that it all arises at the highest temperature. The cell pressure is then changed to atmospheric by lowering the mercury in tube U and bubbling helium through the tube. The solution is removed in a hypodermic syringe with a long flexible needle. A dimple at the bottom of the cell permits nearly complete removal. Samples are weighed directly from the syringe and analyzed gravimetrically for chloride (*17*). All weighings are corrected to masses. The precision of the determination of the molality is ±0.05%.

The volume of the cell is determined by expanding helium at a known pressure into an evacuated bulb of known volume. It depends upon the levels of mercury in N and in U. These are always set so that the volume is 37.2 cm^3. Since the volume of the vapor is only about five times that of the solution, the fraction of water in the vapor phase is negligible at low temperatures, as shown by the values at 298K and 323K in Table I. At 348K the molality is about 0.1% greater than at 298K, and at 373K it is about 0.3% greater.

Results

We desire the logarithm of the activity of the water or, better, the osmotic coefficient. These are given by

$$\ln a_1 = \ln (p_1/p_1^\circ) + (\beta - \bar{V}_1)(p_1 - p_1^\circ)/RT \quad (1)$$

$$\phi = -(M_1 \nu m)^{-1} \ln a_1 \quad (2)$$

where a_1 is the activity of water, p_1 the vapor pressure of the solution, p_1° that of pure water at the same temperature, β is $(\bar{V}_{1,g} - RT/p)$, $\bar{V}_{1,g}$ is the molar volume of water vapor, and $\bar{V}_1$ the molar volume of liquid water, ϕ is the osmotic coefficient, M_1 is the molar mass of water, ν is 2 for NaCl, and m is the molality of NaCl. For β we use the equation of Keyes et al. (*15*):

$$\beta/(cm^3\ mol^{-1}) = 34.0 - (47549\ K/T)\,10^{80870(K/T)^2} \quad (3)$$

Table I. Osmotic Coefficients of Sodium Chloride Solutions

m, mol kg^{-1}	T, K	ϕ	$\phi - \phi_{calcd}$
1.046	298.15	0.9391	0.0011
1.046	323.15	0.9427	−0.0013
1.047	348.15	0.9420	−0.0001
1.049	373.15	0.9316	−0.0048
1.862	298.15	0.9671	(−0.0092)[a]
1.863	323.15	0.9854	−0.0013
1.864	348.15	0.9837	−0.0016
1.868	373.15	0.9747	−0.0023
2.508	298.15	1.0073	−0.0061
2.509	310.65	1.0229	0.0012
2.509	323.15	1.0271	0.0016
2.510	335.65	1.0266	0.0009
2.511	348.15	1.0253	0.0020
2.513	360.65	1.0193	0.0007
2.516	373.15	1.0160	0.0037
3.033	298.15	1.0455	−0.0013
3.034	310.65	1.0553	0.0000
3.035	323.15	1.0588	−0.0002
3.036	335.65	1.0576	−0.0012
3.036	348.15	1.0574	0.0018
3.039	360.65	1.0492	−0.0007
3.043	373.15	1.042	−0.0002
3.725	298.15	1.0887	−0.0056
3.726	323.15	1.1038	−0.0013
3.731	348.15	1.1021	0.0027
3.738	373.15	1.0854	0.0025
4.883	298.15	1.1773	−0.0030
4.885	310.65	1.1842	−0.0013
4.886	323.15	1.1852	0.0000
4.887	335.65	1.1827	0.0020
4.890	348.15	1.1740	0.0009
4.894	360.65	1.1655	0.0025
4.900	373.15	1.1509	0.0021
5.102	298.15	1.1949	−0.0023
5.104	323.15	1.2023	0.0018
5.108	348.15	1.1871	0.0003
5.113	360.65	1.1748	−0.0012
5.119	373.15	1.1572	−0.0059
5.646	298.15	1.2385	−0.0017
5.649	323.15	1.2398	0.0012
5.652	348.15	1.2199	−0.0004
5.666	373.15	1.1889	−0.0036
6.102	298.15	1.2748	−0.0023
6.103	310.65	1.2747	−0.0016
6.104	323.15	1.2718	0.0015
6.105	335.65	1.2637	0.0034
6.108	348.15	1.2503	0.0030
6.112	360.65	1.2353	0.0033
6.117	373.15	1.2166	0.0019
6.120	298.15	1.2730	−0.0055
6.121	310.65	1.2742	−0.0035
6.122	323.15	1.2719	0.0003
6.123	335.65	1.2627	0.0012
6.126	348.15	1.2495	0.0011
6.130	360.65	1.2351	0.0022
6.135	373.15	1.2153	−0.0002

[a] This point not included in least-squares analysis.

The quantity $\bar{V}_1$ is negligibly small. The correction to ϕ from β is nearly independent of the salt concentration and increases from about −0.0016 at 298K to −0.016 at 373K.

Analytical expression. Even though the Gibbs function G is never itself measured directly, it is convenient to start with G or the dimensionless G/RT to obtain analytical expressions of the thermodynamic functions when the state variables are temperature, pressure, and amounts of the components, for the other functions may then be obtained by differentiation and simple arithmetical operations.

We express G/RT as an ideal term and an approximate Debye-Hückel term plus an integral power series in the molalities of the solute species. For a single salt this gives the following expression for the excess Gibbs function G^E:

$$G^E/RT = G/RT - n_1G_1^\circ/RT - \Sigma_i n_i(G_i^\circ/RT) - \Sigma_i \nu_i n_s[-1 + \ln (m_i/m^\circ)] = -2SXIW_1/a' + n_s\sum_{j=1}^{r} j^{-1}D_j m^j \quad (4)$$

where R is the gas constant; T is the thermodynamic temperature; $\nu_i n_s$ is the number of moles of ion i, and z_i its charge number; n_s is the number of moles of salt, and m is its molality; G_1° is the standard molar Gibbs function of the solvent, and G_i° is that of the species i in the solvent 1; W_1 is the mass of solvent; S is the Debye-Hückel limiting slope; X is a function of x defined in Equation 6, where $x = a'I^{1/2}$, and a' is the ion size parameter; I is the ionic strength: $I = \Sigma_i m_i z_i^2/2$; and m° is a standard value of molality chosen here as 1 mol kg^{-1}.

The Debye-Hückel functions are:

$$S = N_A{}^2e^3(2\pi\rho_1)^{1/2}/(4\pi\epsilon_0 D_1 RT)^{3/2} \quad (5)$$

in which N_A is Avogadro's constant, e is the charge on the proton, ρ_1 is the density of the solvent, and D_1 is its dielectric constant, and

$$X = [x^2 - 2x + 2\ln(1 + x)]/x^2 \quad (6)$$

We need two related functions

$$Z = (x/2)(dX/dx) = \{1 + x - [1/(1 + x)] - 2\ln(1 + x)\}/x^2 \quad (7)$$

$$Y = X + Z = x/(1 + x) \quad (8)$$

For the osmotic coefficient ϕ and the mean ionic activity coefficient $\gamma_\pm$ we have

$$\phi = 1 - (M_1\Sigma_i m_i)^{-1}\partial(G^E/RT)/\partial n_1 = 1 - 2SZI/a'\Sigma_i m_i + \sum_{j=1}^{r} D_j m^j \quad (9)$$

$$\ln \gamma_\pm = (\Sigma_i m_i)^{-1}\Sigma_i[m_i\partial(G^E/RT)/\partial n_i] = -2SYI/a'\Sigma_i m_i + \sum_{j=1}^{r} D_j(1 + j^{-1})m^j \quad (10)$$

We assume that the excess enthalpy function per mole of solute may be represented by a Taylor series expansion about a standard temperature T_s, which we choose as 298.16K:

$$H^E/n_s = (2RXI/a'm)(T^2dS/dT) + \sum_{j=1}^{r}(m^j/j)\sum_{k=0}^{\omega}(D_j{}^{(k)}/k!)\tau^k \quad (11)$$

where $\tau = T - T_s$. Then for each function of temperature in Equation 9, which we will call D,

$$D = D^{(s)} - (2R)^{-1}\sum_{k=0}^{\omega}(D^{(k)}/k!)\int_0^T t^k[(t + T_s)^2]^{-1}dt \quad (12)$$

The resulting equations for S and the D_j coefficients of Equation 9 are given for $\omega = 3$ by Equations 2 and 4 of ref. *10*. Once the form of S is chosen, the coefficients are determined by the values of the quantity $[\rho_1{}^{1/2}/(TD_1)^{3/2}]$. For water we used the International Critical Table (*14*) values of ρ_1 and the measurement of the dielectric constant by Owen et al. (*24*) and Åkerlöf and Oshry (*1*) from 273 to 523K. Above 373K the equation applies at the vapor pressure of water instead of at 1 atm. It extends to 523K. We assume that a' is equal to 1.5 and is independent of temperature.

Table II gives the parameters derived for aqueous sodium chloride. We also computed parameters for a quadratic, a cubic, and a quintic equation in m, which led to 10, 15, and 25 parameters in Equations 4, 9, and 10. The eight $D_i{}^{(0)}$ and $D_i{}^{(1)}$ parameters were determined by a method described by Gibbard (*7*), from the enthalpy and heat capacity values at 298.15K tabulated by Parker (*25*).

The remaining 12 parameters were computed from 251 values of the osmotic coefficient, the sources of which are described in Table III. The osmotic coefficients of Liu and Lindsay (*19*) at 1.0 mol kg^{-1} and below were omit-

Table II. Parameters of Equation 9

$D_1^{(s)} = 1.931487 \times 10^{-2}$	$D_1^{(2)} = -2.525002 \times 10^{-1}$
$D_2^{(s)} = 1.082203 \times 10^{-2}$	$D_2^{(2)} = 1.584023 \times 10^{-1}$
$D_3^{(s)} = -9.568554 \times 10^{-4}$	$D_3^{(2)} = -3.569951 \times 10^{-2}$
$D_4^{(s)} = 3.830374 \times 10^{-5}$	$D_4^{(2)} = 2.619678 \times 10^{-3}$
$D_1^{(0)} = -2.880375 \times 10^{2}$	$D_1^{(3)} = 3.292619 \times 10^{-3}$
$D_2^{(0)} = 7.456777 \times 10^{1}$	$D_2^{(3)} = -2.169034 \times 10^{-3}$
$D_3^{(0)} = -8.242194$	$D_3^{(3)} = 5.003646 \times 10^{-4}$
$D_4^{(0)} = 5.338942 \times 10^{-1}$	$D_4^{(3)} = -3.729485 \times 10^{-5}$
$D_1^{(1)} = 8.999579$	
$D_2^{(1)} = -3.315856$	
$D_3^{(1)} = 6.235031 \times 10^{-1}$	
$D_4^{(1)} = -4.268129 \times 10^{-2}$	

Table III. Osmotic Coefficients Used in Least-Squares Treatment

No. of values	Technique	Molality range	Temp range	SD	Ref
55	Static vapor pressure	1.0–6.1	298–373	0.0024	This work
24	Freezing-point depression	0.01–1.3	273–269	0.0012	*28*
10	Static vapor pressure	1.0–5.8	298	0.0037	*26*
39	Freezing-point depression	0.01–3.6	273–260	0.0024	*8*
19	Freezing-point depression	0.04–3.1	273–262	0.0017	*21*
21	Static vapor pressure	1.0–3.0	395–541	0.0052	*5, 6*
26	Static vapor pressure	3.8–6.1	373–573	0.0039	*19, 20*
36	Static vapor pressure	2.3–6.1	293–303	0.0023	*23*
21	Static vapor pressure	1.0–5.8	293–298	0.0030	*22*

ted, as were their values above 6.0 mol kg^{-1} (*20*). Inclusion of these results produced a poorer fit of the measurements below 373K. All of the parameters were determined by the method of least squares on the IBM 360/50 computer of the Southern Illinois University computation center. Each measurement which was given any weight was given unit weight in the least-squares treatment of the osmotic coefficient.

Table I contains the results of our own measurements. The first column is the molality, the second is the temperature, the third is the osmotic coefficient, and the fourth is the difference between the measured osmotic coefficient and that calculated by Equation 9. Table IV gives the calculated values from Equation 9 of ϕ for rounded temperatures, every 25K, and molalities, those in the tables of Robinson and Stokes (*27*) plus 1.5 mol

Table IV. Osmotic Coefficients at Rounded Temperatures and Molalities

	T, K								
m, mol kg^{-1}	273.15	298.15	323.15	348.15	373.15	398.15	423.15	448.15	473.15
0.1	0.9329	0.9338	0.9317	0.9281	0.9238	0.9187	0.9126	0.9051	0.8955
0.2	0.9214	0.9249	0.9235	0.9198	0.9150	0.9093	0.9023	0.8934	0.8817
0.3	0.9157	0.9220	0.9214	0.9179	0.9129	0.9069	0.8994	0.8897	0.8766
0.4	0.9127	0.9215	0.9219	0.9185	0.9135	0.9073	0.8994	0.8890	0.8748
0.5	0.9111	0.9224	0.9237	0.9206	0.9156	0.9091	0.9009	0.8898	0.8746
0.6	0.9106	0.9241	0.9264	0.9236	0.9185	0.9118	0.9031	0.8915	0.8753
0.7	0.9109	0.9266	0.9297	0.9271	0.9219	0.9149	0.9058	0.8935	0.8765
0.8	0.9118	0.9294	0.9335	0.9311	0.9258	0.9184	0.9088	0.8959	0.8779
0.9	0.9132	0.9327	0.9376	0.9354	0.9299	0.9222	0.9120	0.8984	0.8795
1.0	0.9150	0.9363	0.9419	0.9399	0.9342	0.9261	0.9154	0.9009	0.8812
1.2	0.9199	0.9443	0.9513	0.9496	0.9434	0.9343	0.9223	0.9063	0.8848
1.4	0.9261	0.9531	0.9614	0.9598	0.9531	0.9429	0.9293	0.9117	0.8885
1.5	0.9296	0.9578	0.9666	0.9652	0.9581	0.9472	0.9329	0.9144	0.8903
1.6	0.9334	0.9627	0.9720	0.9706	0.9631	0.9517	0.9366	0.9172	0.8922
1.8	0.9418	0.9730	0.9831	0.9816	0.9735	0.9607	0.9440	0.9228	0.8961
2.0	0.9510	0.9838	0.9946	0.9930	0.9840	0.9699	0.9516	0.9286	0.9002
2.5	0.9774	1.0129	1.0249	1.0226	1.0114	0.9939	0.9714	0.9441	0.9115
3.0	1.0077	1.0447	1.0567	1.0533	1.0398	1.0191	0.9929	0.9616	0.9252
3.5	1.0412	1.0785	1.0898	1.0847	1.0689	1.0454	1.0160	0.9813	0.9414
4.0	1.0773	1.1141	1.1238	1.1166	1.0984	1.0724	1.0404	1.0029	0.9599
4.5	1.1158	1.1511	1.1583	1.1484	1.1277	1.0995	1.0653	1.0254	0.9796
5.0	1.1566	1.1893	1.1932	1.1800	1.1565	1.1258	1.0893	1.0472	0.9988
5.5	1.2000	1.2286	1.2282	1.2110	1.1839	1.1500	1.1108	1.0661	1.0152
6.0	1.2462	1.2687	1.2631	1.2410	1.2091	1.1708	1.1274	1.0792	1.0256

Table V. Activity Coefficients[a] at Rounded Temperatures and Molalities

	T, K								
m, mol kg^{-1}	273.15	298.15	323.15	348.15	373.15	398.15	423.15	448.15	473.15
0.1	0.8934	0.8925	0.8882	0.8821	0.8750	0.8666	0.8567	0.8446	0.8298
0.2	0.8664	0.8673	0.8628	0.8555	0.8467	0.8364	0.8242	0.8091	0.7901
0.3	0.8496	0.8525	0.8482	0.8403	0.8306	0.8192	0.8054	0.7883	0.7666
0.4	0.8376	0.8425	0.8386	0.8304	0.8200	0.8077	0.7928	0.7742	0.7503
0.5	0.8284	0.8353	0.8319	0.8235	0.8126	0.7996	0.7838	0.7638	0.7381
0.6	0.8211	0.8300	0.8271	0.8186	0.8073	0.7937	0.7770	0.7559	0.7284
0.7	0.8152	0.8260	0.8237	0.8151	0.8035	0.7892	0.7718	0.7496	0.7206
0.8	0.8105	0.8231	0.8214	0.8128	0.8007	0.7859	0.7677	0.7445	0.7141
0.9	0.8066	0.8210	0.8198	0.8112	0.7988	0.7835	0.7645	0.7403	0.7086
1.0	0.8035	0.8196	0.8190	0.8103	0.7976	0.7817	0.7620	0.7368	0.7039
1.2	0.7990	0.8183	0.8188	0.8101	0.7967	0.7797	0.7586	0.7315	0.6962
1.4	0.7965	0.8187	0.8202	0.8115	0.7975	0.7793	0.7567	0.7277	0.6902
1.5	0.7959	0.8194	0.8214	0.8127	0.7983	0.7796	0.7562	0.7263	0.6877
1.6	0.7956	0.8204	0.8229	0.8142	0.7994	0.7801	0.7559	0.7251	0.6854
1.8	0.7961	0.8232	0.8266	0.8177	0.8022	0.7818	0.7561	0.7235	0.6817
2.0	0.7976	0.8269	0.8311	0.8221	0.8058	0.7842	0.7570	0.7226	0.6788
2.5	0.8055	0.8393	0.8451	0.8356	0.8174	0.7928	0.7618	0.7231	0.6746
3.0	0.8180	0.8553	0.8621	0.8519	0.8317	0.8042	0.7697	0.7270	0.6740
3.5	0.8342	0.8741	0.8813	0.8702	0.8480	0.8178	0.7800	0.7336	0.6766
4.0		0.8951	0.9023	0.8898	0.8656	0.8329	0.7922	0.7425	0.6817
4.5		0.9179	0.9245	0.9104	0.8842	0.8490	0.8057	0.7530	0.6887
5.0		0.9423	0.9476	0.9316	0.9031	0.8656	0.8197	0.7641	0.6966
5.5		0.9680	0.9715	0.9532	0.9221	0.8818	0.8331	0.7746	0.7040
6.0		0.9948	0.9960	0.9747	0.9405	0.8969	0.8449	0.7831	0.7093

[a] Quantity tabulated is $1 + \log_{10} \gamma_{\pm}$.

kg^{-1}. Table V gives the corresponding mean activity coefficients as $(1 + \log_{10} \gamma_{\pm})$. Table VI gives the corresponding apparent partial molar enthalpy, and Table VII gives the corresponding apparent partial molar heat capacity, less the partial molar heat capacity of the solute at infinite dilution.

Figure 2 shows the deviations from Equation 9 of the values of ϕ from our vapor-pressure measurements at 298.15K, as well as those of Olynyk and Gordon (*23*) at 293.15, 298.15, and 303.15K, Pepela and Dunlop (*26*) at 298.15K, and Negus and Norris (*22*) at 293.15 and 298.15K. It also shows the deviations of ϕ from the values tabulated by Scatchard et al. (*30*) and Robinson and Stokes (*27*). The latter two are about 0.0016 too high above about 1 mol kg^{-1} because they are determined from vapor-pressure measurements without correcting for

Table VI. Apparent Molar Enthalpy[a] at Rounded Temperatures and Molalities

	T, K								
m, mol kg^{-1}	273.15	298.15	323.15	348.15	373.15	398.15	423.15	448.15	473.15
0.1	−8	84	155	219	291	387	521	708	964
0.2	−51	88	189	275	368	490	665	914	1260
0.3	−97	81	207	309	416	556	759	1052	1464
0.4	−143	70	218	334	451	606	830	1159	1625
0.5	−189	57	224	352	480	645	888	1247	1761
0.6	−234	42	228	367	503	679	938	1324	1880
0.7	−278	26	230	380	524	709	983	1393	1987
0.8	−320	10	230	390	542	736	1024	1456	2084
0.9	−362	−6	230	400	559	762	1062	1515	2174
1.0	−402	−23	228	408	575	786	1098	1570	2258
1.2	−479	−55	224	424	605	831	1166	1672	2413
1.4	−551	−87	219	437	633	874	1230	1767	2553
1.5	−585	−103	216	443	646	896	1261	1812	2619
1.6	−619	−118	214	449	660	917	1292	1857	2683
1.8	−682	−148	208	461	686	958	1352	1942	2805
2.0	−741	−177	202	472	712	999	1411	2025	2920
2.5	−875	−242	188	500	777	1101	1555	2222	3185
3.0	−989	−300	178	529	842	1201	1694	2407	3427
3.5	−1089	−349	171	560	906	1299	1828	2582	3651
4.0		−390	169	591	968	1393	1955	2747	3861
4.5		−423	171	624	1030	1482	2075	2903	4060
5.0		−449	179	660	1091	1569	2190	3051	4249
5.5		−468	192	698	1152	1653	2300	3192	4429
6.0		−478	210	741	1216	1738	2408	3328	4601

[a] Quantity tabulated is Φ_L/(cal mol^{-1}).

Table VII. Relative Apparent Molar Heat Capacity[a] at Rounded Temperatures and Molalities

	T, K								
m, mol kg^{-1}	273.15	298.15	323.15	348.15	373.15	398.15	423.15	448.15	473.15
0.1	4.3	3.2	2.6	2.6	3.3	4.5	6.3	8.8	11.8
0.2	6.6	4.7	3.6	3.4	4.2	5.8	8.3	11.7	16.1
0.3	8.6	5.9	4.4	4.0	4.8	6.7	9.7	13.9	19.3
0.4	10.3	7.0	5.0	4.4	5.2	7.3	10.8	15.7	21.9
0.5	11.9	8.0	5.6	4.8	5.6	7.9	11.8	17.2	24.2
0.6	13.4	8.9	6.2	5.2	6.0	8.4	12.6	18.5	26.2
0.7	14.8	9.8	6.8	5.6	6.3	8.9	13.3	19.8	28.0
0.8	16.1	10.7	7.3	5.9	6.6	9.3	14.1	20.8	29.7
0.9	17.4	11.5	7.8	6.2	6.9	9.7	14.7	21.9	31.2
1.0	18.5	12.2	8.2	6.5	7.2	10.1	15.3	22.8	32.6
1.2	20.7	13.6	9.2	7.2	7.7	10.8	16.4	24.5	35.1
1.4	22.6	15.0	10.0	7.8	8.3	11.5	17.4	26.0	37.3
1.5	23.5	15.6	10.5	8.1	8.6	11.8	17.9	26.7	38.3
1.6	24.3	16.2	10.9	8.4	8.9	12.2	18.3	27.4	39.2
1.8	25.9	17.3	11.7	9.1	9.4	12.8	19.2	28.6	40.9
2.0	27.3	18.3	12.5	9.7	10.0	13.5	20.0	29.7	42.4
2.5	30.4	20.7	14.3	11.2	11.5	15.0	21.9	32.0	45.5
3.0	33.0	22.8	16.0	12.7	12.9	16.5	23.5	34.1	48.0
3.5	35.2	24.6	17.6	14.1	14.2	17.8	25.1	35.9	50.2
4.0		26.3	19.0	15.4	15.4	19.1	26.5	37.5	52.2
4.5		27.9	20.3	16.6	16.5	20.3	27.8	39.1	54.1
5.0		29.3	21.5	17.6	17.5	21.3	29.0	40.5	55.9
5.5		30.7	22.7	18.6	18.4	22.2	30.1	41.9	57.7
6.0		32.0	23.7	19.4	19.3	23.2	31.1	43.2	59.3

[a] Quantity tabulated is $[\Phi(C_p) - \Phi(C_p)^c]$/(cal K^{-1} mol^{-1}).

the deviations from the perfect gas laws. Scatchard et al. did not have the advantage of the measurements of Olynyk and Gordon and of those of Shankman and Gordon (*36*) on sulfuric acid. The values of Robinson and Stokes would be in good agreement if corrected for the difference between p/p° and a. The deviations of our measurements from Equation 9 at other temperatures are given in Table I.

Figure 3 gives the values of the osmotic coefficients from 273 to 373K calculated from Equation 9 and also those calculated by Smith and Hirtle (*37*) from their boiling-point elevations from 333 to 373K and from the measurements of Harned and Nims (*12*) of the emf's of concentration cells with sodium amalgam and silver, silver chloride electrodes from 273 to 313K. It also contains the values of Vlasov (*39*) from static vapor-pressure measurements at 318K. The perpendicular crosses are his smoothing to even molalities; the diagonal crosses are our smoothing of the same measurements. We put more weight on his measurement at 6.167 mol kg^{-1} and zero weight on his measurement at 6.26 mol kg^{-1}, which deviates from Equation 9 more than three times as much as any of the nine other measurements and nearly six times the average deviation. Moreover, the solubility at 318K listed in the ICT is only 6.24 mol kg^{-1}.

The high-temperature osmotic coefficients of Gardner et al. (*5, 6*) and Liu and Lindsay (*19, 20*) are compared with Equation 9 in Figures 4 and 5.

Freezing points. For the freezing-point measurements of Scatchard and Prentiss (*28*), Gibbard and Gossmann (*8*), Fong (*8*), and Momicchioli et al. (*21*), we calculated osmotic coefficients by Equation A1 of Scatchard et al. (*32*). For the dilute solutions their simpler Equation A2 was used. The deviations from Equation 9 are shown in Figure 6. The four sets of measurements are in good agreement and are fit fairly well by the equation, except that the deviations are consistently positive above about 0.5 mol kg^{-1}. However, the average deviation from Equation 9 of all the osmotic coefficients above 0.5 mol kg^{-1} is only 0.0018.

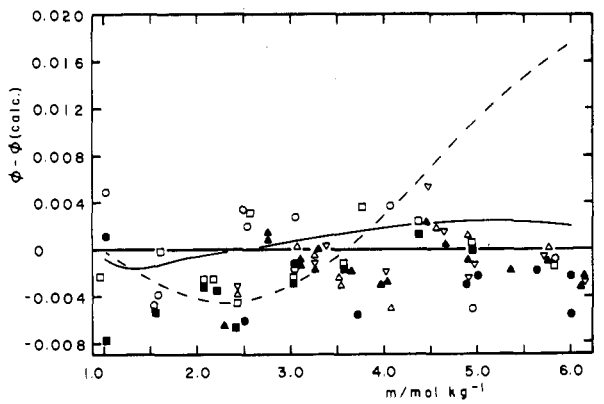

Figure 2. Osmotic coefficient deviations near 298K

● This work, 298.15K; ■ Negus (*22*), 298.15K; □ Norris (*22*), 293.15 and 298.15K; △ Olynyk and Gordon (*23*), 293.15K; ▲ Olynyk and Gordon (*23*), 298.15K; ▽ Olynyk and Gordon (*23*), 303.15K; ○ Pepela and Dunlop (*26*), 298.15K; — Robinson and Stokes (*27*), 298.15K; - - - Scatchard et al. (*30*), 298.15K

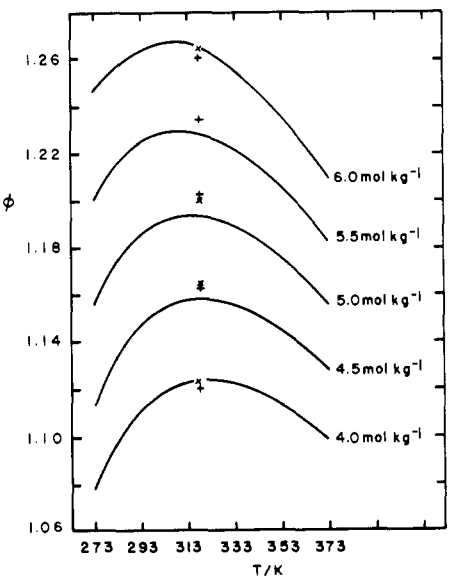

Figure 3b. Osmotic coefficients of aqueous sodium chloride from 273 to 373K, 4.0–6.0 mol kg^{-1}

x + Vlasov (*39*) (where only one cross is shown, Vlasov's smoothed value agrees with our smoothing of his results); — calculated from Equation 9

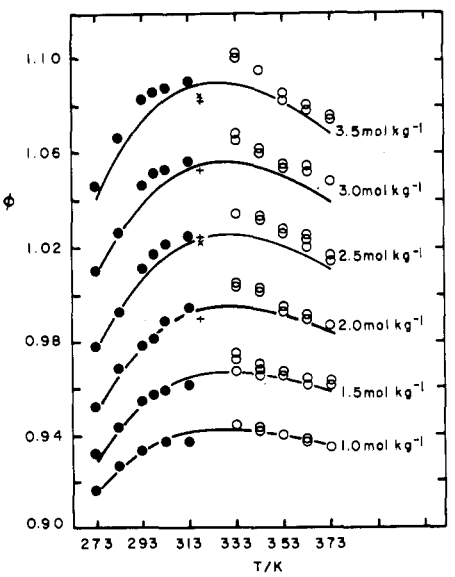

Figure 3a. Osmotic coefficients of aqueous sodium chloride from 273 to 373K, 1.0–3.5 mol kg^{-1}

● Harned and Nims (*12, 13*); ○ Smith and Hirtle (*37*); x + Vlasov (*39*) (where only one cross is shown, Vlasov's smoothed value agrees with our smoothing of his results); — calculated from Equation 9

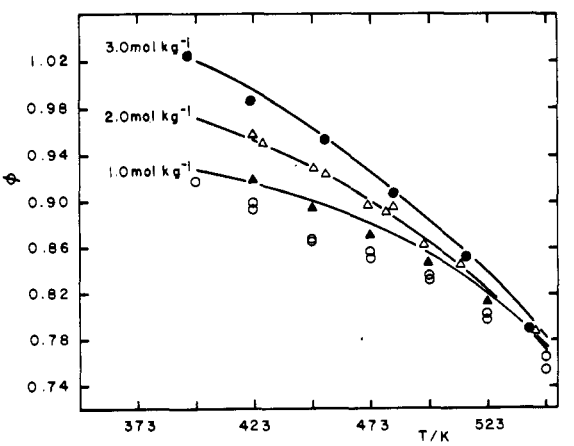

Figure 4. Osmotic coefficients of aqueous sodium chloride from 398 to 548K

○ Liu and Lindsay (*19*), 1.0 mol kg^{-1}; ▲ Gardner et al. (*5, 6*), 1.0 mol kg^{-1}; △ Gardner et al., 2.0 mol kg^{-1}; ● Gardner et al., 3.0 mol kg^{-1}; — calculated from Equation 9

Recently, Platford (*26a*) reported osmotic coefficients for aqueous sodium chloride at 273.15K from isopiestic measurements, with aqueous urea as a standard. Comparison of the values given from 0.1 to 6.0 mol kg^{-1} in Platford's Table II with those from our Table IV shows excellent agreement. The maximum deviation is 0.003, and the standard deviation of his values from ours is 0.0014.

Electromotive force and activity coefficients. Figure 7 shows deviations from Equation 10 of the logarithm of the activity coefficients of NaCl at 298.15K. Deviations are shown for the values tabulated by Robinson and Stokes (*27*) and measured by Harned and Nims (*12*) and Caramazza (*2*) with NaCl concentration cells with sodium amalgam and silver, silver chloride electrodes, and by Lanier (*18*) with alkali-sensitive glass and silver, silver chloride electrodes.

The three sets of measurements agree well up to 4 mol kg^{-1}, and below 1 mol kg^{-1}, they agree with the values tabulated by Robinson and Stokes which were obtained largely from ref. *13* and from measurements on other salts extrapolated similarly to zero molality. Above 2 mol kg^{-1} the deviations increase rapidly with increasing molality. This discrepancy was explained by Gibbard (*11*) as the result of the formation of silver chloride, sodium chloride solid solutions.

Enthalpies and heat capacities. The use of Equation 11 and its derivative with respect to temperature to fit the excess enthalpy and heat capacity values of Parker (*25*) constrains our equation to agree with the calorimetric quantities at 298K. The standard deviations of the least-squares treatments are 0.51 cal mol^{-1} for Φ_L, which Parker tabulates to the nearest calorie per mole, and 0.19 cal K^{-1} mol^{-1} for $\Phi(C_p)$, which she gives to 0.1 cal K^{-1} mol^{-1}.

Recently, Messikomer and Wood (*20a*) measured the enthalpy of dilution of aqueous sodium chloride from 298.15 to 373.15K. Their values of the excess enthalpy from 0.1 to 5.0 mol kg^{-1} and from 298.15 to 348.15K are in excellent agreement with the values given in Table VI; the average deviation is 9.6 cal mol^{-1}. The deviations increase at higher temperatures; above 348.15K our values are consistently lower than those of Messikomer and Wood. The average deviations at higher temperatures are: 21 cal mol^{-1} at 353.15K, 46 cal mol^{-1} at 363.15K, and 73 cal mol^{-1} at 373.15K. The agreement of our excess enthalpies with those of Ensor and Anderson (*4a*) is somewhat poorer at low temperatures and better at higher temperatures. For 0.1–6.0 mol kg^{-1} aqueous sodium chloride from 313.15 to 353.15K, the average deviation of Ensor and Anderson's values from those in Table VI is 19 cal mol^{-1}. However, at 353.15K the average deviation is only 12 cal mol^{-1}.

Eigen and Wicke (*4*) measured the heat capacities of 0.405, 0.573, and 1.120 mol kg^{-1} aqueous sodium chloride from 283 to 393 or 403K. Figure 8 shows the values of the apparent partial molar heat capacity at infinite dilution, $\Phi(C_p)^\circ$ computed from their measurements and the values of $\Phi(C_p) - \Phi(C_p)^\circ$ computed from the temperature derivative of Equation 11.

The full curve passes through the mean value at each temperature. The average deviations of the values from the mean are: 0.17 cal K^{-1} mol^{-1} at 283K, 0.43 cal K^{-1} mol^{-1} at 293K, 0.30 cal K^{-1} mol^{-1} at 313 and at 333K, 0.13 cal K^{-1} mol^{-1} at 353K, 0.90 cal K^{-1} mol^{-1} at

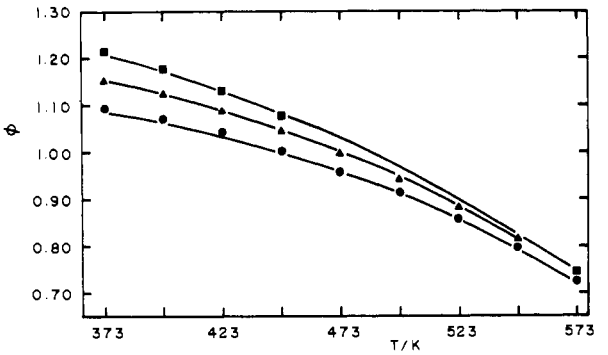

Figure 5. Osmotic coefficients of aqueous sodium chloride from 373 to 573K

● Liu and Lindsay (*20*), 3.4 mol kg^{-1}; ▲ Liu and Lindsay, 4.9 mol kg^{-1}; ■ Liu and Lindsay, 6.0 mol kg^{-1}; — calculated from Equation 9. Molalities given apply at 373K but increase with increasing temperature

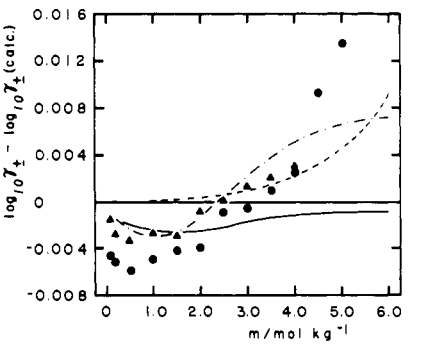

Figure 7. Deviations of activity coefficients at 298.15K from Equation 10

▲ Harned and Cook (*13*); ● Caramazza (*2*); — Robinson and Stokes (*27*); -·- Lanier (*18*); - - - Gibbard (*11*), calculated on basis of imperfection of Ag, AgCl electrode

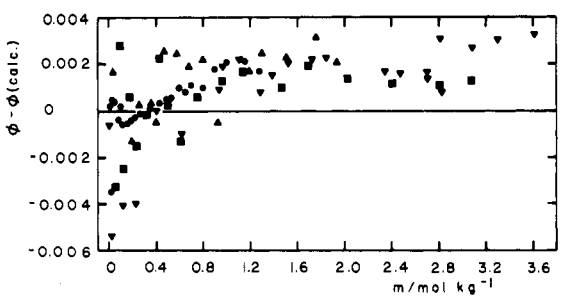

Figure 6. Osmotic coefficient deviations at freezing points of solutions

● Scatchard and Prentiss (*28*); ■ Momicchioli et al. (*21*); ▼ Gibbard and Gossmann (*8*); ▲ Fong (*8*)

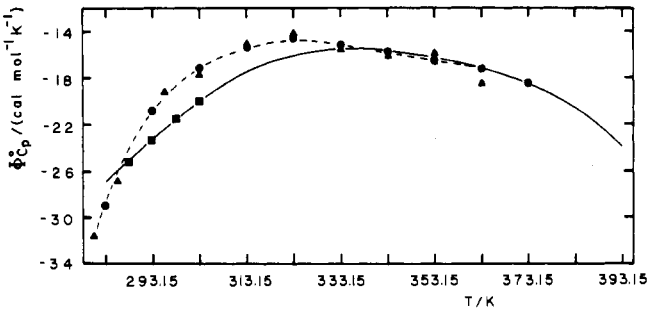

Figure 8. Temperature dependence of apparent partial molar heat capacity of sodium chloride at infinite dilution

■ Parker (*25*); ▲ Criss and Cobble (*3*), "measured"; ● Criss and Cobble, "smoothed"; curves are described in text

373K, and 1.63 cal K^{-1} mol^{-1} at 393K. The broken curve goes through the smoothed values from Table IV of Criss and Cobble (*3*), represented by the circles. Any smooth curve through these points must have a peculiar inflection near 323K.

The agreement between the values of Criss and Cobble and those computed from experimental heat capacities and our equation is remarkable. Even more remarkable is that when calorimetric quantities at 298K are omitted and all of the parameters of our equation are determined from solvent activities, the maximum deviation from Criss and Cobble is only 3.0 cal K^{-1} mol^{-1}. This requires that the fourth derivative of G^E/RT with respect to temperature be approximately correct. This is possible only for an equation derived from accurate solvent activities over a wide temperature range.

Literature Cited

(1) Åkerlöf, G. C., Oshry, H. I., *J. Amer. Chem. Soc.*, **72**, 2844 (1950).
(2) *Caramazza, R., Gazz. Chim. Ital.*, **90**, 1839 (1960).
(3) Criss, C. M., Cobble, J. W., *J. Amer. Chem. Soc.*, **83**, 3223 (1961).
(4) Eigen, M., Wicke, E., *Z. Elektrochem.*, **55**, 354 (1951).
(4a) Ensor, D. D., Anderson, H. L., *J. Chem. Eng. Data*, **18**, 205 (1973).
(5) Gardner, E. R., Jones, P. J., deNordwall, H. J., *Trans. Faraday Soc.*, **59**, 1994 (1963).
(6) Gardner, E. R., Jones, P. J., deNordwall, H. J., private communication, 1965.
(7) Gibbard, Jr., H. F., *J. Phys. Chem.*, **73**, 2382 (1969).
(8) Gibbard, Jr., H. F., Gossmann, A. F., *J. Solut. Chem.*, in press (1974).
(9) Gibbard, Jr., H. F., Scatchard, G., *J. Chem. Eng. Data*, **17** (4), 498 (1972).
(10) Gibbard, Jr., H. F., Scatchard, G., *ibid.*, **18** (2), 293 (1973).
(11) Gibbard, Jr., H. F., *J. Electrochem. Soc.*, **120**, 624 (1973).
(12) Harned, H. S., Nims, L. F., *J. Amer. Chem. Soc.*, **54**, 423 (1932).
(13) Harned, H. S., Cook, M. A., *ibid.*, **61**, 495 (1939).
(14) International Critical Tables, III, pp 25, 26, 234, McGraw-Hill, New York, N.Y., 1928.
(15) Keyes, F. G., Smith, L. B., Gerry, H. T., *Proc. Amer. Acad. Arts Sci.*, **70**, 319 (1936).
(16) Keyes, F. G., *J. Chem. Phys.*, **15**, 602 (1947).
(17) Kolthoff, I. M., Sandell, E. B., "Textbook of Quantitative Inorganic Analysis," Macmillan, New York, N.Y., 1952.
(18) Lanier, R. D., *J. Phys. Chem.*, **69**, 2697 (1965).
(19) Liu, C., Lindsay, W. T., *ibid.*, **74**, 341 (1970).
(20) Liu, C., Lindsay, W. T., "Thermodynamic Properties of Aqueous Solutions at High Temperatures," final report to Office of Saline Water under Contract 14-01-0001-2126, 1971.
(20a) Messikomer, E. E., Wood, R. H., *J. Chem. Thermodyn.*, in press.
(21) Momicchioli, F., Devoto, O., Cocco, G., Grandi, G., *Ber. Bunsenges. Phys. Chem.*, **74**, 59 (1970).
(22) Negus, S. S., thesis, Johns Hopkins University, Baltimore, Md., 1922.
(23) Olynyk, P., Gordon, A. R., *J. Amer. Chem. Soc.*, **65**, 224 (1943).
(24) Owen, B. B., Miller, R. C., Milner, C. E., Cogan, H. L., *J. Phys. Chem.*, **65**, 2065 (1961).
(25) Parker, V. B., "Thermal Properties of Aqueous Uni-Univalent Electrolytes," National Standard Reference Data Series, National Bureau of Standards 2, 1965.
(26) Pepela, C. N., Dunlop, P. J., *J. Chem. Thermodyn.*, **4**, 255 (1972).
(26a) Platford, R. F., *J. Chem. Eng. Data*, **18**, 215 (1973).
(27) Robinson, R. A., Stokes, R. H., "Electrolyte Solutions," 2nd ed., Butterworths, London, England, 1959.
(28) Scatchard, G., Prentiss, S. S., *J. Amer. Chem. Soc.*, **55**, 4355 (1933).
(29) Scatchard, G., Raymond, C. L., Gilmann, H. H., *ibid.*, **60**, 1275 (1938).
(30) Scatchard, G., Hamer, W. J., Wood, S. E., *ibid.*, p 3061.
(31) Scatchard, G., Kavanagh, G. M., Ticknor, L. B., *ibid.*, **74**, 3715 (1952).
(32) Scatchard, G., Vonnegut, B., Beaumont, D. W., *J. Phys. Chem.*, **33**, 1292 (1960).
(33) Scatchard, G., Wilson, G. M., Satkiewicz, F. G., *J. Amer. Chem. Soc.*, **86**, 125 (1964).
(34) Scatchard, G., Satkiewicz, F. G., *ibid.*, p 130.
(35) Scatchard, G., Wilson, G. M., *ibid.*, p 133.
(36) Shankman, S., Gordon, A. R., *ibid.*, **61**, 2370 (1939).
(37) Smith, R. P., Hirtle, D. S., *ibid.*, p 1123.
(38) Taylor, R. K., *ibid.*, **52**, 3577 (1930).
(39) Vlasov, Y. G., *Russ. J. Phys. Chem.*, **37**, 1399 (1963).

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NEW COMPOUND SECTION

Synthesis and Spectral Data for Some Derivatives of *N*-Aryloxamic Acid Hydrazides

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By condensation of diethyl oxalate with aromatic amines, 21 ethyl *N*-aryloxamates were prepared. Subsequent reaction with hydrazine afforded the corresponding *N*-aryloxamic acid hydrazides; these were converted into 80 hydrazones, 10 *N*-phosphoryl, 26 *N*-sulfonyl, nine *N,N*-dimethylcarbamoyl, and six *N*-ethoxycarbonyl derivatives. The ir and nmr spectral data of the various compounds and their biological activities are presented.

The *N*-aryloxamic acid hydrazides (I) (Table II) were obtained by hydrazinolysis of the appropriate ethyl *N*-aryloxamate (II) (Table I) (*24*). The latter were prepared by condensation of the arylamine with diethyl oxalate following the method of Pierce et al. (*22*):

$$(CO_2C_2H_5)_2 \xrightarrow{RNH_2} \underset{(II)}{R{\cdot}NH{\cdot}COCO_2C_2H_5} + \underset{(IV)}{RNHCOCONHR}$$

$$\underset{(II)}{R{\cdot}NH{\cdot}COCO_2C_2H_5} \xrightarrow{N_2H_4H_2O} \underset{(I)}{RNH_a{\cdot}COCO{\cdot}NH_bNH_2} \xrightarrow{R'R''CO} \underset{(III)}{RNHCOCONHN{=}CR'R''}$$

The hydrazides (I) were converted into hydrazones (III) (Table III) by treatment with the appropriate carbonyl compound: the reaction was catalyzed by a trace of io-