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THERMODYNAMIC PROPERTIES OF AQUEOUS NaCl FROM 273 TO 823 K WITH  
ESTIMATES FOR HIGHER TEMPERATURES

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(Abstract)

Equations based on theory, to the degree feasible, are developed which represent the various thermodynamic properties of aqueous NaCl. In the range 273-573 K, 0-1 kbar, and to saturation molality, the experimental data base is excellent. An equation based on a virial expansion and a Debye-Hückel term represents the data accurately. This form of equation has been generalized to multicomponent systems; hence these results are readily extended to complex brines as the properties for other components become known.

In the range above 573 K the data are more limited and of less accuracy, but a comprehensive treatment is still possible. The equation is one used before for ionic systems miscible to a fused salt. The supercooled liquid NaCl is taken as a reference state. The equation is valid from 423 to 823 K and thus has an extensive overlap with the lower-temperature equation. Estimates are also presented for temperatures above 823 K.

INTRODUCTION

The thermodynamic properties of aqueous sodium chloride are important in many areas including geochemistry, oceanography, and many industrial processes. In practical steam power generation the water is not perfectly pure and the most common impurity is NaCl. For many purposes the properties of seawater and other natural waters may be approximated by sodium chloride solutions of appropriate composition. Since aqueous NaCl is the electrolyte which has been most widely investigated, it is of theoretical interest as the prototype of an ionic system including a polar molecular solvent.

There are various empirical compilations of the volumetric and thermodynamic properties of NaCl-H<sub>2</sub>O, including a comprehensive one by Khaibullin (1980). The primary purposes of the present investigations have been, (a) to represent the experimental data by analytical equations, and (b) to incorporate very recent measurements of high accuracy. An equation of state has the advantage that the various properties interrelated by thermodynamics are all given by the appropriate derivatives of the parent equation. This makes available convenient computation of any desired property and assures consistency with all thermodynamic relationships. It was possible to use equations where the composition dependence has a theoretical basis in molecular-statistical terms and where this compositional dependence can be generalized to multicomponent systems.

Although the properties of aqueous NaCl are known over a very wide range of temperature, pressure, and composition, the accuracy and completeness of the measurements varies greatly for different ranges of temperature and pressure. Also the character of water changes greatly and therewith the extent to which water modifies the interionic forces. For both sets of reasons, it is difficult to use a single equation to express the properties over the entire range. Fortunately, there is an equation of state for pure water valid in good approximation over the entire range of interest and having a theoretically based form so that extrapolation to higher temperature is probably reliable. We use the equation of Haar, et al. (1981) without correction for the region immediately around the critical point (Kestin, et al. 1984). For the dielectric constant (relative permittivity) of water the empirical equation of Uematsu and Franck (1980) is valid from 273 to 823 K, but its form does not allow extrapolation to higher temperature. Since one of our objectives is to develop equations valid at still higher temperatures, we have chosen to use a theoretically based equation (Pitzer, 1983a) for the dielectric constant which should be reasonably accurate to very high temperature above the range of experimental measurement; it fits the experimental measurements for liquid-like densities above 573 K, which extend to 823 K, and is valid for steam at any temperature. At lower temperatures the relatively simple equation of Bradley and Pitzer (1979) fits the data for the liquid and agrees very precisely with the values recommended by the International Union of Pure and Applied Chemistry (Kienitz and Marsh, 1981).

Recently my colleagues and I have developed two equations for the thermodynamic properties of aqueous NaCl. The first, by Pitzer, Peiper, and Busey (1984), depends on an earlier equation of Rogers and Pitzer (1982) for the volumetric properties as well as a large array of activity, enthalpy and heat capacity measurements extending to 573 K, 1 kbar, and saturation molality. This equation, designated PPB hereafter, follows the pattern used for room-temperature electrolyte thermodynamics in using molality as the measure of composition and in adopting a form known to be accurate for many aqueous electrolytes, including mixtures, near 298 K. Since the PPB equation has been described rather comprehensively, the present paper will include only a general description and, in the Appendix, a concise statement of the exact mathematical expressions and parameters.

The second equation, by Pitzer and Li (1983) was designed for application over a much higher temperature range extending even to pure fused NaCl. While presently available experimental data allowed evaluation of parameters only to 823 K, there is every reason to expect the form of the equation to continue to be useful to much higher temperature provided the density remains fairly high. While there are many differences between this second, PL, equation and the PPB equation, both assume that the NaCl is present primarily as ions. At low densities, such as the steam side of the two-phase region, there is extensive ion pairing which must be recognized in an accurate treatment. The extent to which the PL equation gives useful estimates at intermediate densities and concentrations is discussed in the last section of this paper.

The original publication of Pitzer and Li(1983) presented the development of the PL equation for activities of both H<sub>2</sub>O and NaCl but gave only very brief comments about other properties. In this paper the development of the PL equation is reviewed; the differences from the PPB equation are clearly described, and then new calculations are presented of the enthalpy and entropy from the PL equation for the range above 573 K.

Finally, there is a discussion of the few data and of estimates of the properties of NaCl-H<sub>2</sub>O above 823 K.

TREATMENT VALID TO 573 K (PPB EQUATION)

There are extensive measurements of several thermodynamic properties for NaCl-H<sub>2</sub>O in the range to 573 K or in some cases a little higher temperature. A set of equations representing these properties to nearly full experimental accuracy has been developed and published very recently (Pitzer, et al. 1984). Extensive tables are included as well as references to the sources of experimental data. It would be inappropriate to repeat that presentation in full detail, hence, I present only a general description and include in the Appendix a concise statement of the exact equations with a listing of the numerical parameters.

The composition dependence at any given temperature and pressure is represented by a simple, theoretically-based equation (Pitzer, 1973) which has the advantage that it has been successfully extended to multi-component systems (Pitzer and Kim, 1974). The pure electrolyte parameters are the dominant terms for the more complex systems. The PPB equation uses molality which is the most widely used composition variable for aqueous electrolytes.

For a single solute with singly charged ions one may define the excess Gibbs energy in the molality system as

$$G^{EX} = G - n_1 G_1^\circ - n_2 \bar{G}_2^\circ + 2n_2 RT(1 - \ln m) \quad (1)$$

where  $n_1$  and  $n_2$  give the content in moles of solvent and salt of molar Gibbs energies  $G_1^\circ$  and  $\bar{G}_2^\circ$  in their reference states, respectively, and  $m$  is the molality. Then it is assumed that

$$G^{EX}/n_w RT = f(I) + 2m^2 B(I) + 2m^3 C \quad (2)$$

where  $n_w$  is the number of kg of solvent ( $n_1/n_w \cong 55.5 \text{ mol}\cdot\text{kg}^{-1}$ ) and  $f(I)$  is a function of a Debye-Hückel type representing the effect of long-range electrostatic forces.  $B$  and  $C$  are second and third virial coefficients representing the effect of short-range, solvent-modulated forces between pairs and triplets of solute particles respectively. Higher virial terms could be included but are not needed for NaCl or for most solutes. Although for the 1:1 electrolyte the ionic strength  $I$  is equal to the molality  $m$ , the separate symbol  $I$  is used to

emphasize a dependency on ionic strength in a multicomponent solution. For a different salt  $f(I)$  remains the same, but B and C are solute specific. The ionic strength dependence of B, however, is given by a general expression which has a theoretical basis (Pitzer, 1973). The detailed forms of  $f(I)$  and  $B(I)$  are given in the Appendix.

The chemical potential and the activity for either component are given by the usual definitions

$$\mu_i = (\partial G / \partial n_i)_{T,P,n_j} \quad (3)$$

$$\ln a_i = (\mu_i - G_i^\circ) / RT. \quad (4)$$

The molality,  $m = 1000 n_2 / M_1 n_1$  with  $M_1$  the molecular mass of the solvent, is unsymmetrically related to  $n_1$  and  $n_2$ . Hence, there are different expressions for  $a_1$  and  $a_2$

$$\ln a_1 = \frac{M_1}{1000} \left[ -2m + \frac{G^{EX}}{n_w RT} - m \left( \frac{\partial (G^{EX} / n_w RT)}{\partial m} \right)_{P,T} \right] \quad (5)$$

$$\ln a_2 = 2 \ln m + \left[ \frac{\partial (G^{EX} / n_w RT)}{\partial m} \right]_{P,T} \quad (6)$$

In the molality system the activity coefficient of a symmetrical ionic solute is

$$\gamma_{\pm} = a_2^{1/2} / m \quad (7)$$

$$\ln \gamma_{\pm} = (1/2) \left[ \frac{\partial (G^{EX} / n_w RT)}{\partial m} \right]_{P,T} \quad (8)$$

while the osmotic coefficient is defined to represent solvent activity as

$$\phi = -(1000 / 2M_1 m) \ln a_1 \quad (9a)$$

$$\phi - 1 = \frac{1}{2} \left[ \left( \frac{\partial (G^{EX} / n_w RT)}{\partial m} \right)_{P,T} - \frac{G^{EX}}{n_w RT m} \right] \quad (9b)$$



The detailed expressions for  $\gamma_{\pm}$  and  $\phi$  with the forms adopted for  $f(I)$  and  $B(I)$  are given in the Appendix.

The excess enthalpy, entropy, heat capacity, volume, and related quantities are all given by appropriate derivatives of the excess Gibbs energy. If  $Y^{\text{EX}}$  represents any of these excess quantities, it has the same composition dependence as  $G^{\text{EX}}$  since the molality is independent of  $P$  or  $T$ . Thus

$$Y^{\text{EX}}/n_w = f^Y(I) + 2m^2 B^Y(I) + 2m^3 C^Y \quad (10)$$

where the ionic strength dependence of  $f^Y(I)$  is the same regardless of  $Y$  and the same is true for  $B^Y(I)$ .

The only temperature and pressure dependent quantity in  $f(I)$  is the Debye-Hückel parameter which is fully determined by the properties of water. Both  $B$  and  $C$  contain parameters dependent on temperature and pressure which are expressed empirically. The appropriate derivatives then give  $B^{\text{H}}$  for enthalpy,  $B^{\text{S}}$  for entropy,  $B^{\text{V}}$  for volume, etc. The full array of parameters are given in the Appendix.

The full list of experimental data which were considered is given in the detailed paper. I only comment here about a few very important investigations including the precise osmotic coefficient measurements of Liu and Lindsay (1972) and the very recent heat of dilution measurements of Busey, et al. (1984). These two sets of data are consistent to high accuracy and determine the composition dependency at the higher temperatures. The absolute enthalpy and entropy values depend primarily on the heat capacity measurements at  $3 \text{ mol kg}^{-1}$  by White and Wood (1982). Most important for the volumetric data base are the measurements of Hilbert (1979). These comments all relate to the higher temperatures; there are many accurate measurements at lower temperatures.

The final PPB equation gives the Gibbs energy as a function of temperature, pressure, and molality. Appropriate derivatives yield activity and osmotic coefficients, as well as the enthalpy, entropy, heat capacity, volume (or density), expansivity and compressibility. Tables are included giving the various parameters for various values of  $T$  and  $P$ . From these parameters it is a very simple calculation to insert the dependency on molality and to obtain any of the properties

at a given value of  $m$ . In addition, there are tables of the various thermodynamic properties at appropriately spaced intervals of  $T$ ,  $P$ ,  $m$  for linear interpolation.

The pressure dependency of the Gibbs energy, which yields the volumetric properties, was developed by Rogers and Pitzer (1982) and was retained without change in the more complete PPB equation. Likewise, the earlier 1982 paper should be consulted for the details of the experimental volumetric data and for the tables of volumetric parameters and explicit values of the specific volume, expansivity, and compressibility. In order to maintain optimum accuracy for the low temperature range where there are very precise experimental data, a "low temperature" fit (valid to 358 K) was made in addition to the general fit valid from 273 to 573 K with lower precision.

Table 1 gives a list of the tables of parameters as functions of  $T$  and  $P$  and a list of tables of properties as functions of  $T$ ,  $P$ , and  $m$  which are available in one or the other paper. As samples of the property tables and for use in comparison with results for higher temperatures, Tables 2 and 3 give the specific enthalpy and the specific entropy for 1000 bar.

The absolute reference state of energy or enthalpy for  $H_2O$  is the gas at zero Kelvin while for  $NaCl$  it is the infinitely dilute solute standard state at 298.15 K and 1 atm. Another set of reference states in common use is pure liquid water and infinitely dilute  $NaCl$ , both at 273.15 K ( $0^\circ C$ ). For conversion of our values in Table 2 to the latter reference states, add  $1997.65 \text{ J}\cdot\text{g}^{-1}$  for  $H_2O$  and subtract  $52.1 \text{ J}\cdot\text{g}^{-1}$  for  $NaCl$ . Our entropies are absolute values, i.e., they are referenced to states of  $H_2O$  and  $NaCl$  which approach zero entropy as  $T \rightarrow 0 \text{ K}$ .

Estimates of uncertainty are given in Table 4 for calculated values of various thermodynamic quantities as a function of temperature, pressure, and molality. The uncertainties are very small over most of the range of conditions but increase considerably near 573 K and especially above 200 bar and near 573 K. The solubility of solid  $NaCl$  was not used in the evaluation of the PPB equation, but it is shown that the final results for the activity coefficient are consistent with the measured solubility (to 1% at the extremes of temperature and to 0.2% over most of the range).

Table 1. Tables of Parameters as Functions of T and P and of Thermodynamic Properties as Functions of T, P, and m Based on the PPB Equation for NaCl-H<sub>2</sub>O

Parameter tables: all given by Pitzer, et al. (1984);  
the last three also given by Rogers and Pitzer (1982).

1. Standard Gibbs energies, Debye-Hückel  $A_\phi$  parameter, and virial coefficients for NaCl(aq)
2. Standard entropies, Debye-Hückel  $A_S$  parameter, and virial coefficients for the NaCl(aq) entropy
3. Standard enthalpies, Debye-Hückel  $A_L$  parameter, and virial coefficients for the NaCl(aq) enthalpy
4. Standard heat capacities, Debye-Hückel  $A_J$  parameter, and virial coefficients for the NaCl(aq) heat capacity
5. Standard volumes, Debye-Hückel  $A_V$  parameter, and virial coefficients for the NaCl(aq) volume
6. Standard expansivities, Debye-Hückel  $A_x$  parameter, and virial coefficients for the NaCl(aq) expansivity
7. Standard compressibilities, Debye-Hückel  $A_K$  parameter, and virial coefficients for the NaCl(aq) compressibility

Property Tables

A. Tables given by Pitzer, et al. (1984)

1. Activity coefficient of NaCl(aq)
2. Osmotic coefficient of NaCl(aq)
3. Entropy of solution of NaCl(aq)
4. Enthalpy of solution of NaCl(aq)
5. Relative entropy of NaCl(aq)
6. Relative enthalpy of NaCl(aq)
7. Relative heat capacity of NaCl(aq)
8. Density of NaCl(aq)
9. Specific entropy of NaCl(aq)
10. Specific enthalpy of NaCl(aq)

B. Tables given by Rogers and Pitzer (1982)

11. Specific volumes of NaCl(aq)
12. Expansivities of NaCl(aq)
13. Compressibilities of NaCl(aq)

Table 2. The Specific Enthalpy ( $\text{J}\cdot\text{g}^{-1}$ ) of  $\text{NaCl}(\text{aq})$  at 1000 bar

t °C	m=0.1 mol/kg	m=0.25 mol/kg	m=0.5 mol/kg	m=0.75 mol/kg	m=1.0 mol/kg	m=2.0 mol/kg	m=3.0 mol/kg	m=4.0 mol/kg	m=5.0 mol/kg	m=6.0 mol/kg
0.0	-1891.2	-1874.8	-1848.2	-1822.4	-1797.4	-1704.8	-1622.1	-1547.9	-1480.6	-1419.2
10.0	-1852.2	-1836.2	-1810.0	-1784.7	-1760.2	-1669.0	-1587.6	-1514.3	-1447.9	-1387.1
20.0	-1812.9	-1797.2	-1771.6	-1746.8	-1722.7	-1633.1	-1552.9	-1480.6	-1414.9	-1354.9
25.0	-1793.2	-1777.6	-1752.3	-1727.7	-1703.9	-1615.0	-1535.5	-1463.7	-1398.5	-1338.7
30.0	-1773.4	-1758.0	-1732.9	-1708.6	-1685.0	-1597.0	-1518.1	-1446.8	-1382.0	-1322.5
40.0	-1733.6	-1718.6	-1694.0	-1670.2	-1647.1	-1560.7	-1483.1	-1412.9	-1348.9	-1290.2
50.0	-1693.8	-1679.1	-1655.1	-1631.8	-1609.1	-1524.4	-1448.2	-1379.1	-1315.9	-1257.9
60.0	-1654.0	-1639.6	-1616.1	-1593.3	-1571.1	-1488.0	-1413.2	-1345.2	-1283.0	-1225.6
70.0	-1614.0	-1600.0	-1577.1	-1554.7	-1533.0	-1451.7	-1378.2	-1311.3	-1249.9	-1193.3
80.0	-1574.1	-1560.4	-1538.0	-1516.2	-1494.9	-1415.2	-1343.1	-1277.4	-1217.0	-1161.2
90.0	-1534.0	-1520.7	-1498.8	-1477.5	-1456.8	-1378.8	-1308.1	-1243.5	-1184.2	-1129.1
100.0	-1493.9	-1480.9	-1459.6	-1438.9	-1418.6	-1342.4	-1273.1	-1209.7	-1151.3	-1097.2
110.0	-1453.8	-1441.1	-1420.4	-1400.1	-1380.4	-1305.9	-1238.1	-1175.9	-1118.6	-1065.3
120.0	-1413.5	-1401.2	-1381.1	-1361.3	-1342.1	-1269.4	-1203.0	-1142.1	-1085.8	-1033.5
130.0	-1373.1	-1361.2	-1341.7	-1322.5	-1303.8	-1232.9	-1168.0	-1108.4	-1053.2	-1001.8
140.0	-1332.7	-1321.2	-1302.2	-1283.6	-1265.4	-1196.4	-1133.0	-1074.6	-1020.5	-970.1
150.0	-1292.2	-1281.1	-1262.7	-1244.7	-1227.0	-1159.9	-1098.1	-1040.9	-987.9	-938.5
160.0	-1251.6	-1240.9	-1223.2	-1205.7	-1188.6	-1123.4	-1063.1	-1007.3	-955.4	-906.9
170.0	-1210.9	-1200.6	-1183.5	-1166.7	-1150.2	-1086.9	-1028.2	-973.7	-922.8	-875.3
180.0	-1170.1	-1160.3	-1143.9	-1127.7	-1111.7	-1050.4	-993.3	-940.1	-890.4	-843.8
190.0	-1129.2	-1119.8	-1104.1	-1088.6	-1073.2	-1014.0	-958.5	-906.5	-857.9	-812.3
200.0	-1088.2	-1079.3	-1064.3	-1049.4	-1034.7	-977.6	-923.7	-873.0	-825.5	-780.7
210.0	-1047.1	-1038.6	-1024.4	-1010.2	-996.1	-941.2	-888.9	-839.6	-793.0	-749.2
220.0	-1005.8	-997.9	-984.5	-971.0	-957.5	-904.8	-854.2	-806.2	-760.6	-717.7
230.0	-964.4	-957.0	-944.4	-931.7	-918.9	-868.4	-819.6	-772.8	-728.3	-686.1
240.0	-922.8	-915.9	-904.2	-892.3	-880.2	-832.1	-785.0	-739.5	-695.9	-654.4
250.0	-881.0	-874.7	-863.9	-852.8	-841.5	-795.9	-750.5	-706.2	-663.5	-622.7
260.0	-838.9	-833.3	-823.5	-813.2	-802.8	-759.7	-716.0	-673.0	-631.1	-590.9
270.0	-796.7	-791.7	-782.9	-773.6	-764.0	-723.6	-681.7	-639.8	-598.7	-559.0
280.0	-754.1	-749.9	-742.2	-733.9	-725.2	-687.6	-647.5	-606.8	-566.3	-526.9
290.0	-711.3	-707.9	-701.4	-694.2	-686.4	-651.7	-613.5	-573.8	-533.7	-494.4
300.0	-668.2	-665.7	-660.5	-654.4	-647.7	-616.2	-579.8	-540.8	-501.0	-461.5

Table 3. The Specific Entropy ( $\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ ) of  $\text{NaCl}(\text{aq})$  at 1000 bar

t °C	m=0.1 mol/kg	m=0.25 mol/kg	m=0.5 mol/kg	m=0.75 mol/kg	m=1.0 mol/kg	m=2.0 mol/kg	m=3.0 mol/kg	m=4.0 mol/kg	m=5.0 mol/kg	m=6.0 mol/kg
0.0	3.504	3.495	3.477	3.458	3.437	3.350	3.260	3.171	3.085	3.002
10.0	3.644	3.634	3.614	3.593	3.571	3.478	3.384	3.292	3.202	3.117
20.0	3.780	3.769	3.748	3.725	3.701	3.603	3.505	3.409	3.317	3.229
25.0	3.847	3.835	3.813	3.789	3.765	3.664	3.564	3.466	3.373	3.284
30.0	3.913	3.900	3.877	3.853	3.828	3.724	3.622	3.522	3.427	3.337
40.0	4.042	4.028	4.004	3.977	3.951	3.842	3.735	3.632	3.535	3.442
50.0	4.167	4.152	4.126	4.098	4.070	3.956	3.845	3.739	3.638	3.544
60.0	4.288	4.273	4.245	4.216	4.186	4.067	3.951	3.842	3.739	3.642
70.0	4.406	4.390	4.360	4.329	4.298	4.174	4.055	3.942	3.836	3.738
80.0	4.521	4.504	4.472	4.440	4.408	4.279	4.156	4.040	3.931	3.830
90.0	4.633	4.615	4.582	4.548	4.514	4.381	4.253	4.134	4.023	3.920
100.0	4.742	4.723	4.688	4.653	4.618	4.480	4.349	4.226	4.112	4.006
110.0	4.848	4.828	4.792	4.756	4.719	4.576	4.441	4.315	4.199	4.091
120.0	4.952	4.931	4.893	4.856	4.818	4.670	4.531	4.402	4.283	4.173
130.0	5.053	5.031	4.992	4.953	4.914	4.762	4.619	4.487	4.365	4.252
140.0	5.152	5.129	5.089	5.048	5.008	4.851	4.705	4.570	4.445	4.330
150.0	5.249	5.225	5.183	5.141	5.100	4.939	4.789	4.650	4.523	4.406
160.0	5.344	5.319	5.276	5.233	5.189	5.024	4.870	4.729	4.599	4.479
170.0	5.437	5.411	5.366	5.322	5.277	5.107	4.950	4.806	4.673	4.551
180.0	5.528	5.501	5.455	5.409	5.363	5.188	5.028	4.881	4.746	4.622
190.0	5.617	5.589	5.542	5.494	5.447	5.268	5.104	4.954	4.817	4.691
200.0	5.705	5.676	5.627	5.578	5.529	5.346	5.178	5.025	4.886	4.758
210.0	5.791	5.761	5.710	5.660	5.610	5.422	5.251	5.095	4.954	4.824
220.0	5.875	5.844	5.792	5.740	5.689	5.497	5.322	5.164	5.020	4.889
230.0	5.959	5.926	5.872	5.819	5.767	5.569	5.392	5.231	5.085	4.952
240.0	6.041	6.007	5.951	5.897	5.843	5.641	5.460	5.296	5.149	5.014
250.0	6.121	6.087	6.029	5.973	5.917	5.711	5.526	5.361	5.211	5.075
260.0	6.201	6.165	6.106	6.048	5.991	5.779	5.591	5.424	5.273	5.136
270.0	6.279	6.242	6.181	6.121	6.063	5.847	5.655	5.485	5.333	5.195
280.0	6.357	6.319	6.255	6.194	6.134	5.912	5.718	5.546	5.392	5.254
290.0	6.434	6.394	6.329	6.265	6.203	5.976	5.779	5.605	5.450	5.312
300.0	6.510	6.468	6.401	6.335	6.271	6.039	5.838	5.663	5.508	5.370

Table 4. Uncertainty Estimates for the PPB Equation

## Part A. Volumetric Properties

Property	t/°C	p/bar	m	Uncertainties	
				low T fit	high T fit
Volume	0- 25	1.01	0-5.5	120 ppm	150 ppm
	0- 25	1-1000	0-2.0	120 ppm	150 ppm
	25- 85	1-1000	0-5.5	70 ppm	150 ppm
	85-300	1-1000	0-5.5	-	700 ppm
Expansivity	0- 25	1.01	0-4.0	1%	- <sup>a</sup>
	0- 25	1-1000	0-2.0	1%	- <sup>a</sup>
	25- 85	1-1000	0-4.0	1%	5%
	85-300	1-1000	0-4.0	-	5%
Compress- ibility	0- 25	1-1000	0-2.0	.5%	- <sup>a</sup>
	25- 85	1-1000	0-5.0	.5%	5%
	85-300	1-1000	0-5.0	-	5%

<sup>a</sup> Not recommended.

## Part B. Thermal and Activity Properties

Property	m	25°C		200°C		300°C	
		200	1000	200	1000	200	1000
p/bar		200	1000	200	1000	200	1000
$\phi$	0-6	0.002	0.004	0.004	0.008	0.006	0.02
$\ln \gamma_{\pm}$	1.0	0.002	0.006	0.005	0.013	0.015	0.05
	3.0	0.003	0.010	0.008	0.02	0.018	0.06
	6.0	0.004	0.012	0.01	0.03	0.020	0.08
$\Delta H_s^{\circ}/RT$	-	0.06	0.22	0.08	0.30	0.8	2.5
$\phi_L/RT$	1.0	0.01	0.03	0.03	0.09	0.4	1.5
	3.0	0.02	0.10	0.03	0.12	0.5	2.0
	6.0	0.03	0.12	0.04	0.15	0.8	3.0
$\bar{C}_{p,2}^{\circ}/R$	-	0.6	1.8	1.5	4.0	20.	40.
$\phi_C^{\circ}/R$	1-4	0.3	1.2	0.6	2.5	10.	20.

TREATMENT VALID FROM 373 TO 823 K (PL EQUATION)

As the temperature increases substantially above 573 K there are several changes in the NaCl-H<sub>2</sub>O system which are so great that a difference in general formulation of treatment is indicated. Most obviously, pure water at moderate pressure is gas-like rather than liquid-like above the critical temperature. The solute properties in the infinitely dilute reference state display extreme behavior near the critical point

of water. Hence this infinitely dilute state is not a useful reference state for the NaCl. The solubility of solid NaCl increases rapidly. Indeed at its melting point, 1074 K, the system becomes a fluid miscible in all proportions. The molality becomes infinite for a pure fused salt; thus it is not a convenient measure of composition for very soluble systems. Even at 823 K the saturated solution is 63 wt. % NaCl. At temperatures above 700 K and below the critical pressure, the more concentrated of the co-existing phases is liquid-like. The dilute phase is essentially steam; only very near the critical pressure does the concentration of NaCl become substantial. For some purposes, however, the presence of even a very small concentration of NaCl can be very important. The NaCl in the dilute phase exists primarily as ion pairs (Quist and Marshall, 1968; Pitzer, 1983b) whereas in the concentrated phase it is ionized (Pitzer, 1984a). Thus, at these higher temperatures, there is a wide range of composition in which the solvent is liquid-like and the solute is ionized. It is for this range of ionized, liquid-like nature that an equation was developed by Pitzer and Li (1983).

The original publication emphasized the selection of the form of the PL equation and the data for the activity of both  $H_2O$  and NaCl to which it was fitted. After reviewing these aspects, the present paper will emphasize the calculation of enthalpy and entropy. Then there is a discussion of the extent to which the PL equation may yield less accurate but still useful estimates for more dilute solutions or at still higher temperatures or pressures.

Simple 1-1 nitrate salts have much lower melting points than NaCl. They form aqueous solutions of very large solubility at temperatures near 373 K. A very simple equation was found to be adequate (Pitzer, 1981) to describe the behavior of some of these nitrate solutions that are similar in many respects to the NaCl solutions at much higher temperatures. Thus Dr. Li and I first explored the adequacy of this simple equation for NaCl- $H_2O$  in the range below 573 K where the properties are well established. We found remarkably good agreement for a very simple equation from 373 to 573 K, to 1 kbar, and over the entire range of composition. As expected, the accuracy of agreement is less than that of the more complex PPB equation, but the accuracy is high enough to be very useful in a range of less precise experimental data. Consequently, the same equation was fitted to the more limited data in the range to

823 K and good agreement was obtained.

Several differences between this PL treatment and the PPB equation should be emphasized.

1. The measure of composition is mole fraction on an ionized basis,

$$x_1 = n_1 / (n_1 + 2n_2) \quad (11)$$

$$x_2 = 2n_2 / (n_1 + 2n_2) \quad (12)$$

with  $n_1$  and  $n_2$  the numbers of moles of  $H_2O$  and  $NaCl$ , respectively. The terms for ideal behavior are different on a mole fraction basis from those on a molality basis. This yields a different definition of the excess Gibbs energy as follows:

$$G_x^{EX} = G - n_1 G_1^\circ - n_2 G_2^\circ - RT(n_1 \ln x_1 + 2n_2 \ln x_2) \quad (13)$$

where the subscript  $x$  is a reminder of the mole fraction basis.

2. The solute reference state, at any given temperature and pressure, is supercooled liquid  $NaCl$ . At temperatures below 600 K this is evaluated from solution data just as is the case for the infinitely dilute reference state. But one can use the heat of fusion of  $NaCl$ , and the differences in heat capacity and volume between solid and liquid, to extrapolate properties of liquid  $NaCl$  well below the melting point. A smooth curve was adopted interpolating properties of supercooled liquid  $NaCl$  between the values from 373 to 573 K and the extrapolated curve valid at higher temperature. This is expressed as a Gibbs energy of solution (or of fusion)  $\Delta_s G^\circ$  and is shown in Fig. 1 as  $\Delta_s G^\circ / RT$

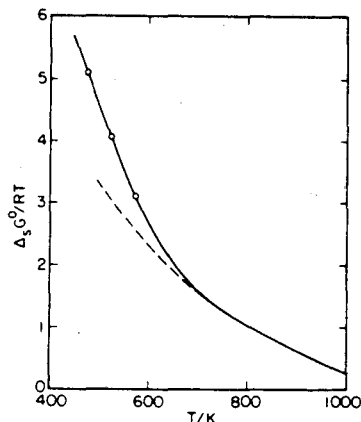


Figure 1. The Gibbs energy of fusion to the supercooled liquid. See text for explanation of the curves.



as a function of T. Now the molar reference-state Gibbs energy of NaCl becomes

$$G_2^\circ = G^\circ(\text{NaCl}, c) + \Delta_S G^\circ \quad (14)$$

where  $G^\circ(\text{NaCl}, c)$  is for crystalline NaCl and all terms are on a molar basis.

3. The Debye-Hückel term in the PL equation contains the limiting law, and is equivalent to the  $f(I)$  of the PPB equation in the limit at low concentration. But the two expressions, although similar in form, differ at any finite concentration and differ substantially at high concentration. The ionic strength is now defined as

$$I_x = \frac{1}{2} \sum z_i^2 x_i \quad (15)$$

with  $z_i$  the charge and  $x_i$  the mole fraction of the  $i^{\text{th}}$  ion. For NaCl this becomes  $I_x = x_2/2$ .

4. The single Margules term in mole fraction for short-range forces in the PL equation is completely different from the power series in molality of the PPB equation. At finite concentration differences in the expressions for short-range forces compensate for differences in the ideal-solution terms and the Debye-Hückel term. The theoretical rationale for the use of a Margules term for an ionic system has been discussed elsewhere (Pitzer, 1981).
5. While the activity of water is the same in either equation and the activity of NaCl differs only from the difference of reference states, the activity coefficients are different. For the solute in the mole fraction system  $\gamma_{\pm, x} = a_2^{1/2}/x_2$  whereas in the molality system  $\gamma_{\pm} = a_2^{1/2}/m$ . For the solvent in the mole fraction system  $\gamma_1 = a_1/x_1$ , but in the molality system one uses instead the osmotic coefficient defined in equation (9a).

In terms of these various definitions the following expression is assumed for the excess Gibbs energy:

$$\frac{G_x^{\text{EX}}}{(n_1 + 2n_2)RT} = wx_1x_2 - \left( \frac{4A}{\rho} \frac{I_x}{x_1x_2} \right) \ln \left( \frac{1 + \rho I_x^{1/2}}{1 + \rho I_x^{-1/2}} \right) \quad (16)$$

By appropriate differentiation the activities and activity coefficients of H<sub>2</sub>O and NaCl are obtained.

$$a_1 = x_1 \gamma_1 \quad (17)$$

$$\ln \gamma_1 = wx_2^2 + 2A_x I_x^{3/2} / (1 + \rho I_x^{1/2}) \quad (18)$$

$$a_{2,x} = (x_2 \gamma_{\pm,x})^2 \quad (19)$$

$$\ln \gamma_{\pm,x} = wx_1^2 - A_x \left\{ \frac{2}{\rho} \ln \left( \frac{1 + \rho I_x^{1/2}}{1 + \rho 2^{-1/2}} \right) + \frac{I_x^{1/2} - 2I_x^{3/2}}{1 + \rho I_x^{1/2}} \right\} \quad (20)$$

In these expressions  $A_x$  is the Debye-Hückel parameter on a mole-fraction basis

$$A_x = (1/3) (2\pi N_A d_1 / M_1)^{1/2} (e^2 / 4\pi \epsilon_0 DkT)^{3/2} \quad (21)$$

with  $d_1$ , and  $D$  the density and dielectric constant (relative permittivity) of water. The permittivity of free space is  $\epsilon_0$ , however, the factor  $4\pi\epsilon_0$  is unity in the e.s.u. system of units in which much electrolyte research is reported. The density is obtained from the equation of Haar, et al. (1981) while the dielectric constant is obtained from the equation of Bradley and Pitzer (1979) below 600 K and the theoretically based equation of Pitzer (1983a) above 600°K. As a measure of the uncertainty related to the joining of the two equations one can compare the results in the temperature range 573-623 K where both equations yield reasonable agreement with experimental dielectric constant data.

The parameter  $\rho$  is related to the hard-core, interionic repulsive distance  $a$  in Debye-Hückel theory,

$$\rho = a(2e^2 N_A d_1 / M_1 \epsilon_0 DkT)^{1/2}. \quad (22)$$

The hard-core model is only an approximation hence it seems best to evaluate  $\rho$  empirically provided the corresponding  $a$ -value is reasonable. Thus we adopt only the factor  $(d_1/DT)^{1/2}$  from equation (22) and evaluate a numerical coefficient to best fit the data for the activity of water in NaCl solutions from 373 to 573 K with the result

$$\rho = 2150(d_1/DT)^{1/2} \quad (23)$$

with  $d_1$  in  $\text{g}\cdot\text{cm}^{-3}$  and  $T$  in K. The numerical factor corresponds to  $a = 5.7 \text{ \AA}$  which is a very reasonable value.

Calculations for 373-573 K: In this fitting of water-activity data the Margules parameter  $w$  is freely adjusted at each temperature while  $A_x$  is determined by the properties of pure water. The osmotic coefficients from the recent comprehensive treatment (Pitzer, et al. 1984) were adopted up to  $4 \text{ mol kg}^{-1}$  while above that molality the directly measured values of Liu and Lindsay (1972) were used. Typical fits of  $\ln a_1$  for the saturation pressure at several temperatures are shown in Fig. 2. The values of  $w$  are given in Table 5 and shown on Fig. 3.

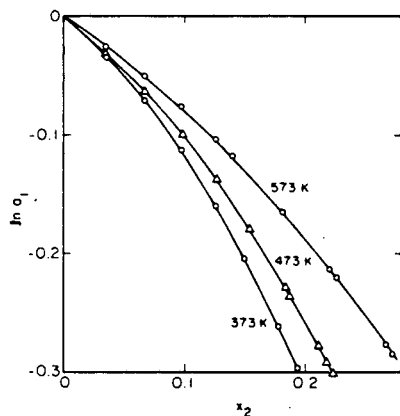


Figure 2. Comparison of curves for water activity calculated from the PL equation with experimental values.

Table 5. Pressure and Temperature Dependence of  $-w$  and  $\Delta_s G^\circ / RT$

T, K	Values with various pressures in bars							
	$P_{\text{sat}}$	$-w$				$\Delta_s G^\circ / RT$		
		400	600	800	1,000	1	$P_{\text{sat}}$	1,000
373	3.14	3.23	3.27	3.30	3.34	7.008	7.008	7.133
423	2.72	2.79	2.82	2.85	2.88	6.207	6.217	6.325
473	2.11	2.15	2.18	2.20	2.22	5.147	5.149	5.261
523	1.48	1.52	1.54	1.57	1.59	4.084	4.088	4.193
573	0.89	0.91	0.93	0.95	0.98	3.075	3.084	3.180
623		0.5	0.5 <sub>3</sub>	0.5 <sub>6</sub>	0.5 <sub>9</sub>	2.35		2.45 <sub>5</sub>
673		0.3 <sub>7</sub>	0.2 <sub>5</sub>	0.2 <sub>5</sub>	0.3	1.81 <sub>5</sub>		1.91 <sub>5</sub>
723			0.2 <sub>5</sub>	0.1 <sub>5</sub>	0.1	1.43		1.53
773				0.2	0.0 <sub>5</sub>	1.14		1.24
823				0.3	0.0 <sub>5</sub>	0.91		1.00 <sub>5</sub>

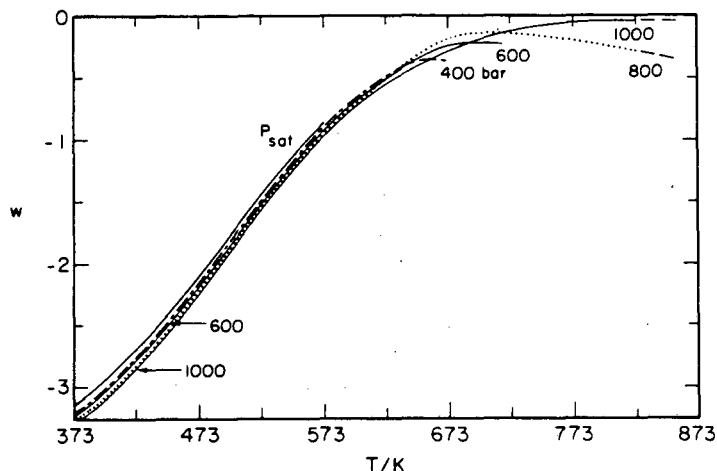


Figure 3. The parameter  $w$  as a function of  $T$  and  $P$ .

For the saturated solution at any temperature, the activity of the NaCl equals that of the solid. If  $\Delta_S G^\circ$  is the Gibbs energy of fusion or solution to the pure supercooled liquid NaCl, which is chosen as the reference state for the mixed system, then

$$\Delta_S G^\circ / RT = -2 \ln(x_{2,y_{\pm,x}})_{\text{sat}} \quad (24)$$

Solubility values were given by Liu and Lindsay (1972), and the resulting values of  $\Delta_S G^\circ / RT$  are given in Table 5 and are plotted in Fig. 1 together with a calculated, extrapolated curve based on the heat of fusion and other properties of liquid and solid NaCl. The latter curve is taken from the JANAF tables (1971) where the pertinent data are assembled. Our values below 600 K are not expected to fit the extrapolated curve, but it is apparent that a very reasonable curve can be interpolated between the values below 600 K and the calculated curve above 700 K.

Calculations were also made for higher pressures. The change with pressure of an activity is given by

$$\left(\frac{\partial \ln a_i}{\partial P}\right)_T = (\bar{V}_i - V_i^\circ) / RT \quad (25)$$

where  $\bar{V}_i$  is the partial molar volume at a given composition while  $V_i^\circ$  is the molar volume of component  $i$  in its reference state. Similarly, the Gibbs energy of solution of the solid changes with pressure

according to

$$(\partial(\Delta_s G^\circ)/\partial P)_T = v_2^\circ(\text{liq}) - v_2^\circ(\text{cry}). \quad (26)$$

The molar volumes of liquid and crystalline NaCl are available (Kirshenbaum, et al., 1962; A.I.P. Handbook, 1972) and the former was extrapolated to lower temperature to allow integration of equation (26). The data for the activity of water in solutions under high pressure are given in the general treatment up to 573 K, 1 kbar, and 6 mol kg<sup>-1</sup>. The volumetric data of Hilbert (1979) were used to convert to higher pressure the data of Liu and Lindsay (1972) for solutions of high molality. Calculations for 573-823 K: In the temperature range above 573 K, the data for water activity are of lower precision but the two-phase, steam-liquid equilibrium is well established through 823 K (Khaibullin and Borisov, 1966; Sourirajan and Kennedy, 1962; Urusova, 1974a,b; Urusova and Ravich, 1971; Khaibullin, 1980; Parisod and Plattner, 1981; Wood, et al., 1984). Volumetric measurements as well as phase equilibria are reported by Urusova (1975), Khaibullin (1980), and by Gehrig, et al. (1983) as well as by earlier investigators. Although the steam phase dissolves more NaCl with increasing temperature, the activity  $a_1$  is close to unity except very near the critical point. We take pure steam as the reference state for water. Then for the saturated liquid at P,  $\gamma_1(\text{sat,liq}) = a_1(\text{vap})/x_1(\text{sat,liq})$  with  $a_1(\text{vap}) \cong 1.0$ .

To interpret these  $\gamma_1$  values, they must be converted to a constant pressure by integration of equation (25). For pure steam the value of  $V_1^\circ$  is obtained from the equation of Haar, et al. (1981). When  $V_1^\circ$  becomes very large, however, it is more convenient to obtain the integral of that term from the difference in Gibbs energy with pressure

$$G_1^\circ(P_2) - G_1^\circ(P_1) = \int_{P_1}^{P_2} V_1^\circ dP \quad (27)$$

which is also given from the equation of state. For the solution  $\bar{V}_1$  and  $\bar{V}_2$  were obtained from the volumetric data of Urusova (1975) by finite difference between values for adjacent mole fractions. The results were smoothed and interpolated graphically and inserted in equation (25), which was integrated graphically.

The available experimental information concerning the solute is the pressure and composition of the liquid at the triple point where

steam, liquid solution, and solid NaCl are in equilibrium. Measurements of the solid solubility are reported by Keevil (1942) in addition to Urusova and others cited above. Thus equation (24) can be applied under these conditions with  $\Delta_s G^\circ$  taken from Table 5 or Fig. 1. Then the resulting  $\gamma_{\pm}$  can be converted to higher pressure by integration of the equation

$$\partial \ln \gamma_{\pm, x} / \partial P = (\bar{V}_2 - V_2^\circ) / 2RT \quad (28)$$

where  $V_2^\circ$  is the molar volume of the supercooled liquid NaCl.

While the accuracy of these  $\bar{V}_1$  and  $\bar{V}_2$  values is not high, it is sufficient to maintain reasonable accuracy in the values of  $\gamma_1$  and  $\gamma_{\pm, x}$  up to 1000 bar at 723, 773, and 823 K. At 623 K and 673 K the data of Urusova (1975) extend only to 225 bar and 600 bar, respectively.

We expect equations (16), (18), and (20) to apply at pressures high enough that pure water has a liquid-like density. Thus we first tested equations (18) and (20) on values of  $\gamma_1$  and  $\gamma_{\pm, x}$  converted to the highest pressure of the volumetric data of Urusova (1000 bar at 723, 773, 823 K, 600 bar at 673 K, 225 bar at 623 K). A good fit was obtained in all cases. Reasonably good fits were obtained at somewhat lower pressures varying from 215 bar at 623 K to 685 bar at 823 K. The resulting values of  $w$  are summarized in Table 5 and are shown on Figs. 3 and 4. Above 573 K the uncertainty in  $w$  is about 0.05 at best and often 0.1 or more. Even so  $\ln \gamma_1$  is determined to about 0.03 and sometimes much better throughout the range of solubility. The uncertainty in  $\ln \gamma_{\pm, x}$  is, likewise, about 0.03 or less for the saturated solution but becomes larger for more dilute solutions. Since the uncertainties

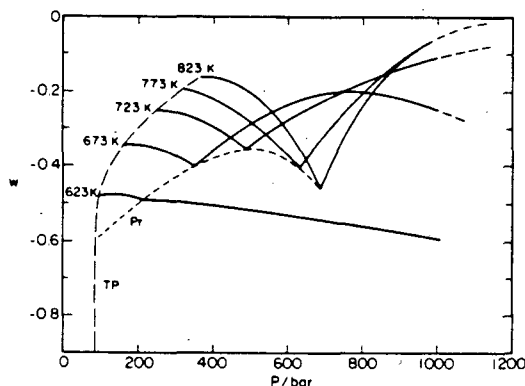


Figure 4. The parameter  $P$  (dashed) and  $w^I$  (solid unlabeled curves).

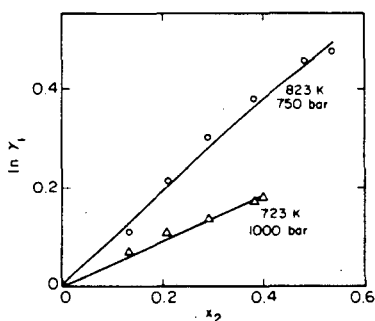


Figure 5. Comparison of calculated curves for the activity coefficient of water with measured values.

in individual points for  $w$  are as large as the difference between curves for adjacent pressures, the points are omitted on Figs. 3 and 4. Figure 5 shows typical fits of experimental values of  $\ln \gamma_1$ .

At 623 and 673 K values of  $w$  were estimated for higher pressures (above 225 and 600 bar, respectively). Some guidance was obtained from the volumetric data of Hilbert (1979) and Gehrig, et al. (1983), but their measurements do not extend near saturation composition. Thus the choice of these  $w$  values was guided primarily by the well-determined values at lower and higher temperatures. From Fig. 3 it is apparent that the  $w$ -values follow a reasonable pattern.

In much of the range of very high temperature, this representation of the properties of NaCl-H<sub>2</sub>O is valid only at  $x_2$  values somewhat above that of the critical point at a given temperature. Consequently, one may question the appropriateness of the Debye-Hückel term. It was found that alternate equations without a Debye-Hückel term required additional empirical parameters to provide an equally good representation of the data. Thus one can justify the retention of the Debye-Hückel term on a purely empirical basis. Also at pressures very substantially above the critical pressure the ion-pairing effect will become small and the present type of equation will then be valid down to zero  $x_2$ .

As the pressure is further reduced, however, the Debye-Hückel term based on the real dielectric constant of steam does become unsatisfactory. The concentrated solution is liquid-like even at the lower pressure and a "liquid-like" Debye-Hückel term is needed. While other methods were tested, our choice of procedure is to adopt at each temperature a reference pressure  $P_r$  and to use the solvent properties for that  $P_r$  for the Debye-Hückel term at all lower pressures. Correspondingly, the activity coefficients of water are modified to refer to a hypothetical "liquid"

H<sub>2</sub>O retaining the volume for P<sub>r</sub> at the lower pressures. This change in γ<sub>1</sub> is given by

$$\ln \gamma_1^* - \ln \gamma_1 = \int_P^{P_r} [V_1^\circ(P_r) - V_1^\circ(P)] dP/RT \quad (29)$$

where γ<sub>1</sub><sup>\*</sup> is the modified activity coefficient. Since the hypothetical liquid water has higher activity than real steam at the same pressure, the activity coefficient is lowered by the correction. The modified γ<sub>1</sub><sup>\*</sup> values were fitted satisfactorily by equation (18) while the γ<sub>±,x</sub> values were fitted by equation (20). Curves for w as a function of P for various temperatures are shown in Fig. 4 as the solid curves above and to the left of the dotted curve which shows P<sub>r</sub>. Table 6 gives values of P<sub>r</sub> and of d<sub>1</sub> at P<sub>r</sub>.

Table 6. Values of P<sub>r</sub> at Various Temperatures and of d<sub>1</sub> at Various Pressures in Bars

T, K	P <sub>r</sub> , bar	d <sub>1</sub>					
		P <sub>r</sub>	200	400	600	800	1,000
623	215	0.6096	0.6008	0.6721	0.7109	0.7393	0.7622
673	353	0.4785	0.1005	0.5237	0.6125	0.6593	0.6926
723	490	0.3918	0.07873	0.2709	0.4799	0.5637	0.6138
773	627	0.3585	0.06771	0.1780	0.3384	0.4570	0.5282
823	686	0.3021	0.06043	0.1434	0.2529	0.3619	0.4444

While it is certainly possible to develop an empirical equation for w, it would have to be quite complicated to represent the complex behavior. Thus it seems best to use graphical methods or simple interpolation formulas for w. Such methods are also adequate for P<sub>r</sub>. In conclusion of this section, previous equations are rearranged and combined to give explicitly the Gibbs energy of the solution

$$G = n_1 G_1^\circ + n_2 [G_2^\circ(c) + \Delta_s G^\circ] + RT(n_1 \ln x_1 + 2n_2 \ln x_2) + (n_1 + 2n_2) RT \left[ w x_1 x_2 - \left( \frac{4A_x I_x}{\rho} \right) \ln \left( \frac{1 + \rho I_x}{1 + \rho 2^{-1/2}} \right) \right] \quad (30)$$



Enthalpy and Entropy from the PL Equation. Since the Gibbs energy is known over a range of temperature, the enthalpy and entropy can be obtained from the appropriate temperature derivatives. However, because  $w$  is known only as a table of values at a series of temperatures and for other reasons, it is more convenient to use finite differences than analytical derivatives for the term in excess Gibbs energy. Both specific enthalpy and specific entropy were calculated from  $(G/T)$  and  $G$ , respectively, with  $50^\circ$  differences in  $T$  for 1000 bar and for 500 bar.

For the calculations above 723 K, 500 bar is less than  $P_r$  as defined above. Here one must calculate the Gibbs energy  $G_1^*$  of the hypothetical water at 500 bar but with the density corresponding to  $P_r$ .

$$G_1^*(P,T) = G_1^\circ(P_r) - (P_r - P)V_1^\circ(P_r). \quad (31)$$

Then equation (30) is modified by the substitution of  $G_1^*$  for  $G_1^\circ$  and the use of  $A_x$  at  $P_r, T$  instead of  $A_x$  at  $P, T$ . Then  $H_1$  and  $S_1$  are calculated by finite differences.

The resulting specific enthalpies and entropies are given in Tables 7 through 10 and shown in Figs. 6 through 9. The absolute reference states are the same as those for the PPB equation as stated above. The results are quite smooth through 648 K but then show some small but unreasonable oscillation at higher temperature and especially at 500 bar. This is to be expected in view of the uncertainties in  $w$  and other parameters at very high temperature. The values of  $H$  and  $S$  above 648 K were smoothed and in some cases rounded. Since the two-phase region extends below 798 K for most of the composition range, Tables 8 and 10 are terminated at 748 K.

The values in Tables 7 and 9 can be compared with those in Tables 2 and 3 for 548 K; the agreement is excellent. Indeed, the  $H$  and  $S$  values from the PL equation can be compared with those from the PPB equation over the temperature range 448-573 K and the full ranges of pressure and molality and the agreement is very good throughout.

A comparison was also made of enthalpies of dilution calculated from our equations with those measured at approximately 400 bar and 623 and 673 K by Busey, et al. (1984). At 673 K the PL equation yields values within 5% of the measurements which is excellent agreement under these circumstances. At 623 K the calculated values are too small by about 15%. The behavior of  $w$  is particularly uncertain near this

Table 7. Specific Enthalpy of NaCl(aq) at 1000 bar in  $\text{J}\cdot\text{g}^{-1}$ 

m	$x_2$	wt %	T/K					
			548	598	648	698	748	798
0.1	0.0036	0.58	-775	-556	-328	- 85	174	445
0.25	0.0089	1.44	-769	-552	-328	- 89	167	430
0.5	0.0177	2.84	-760	-545	-326	- 93	158	410
0.75	0.0263	4.20	-750	-538	-324	- 95	150	395
1.0	0.0348	5.52	-742	-530	-320	- 95	140	380
2.0	0.0672	10.47	-701	-497	-302	- 95	130	350
3.0	0.0976	14.92	-661	-464	-282	- 85	130	330
4.0	0.126	18.95	-621	-430	-259	- 76	130	320
5.0	0.153	22.62	-580	-400	-240	- 60	130	320
6.0	0.178	25.96	-540	-370	-210	- 40	150	320
10.0	0.265	36.9	-400	-250	-120	30	190	330
15.0	0.351	46.7	-260	-130	- 10	100	250	380
20.0	0.419	53.9	-	- 15	70	170	300	410
30.0	0.519	63.7	-	-	200	280	390	480
40.0	0.590	70.0	-	-	-	350	450	540

temperature. Also this is near the respective upper and lower temperature limits of validity of the two equations for dielectric constant. Hence, this agreement is probably as good as could be expected. At each temperature the composition dependence of the heat of dilution is given quite accurately by the PL equation.

Most of the curves on Figs. 6-9 are nearly straight lines with small and slowly changing curvature. The marked exceptions are the enthalpy and entropy curves for pure  $\text{H}_2\text{O}$  at 500 bar. These show S-shapes with steep regions near 700 K which represent the vestige of the vaporization process. Consistent with this picture, the curves for the more dilute solutions intersect the two-phase boundary about 750 K. At 1000 bar this residual of the vaporization effect has diminished and moved near 800 K. It is barely noticeable for pure water and no longer apparent for the solutions. The two-phase region is near 900 K at 1000 bar.

The PL equation assumes an ionized salt and is fitted above the critical temperature of water only to data for solutions more concentrated

Table 8. Specific Enthalpy of NaCl(aq) at 500 bar in  $\text{J}\cdot\text{g}^{-1}$ 

m	$x_2$	wt %	T/K				
			548	598	648	698	748
0.1	0.0036	0.58	-789	-552	-286	(45)	(409) <sup>a</sup>
0.25	0.0089	1.44	-784	-550	-291	(23)	(396)
0.5	0.0177	2.84	-776	-546	-295	(-6)	(377)
0.75	0.0263	4.20	-768	-542	-298	(27)	(362)
1.0	0.0348	5.52	-759	-536	-300	-44	349
2.0	0.0672	10.47	-721	-511	-296	-86	311
3.0	0.0976	14.92	-683	-483	-285	-103	287
4.0	0.126	18.95	-645	-454	-269	-107	270
5.0	0.153	22.62	-607	-425	-251	-103	260
6.0	0.178	25.96	-570	-395	-231	-93	250
10.0	0.265	36.9	-433	-282	-147	-33	250
15.0	0.351	46.7	-286	-159	-40	70	270
20.0	0.419	53.9	-	-56	38	130	310
30.0	0.519	63.7	-	-	175	260	370
40.0	0.590	70.0	-	-	-	350	440

<sup>a</sup> See text for the uncertainty of values at low molality and high temperature.

than the critical composition. It is known that NaCl in steam is largely ion-paired and that this ion-pairing extends to the critical region. At 1000 bar and below 823 K the ion pairing is probably not extensive enough to seriously affect the enthalpy values in Table 7 or the entropies in Table 9. The effect will be much greater at 500 bar and can be evaluated from very recent measurements for 3.2% (0.546 mol·kg<sup>-1</sup>) solution by Bischoff and Rosenbauer (1984). They measured the density over a range of temperature and pressure and calculated the difference from 1000 bar to lower pressures for both H and S. In Table 11 our results for this difference are compared with their values. There is essentially perfect agreement at 548, 598, and 648 K. There is a definite difference at 698 K and a larger difference at 743 K which is the maximum temperature of the experimental measurements. The differences are in the expected direction with the apparent molal enthalpy or entropy of ions smaller than that for ion pairs at a given

Table 9. Specific Entropy of NaCl(aq) at 1000 bar in  $\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ 

m	$x_2$	wt %	T/K					
			548	598	648	698	748	798
0.1	0.0036	0.58	6.32	6.70	7.07	7.43	7.78	8.14
0.25	0.0089	1.44	6.28	6.66	7.02	7.38	7.73	8.07
0.5	0.0177	2.84	6.22	6.59	6.95	7.30	7.64	7.97
0.75	0.0263	4.20	6.16	6.53	6.87	7.22	7.55	7.87
1.0	0.0348	5.52	6.10	6.47	6.80	7.14	7.47	7.78
2.0	0.0672	10.47	5.88	6.24	6.55	6.86	7.1 <sub>5</sub>	7.4 <sub>5</sub>
3.0	0.0976	14.92	5.69	6.03	6.31	6.62	6.9 <sub>0</sub>	7.1 <sub>7</sub>
4.0	0.126	18.95	5.51	5.85	6.11	6.4 <sub>0</sub>	6.6 <sub>5</sub>	6.9 <sub>0</sub>
5.0	0.153	22.62	5.36	5.68	5.9 <sub>5</sub>	6.2 <sub>0</sub>	6.4 <sub>5</sub>	6.7 <sub>0</sub>
6.0	0.178	25.96	5.22	5.53	5.7 <sub>5</sub>	6.0 <sub>0</sub>	6.2 <sub>5</sub>	6.5 <sub>0</sub>
10.0	0.265	36.9	4.77	5.04	5.2 <sub>5</sub>	5.4 <sub>5</sub>	5.7 <sub>0</sub>	5.9
15.0	0.351	46.7	4.4	4.6	4.8 <sub>0</sub>	5.0 <sub>0</sub>	5.2 <sub>0</sub>	5.3 <sub>5</sub>
20.0	0.419	53.9	-	4.3 <sub>5</sub>	4.5 <sub>0</sub>	4.6 <sub>5</sub>	4.80	4.9 <sub>5</sub>
30.0	0.519	63.7	-	-	4.0 <sub>0</sub>	4.1 <sub>5</sub>	4.3 <sub>0</sub>	4.4 <sub>5</sub>
40.0	0.590	70.0	-	-	-	3.9	4.0	4.1

T and P. The dominant cause is the stronger hydration of ions as compared to ion-pairs.

In Tables 8 and 10 the values at low m and high T are enclosed in parentheses to indicate uncertainty from this ion pairing effect. From Table 11 one can estimate the magnitude of the error at 500 bar from the differences in a given function at a particular temperature. The error at 1000 bar should be much smaller and is probably negligible. At molality lower than 0.5 the error per mole of NaCl may be somewhat larger but the net effect on the specific enthalpy or entropy should be no larger than that for the  $0.5 \text{ mol}\cdot\text{kg}^{-1}$  solution.

Discussion of the PL Equation: From Fig. 3 it is apparent that w is large and negative at low temperature. This represents a dominance of ion hydration over the other interparticle interactions. But with increase in temperature w appears to approach a small and relatively constant value. Then the departure from ideal behavior arises primarily from the Debye-Hückel term which arises from the long-range aspect of interionic forces. It appears possible that w may remain small at

Table 10. Specific Entropy of NaCl(aq) at 500 bar in  $\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ 

m	$x_2$	wt %	T/K				
			548	598	648	698	748
0.1	0.0036	0.58	6.40	6.82	(7.24)	(7.73)	(8.24) <sup>a</sup>
0.25	0.0089	1.44	6.36	6.77	(7.19)	(7.65)	(8.17)
0.5	0.0177	2.84	6.30	6.70	7.10	(7.53)	(8.06)
0.75	0.0263	4.20	6.24	6.63	7.02	7.42	(7.96)
1.0	0.0348	5.52	6.18	6.57	6.94	7.32	(7.8)
2.0	0.0672	10.47	5.95	6.32	6.66	7.0	7.5
3.0	0.0976	14.92	5.75	6.10	6.41	6.7	7.2
4.0	0.126	18.95	5.56	5.90	6.19	6.5	6.9
5.0	0.153	22.62	5.40	5.72	6.00	6.3	6.7
6.0	0.178	25.96	5.26	5.57	5.82	6.0	6.5
10.0	0.265	36.9	4.80	5.07	5.28	5.5	5.8
15.0	0.351	46.7	4.41	4.64	4.81	5.0	5.3
20.0	0.419	53.9	-	4.34	4.48	4.7	4.9
30.0	0.519	63.7	-	-	4.05	4.2	4.4
40.0	0.590	70.0	-	-	-	3.9	4.1

<sup>a</sup> See text for the uncertainty of values at low molality and high temperature.

Table 11. Change in Enthalpy and Entropy with Pressure from 500 to 1000 bar for 0.546 molal NaCl

T/K	548	598	648	698	743	Source
$\Delta H/\text{J}\cdot\text{g}^{-1}$	18	0	- 31	- 120	- 273	B.R. <sup>a</sup>
$\Delta H/\text{J}\cdot\text{g}^{-1}$	16	1	- 30	- 85	- 205	P. <sup>b</sup>
$\Delta S/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$	-0.08	-0.10	-0.17	-0.29	-0.50	B.R. <sup>a</sup>
$\Delta S/\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$	-0.08	-0.11	-0.15	-0.23	-0.38	P. <sup>b</sup>

<sup>a</sup> Bischoff and Rosenbauer, 1984.

<sup>b</sup> This research.

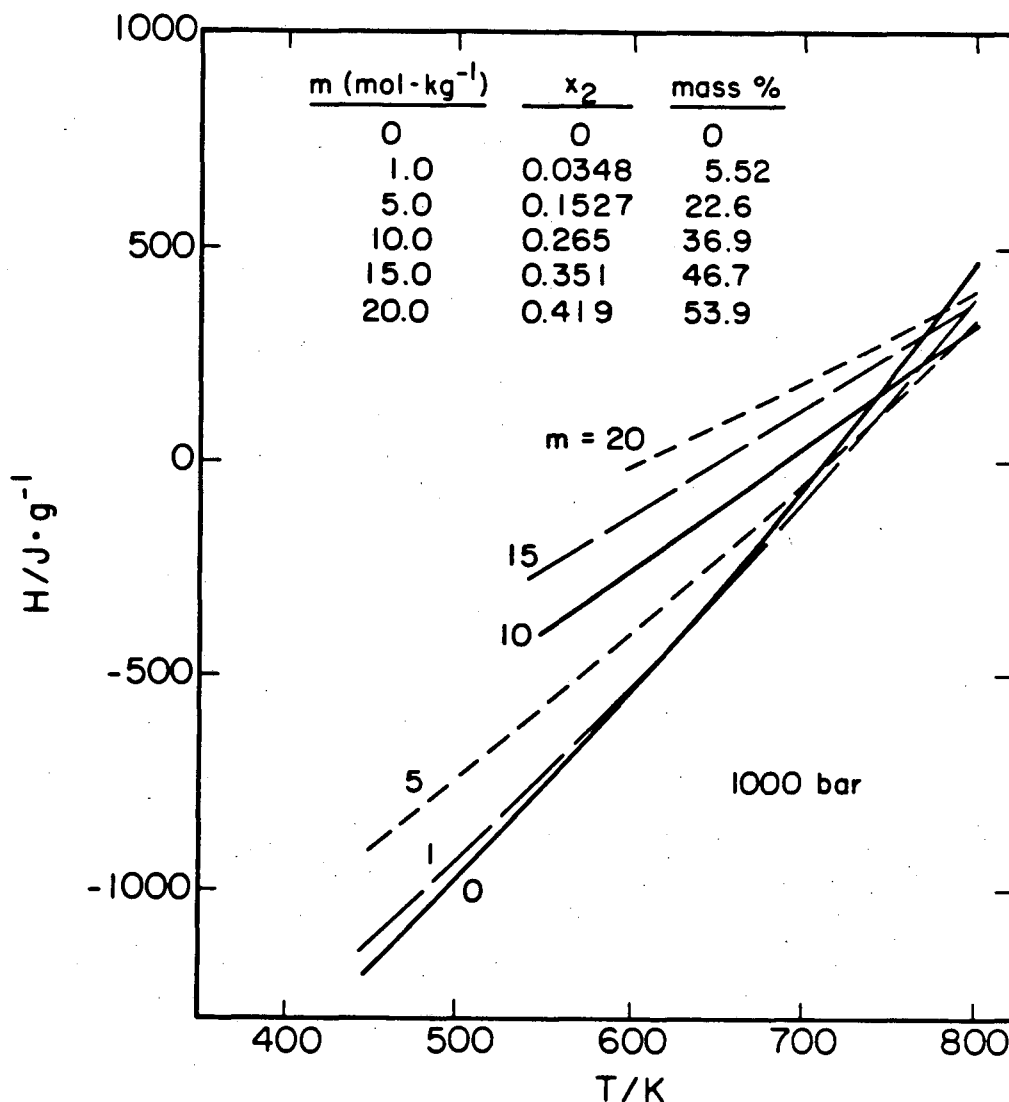


Figure 6. Specific enthalpy of NaCl(aq) at 1000 bar.

still higher temperature, but that will remain a speculation until further evidence becomes available.

The equations and parameters described above provide a full representation of various thermodynamic properties of NaCl-H<sub>2</sub>O for the range 373-823 K, 0-1 kbar, and composition to saturation except for dilute solutions above 573 K where ion-pairing is substantial. With one exception, all of the equations for  $G_x^{EX}$ ,  $\ln\gamma_1$  and  $\ln\gamma_{\pm,x}$  are so simple that there seems to be no need for tabulation of numerical values of these quantities. A simple programmable calculator is adequate for the calculations. The exception is the complex equation of Haar, et al. (1981)

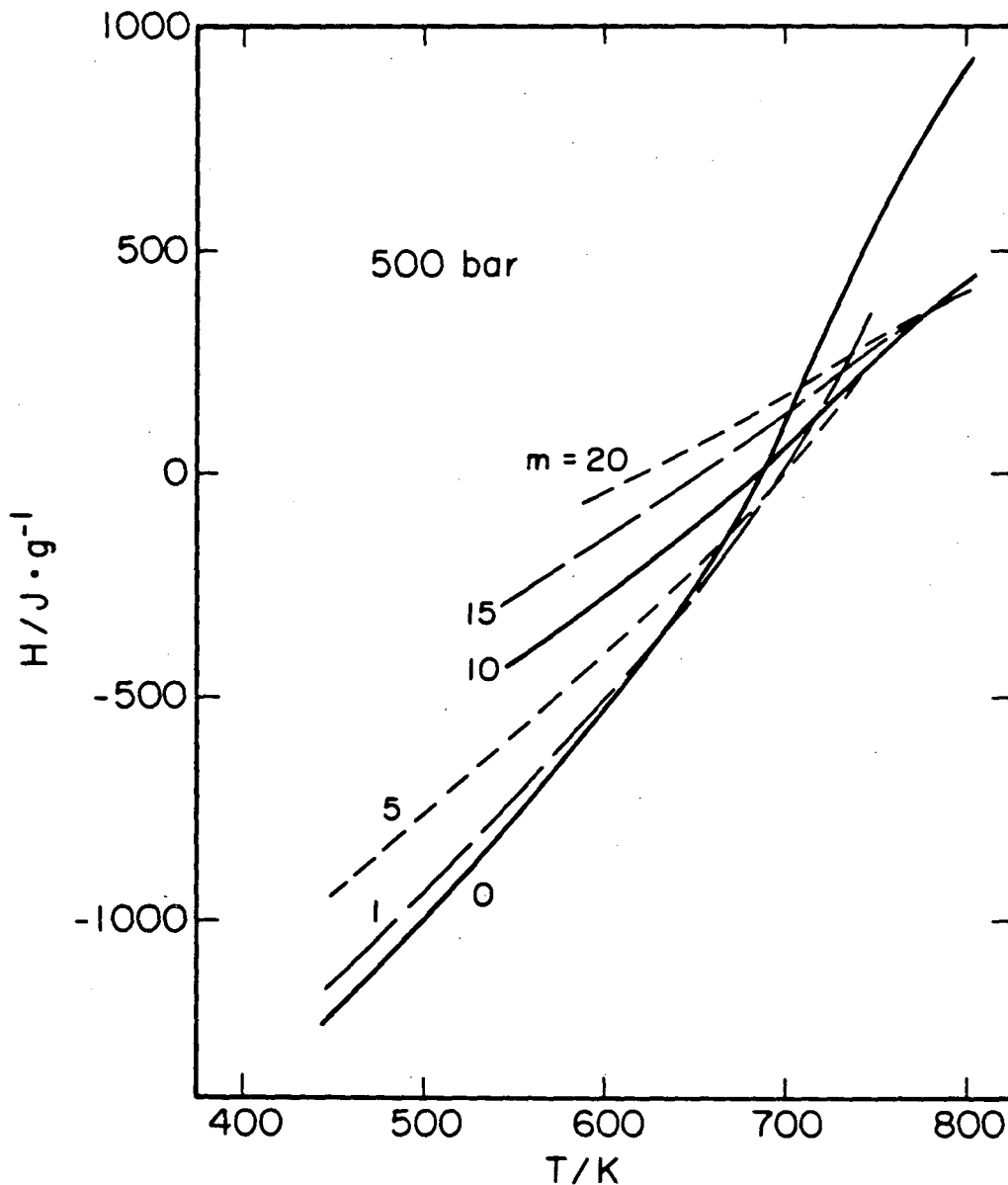


Figure 7. Specific enthalpy of  $\text{NaCl}(\text{aq})$  at 500 bar.

for the density of pure  $\text{H}_2\text{O}$ . For the convenience of users, Table 6 gives densities above 573 K for several pressures, including  $P_r$ . The equations of this paper, together with those of Bradley and Pitzer (1979) or Pitzer (1983a) for the dielectric constant, then yield the Gibbs energy and the activity coefficients directly. Tables of enthalpies and entropies were given in the preceding section. While volumes can be obtained from differences of  $G$  with  $P$ , this is not a useful procedure because of limitations in precision of the PL equation. Volumetric data

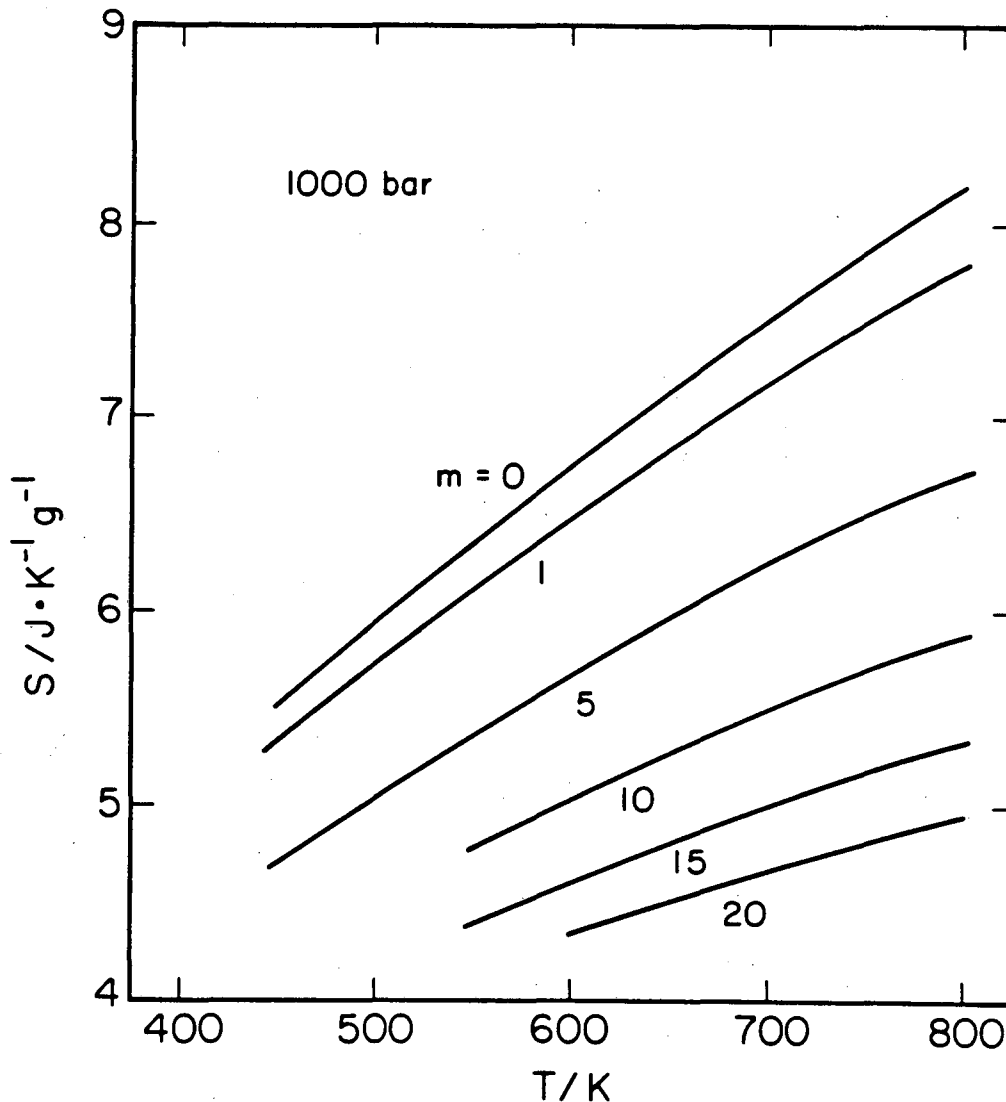


Figure 8. Specific entropy of  $\text{NaCl}(\text{aq})$  at 1000 bar.

above 573 K should be obtained directly from the papers of Urusova (1975) or Gehrig, et al. (1983).

While the PL equation fits the data below 573 K remarkably well in view of the simplicity of the equation, the precision of fit is substantially less than that for the more complex PPB equation. Thus the PPB equation and tables should be used below 573 K unless the simpler equation is adopted as a convenient approximation.



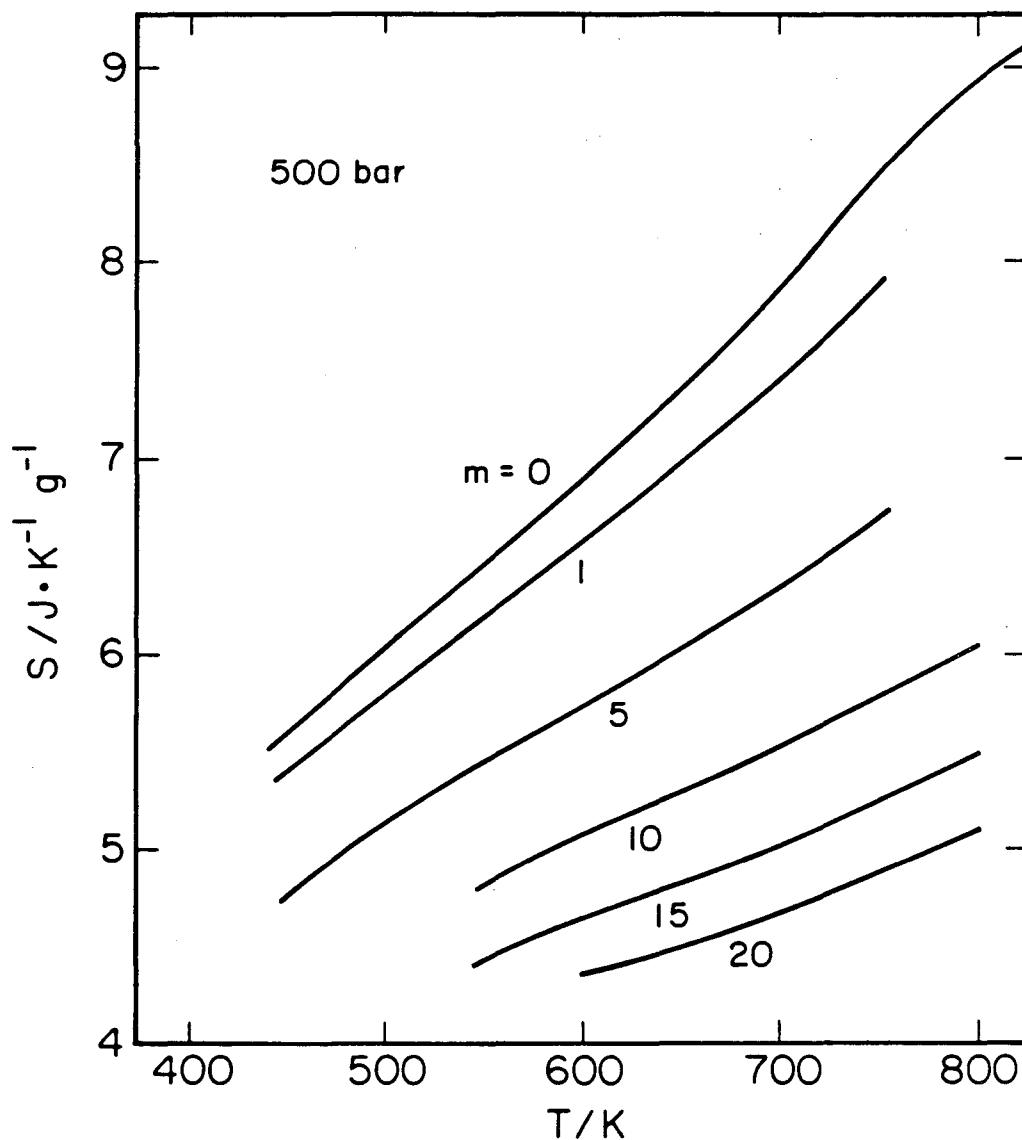


Figure 9. Specific entropy of NaCl(aq) at 500 bar.

ESTIMATES FOR TEMPERATURES ABOVE 823 K

The PL equation and the methods used below 823 K should be applicable at higher temperatures as soon as sufficient experimental data become available. It was noted earlier that the Debye-Hückel term is the primary term for the excess Gibbs energy in the range above 700 K. Thus one can make crude estimates above 823 K with  $w$  either zero or a small negative value extrapolated from Fig. 3. The Debye-Hückel parameter is available from properties of pure water.

The postulate of corresponding states for ionic systems provides another approach which I used (Pitzer, 1984a) to estimate the critical curve all the way to pure NaCl. While the critical properties of pure NaCl have not been measured, theory can be used to guide the extrapolation of known properties of the liquid and vapor to yield good estimates for the critical region (Pitzer, 1984b). The results are  $T_c = 3900$  K,  $V_c = 490 \text{ cm}^3 \cdot \text{mol}^{-1}$ ,  $P_c = 258$  bar. In a mixture one can assume that the only effect of the solvent is that of its dielectric constant  $D$ . Then the product  $DT$  takes the place of  $T$  for pure NaCl.

Of course, a real solvent is not just an inert dielectric. If the nature of the solvent is greatly affected by the ionic solute, this postulate has no value. Thus, near the critical point of water one expects no agreement with this corresponding states relationship to pure NaCl. But at higher temperature and pressure the water properties are less sensitive to the presence of NaCl, and the critical behavior of the NaCl-H<sub>2</sub>O mixture may relate primarily to the NaCl. This is tested by calculating the  $DT$  product along the critical curve for NaCl(aq); the experimental  $P_c$  values above 823 K are from Souririjan and Kennedy (1962). The results are shown in Table 12. In the range above 823 only rough agreement can be expected since the dielectric constant values are extrapolated, although the equation is based on theory. Thus a relatively constant discrepancy of about 10% offers support for this very approximate model. At lower temperature, as expected, there is an increasingly rapid change in pattern as the critical point of water is approached.

The critical curve for NaCl(aq) above 973 K can now be estimated on the basis that at any temperature the critical dielectric constant

Table 12. Test of a Corresponding States Model for the Critical Curve for NaCl(aq)

$T_c$ /K	$P_c$ /bar	$DT$ /K exp'l	$DT$ /K model
973	1237	4360	3900
923	1082	4290	3900
873	922	4220	3900
823	754	4070	3900
723	422	3470	3900

$D_c = 3900/T$ . The density of steam is then calculated to fit this  $D_c$ , and, in turn, the steam pressure may be calculated to fit this density.

Except near the critical point of pure NaCl, the pressure contribution from NaCl can be neglected and the partial pressure of  $H_2O$  taken as the total pressure. Figure 10 is constructed on that basis except that a smooth curve is extended from 3500 K to the critical pressure of pure NaCl at 3900 K. It should be emphasized that the pressures above 1000 K on Fig. 10 are uncertain by at least 20% even if the corresponding states model is generally valid in this range.

A second check on this model is the critical volume which should be the same per mole of NaCl for the mixture as for pure NaCl. The experimental data for critical volumes extend only to 823 K where Urusova (1975) reports a density equivalent to about  $480 \text{ cm}^3 \cdot \text{mol}^{-1}$  in remarkable agreement with the 490 value for pure NaCl. Given a constant critical volume of about  $490 \text{ cm}^3 \cdot \text{mol}^{-1}$ , one can calculate from the density of  $H_2O$

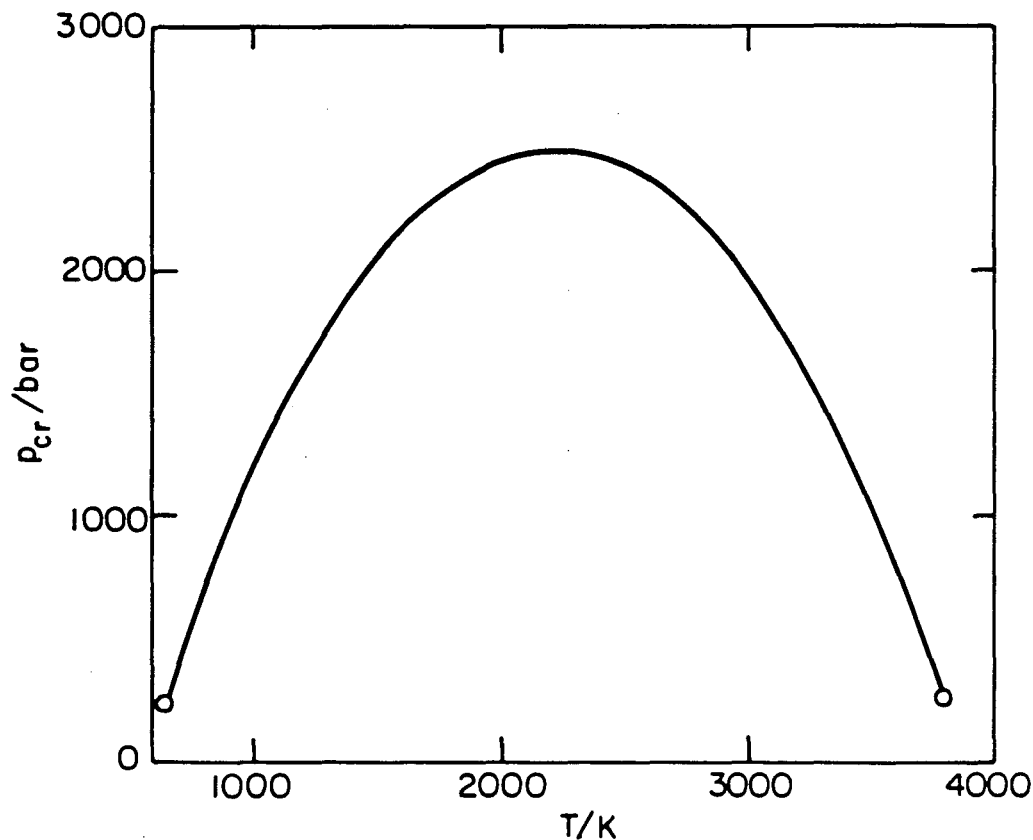


Figure 10. Estimated critical pressure of NaCl(aq).

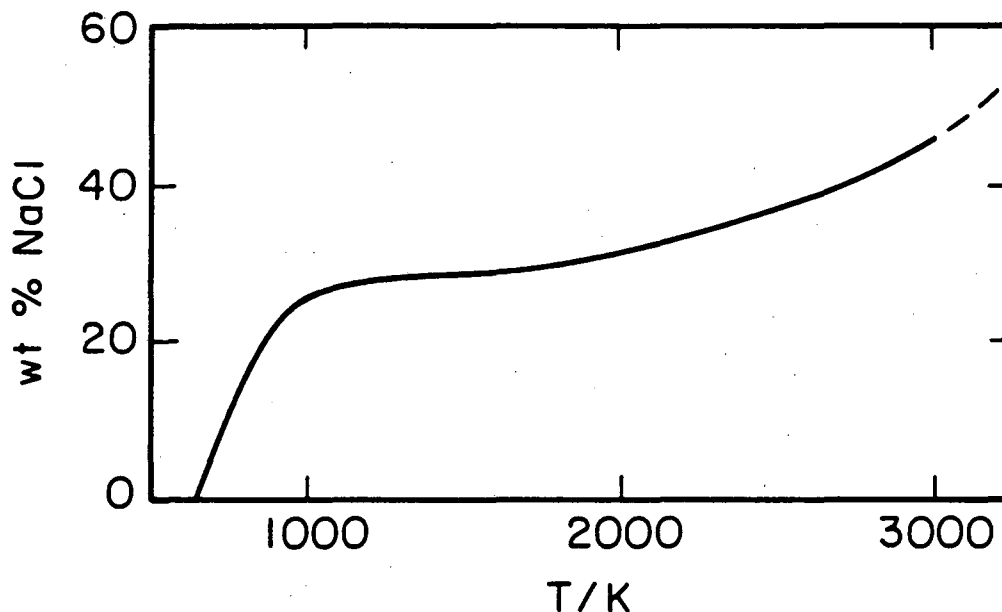


Figure 11. Estimated critical composition of NaCl(aq).

the critical composition. The results are shown in Fig. 11. This curve is terminated near 3000 K in view of the increasing uncertainties, although it must extend to 100% at 3900 K.

The relatively flat portion of the critical composition curve near 30% by weight implies that there are about seven water molecules of hydration per NaCl in this range. This corresponds to a substantial inner shell around either separated ions or an ion pair. The rapid rise in critical pressure allows this relatively constant hydration in the 1000 to 2000 K range. At higher temperatures the degree of hydration decreases as expected.

Finally, one notes that there is need for a better treatment of dilute NaCl in steam. The solubility of solid NaCl in steam has been measured by a number of investigators with less than satisfactory agreement. The ionic dissociation was measured by Quist and Marshall (1968) and this was related to the information from mass spectrometry for hydrated  $\text{Na}^+$  and  $\text{Cl}^-$  by Pitzer (1983b). The thermodynamics of dilute aqueous NaCl at the critical pressure at 723, 773, and 823 K was treated, including the ionization equilibrium, by Pitzer and Li (1984). These initial investigations fall far short of a complete treatment such as is now available for more concentrated solutions, but it should

be possible to build such a complete treatment on the concepts now established.

APPENDIX

PPB Equation: There follows a concise presentation of the equation of Pitzer, Peiper, and Busey (1984) in extension of the general but brief description above. The basic equation is written for the Gibbs energy which is equation (1) rearranged as follows:

$$G = n_1 G_1^\circ + n_2 \bar{G}_2^\circ - 2n_2 RT(1 - \ln m) + G^{EX} \quad (A-1)$$

with  $m$  the molality and  $G^{EX}$  the excess Gibbs energy for which the molality dependence is given by equation (2). The forms assumed for the functions in equation (2) are

$$f(I) = -A_\phi (4I/b) \ln(1 + bI^{1/2}) \quad (A-2)$$

$$B(I) = \beta^{(0)} + 2\beta^{(1)} [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] / \alpha^2 I. \quad (A-3)$$

The two parameters  $b$  and  $\alpha$  are assigned the constant values 1.2 and 2.0 kg<sup>1/2</sup>·mol<sup>-1/2</sup>, respectively, independent of temperature or pressure. Indeed,  $f(I)$  is a universal function. While  $\beta^{(0)}$  and  $\beta^{(1)}$  are specific to the solute, NaCl in this case, the ionic strength function multiplying  $\beta^{(1)}$  is unchanged for most electrolytes. The Debye-Hückel parameter is

$$A_\phi = (1/3) (2\pi N_A d_1 / 1000)^{1/2} (e^2 / 4\pi \epsilon_0 DkT)^{3/2} \quad (A-4)$$

where the various quantities were defined in connection with equation (21).

The osmotic and activity coefficients are obtained from equation (8) and (9b) which yield

$$\phi - 1 = -A_\phi I^{1/2} / (1 + bI^{1/2}) + m[\beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2})] + m^2 C_\phi \quad (A-5)$$

$$\ln \gamma_{\pm} = -A_{\phi} \left[ \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] + m \cdot \left\{ 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 I} \left[ 1 - (1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2}) e^{-\alpha I^{1/2}} \right] + \frac{3m}{2} C^{\phi} \right\} \quad (A-6)$$

The form for the ionic strength dependence of the second virial coefficient was first chosen for the osmotic coefficient, where it is very simple (Pitzer, 1973). The forms for the excess Gibbs energy and the activity coefficient are derived therefrom.

A practical reference state for NaCl was chosen to be the mixture NaCl·10H<sub>2</sub>O or a molality  $m_r = 5.5508 \text{ mol} \cdot \text{kg}^{-1}$ . This avoids a direct expression the extreme behavior of the infinitely dilute reference state as the critical point of water is approached. The Gibbs energy of NaCl in the infinitely dilute is obtained instead from the indirect expression

$$\begin{aligned} \frac{\bar{G}_2^{\circ}(T,P) - \bar{H}_2^{\circ}(298 \text{ K}, 1 \text{ bar})}{RT} &= (z_1 + z_2 P + z_3 P^2 + z_4 P^3) / T \\ &+ z_5 + z_6 P + z_7 P^2 + z_8 P^3 + z_9 \ln T + (z_{10} + z_{11} P + z_{12} P^2) T \\ &+ (z_{13} + z_{14} P) T^2 + z_{15} / T(T-227) + z_{16} / T(680-T) \\ &- \frac{10[G_1^{\circ}(T,P) - H_1^{\circ}(g, 0 \text{ K})]}{RT} - \frac{G^{\text{EX}}(T,P,m_r)}{n_2 RT} \end{aligned} \quad (A-7)$$

Note that the reference state for NaCl is the enthalpy in the infinitely dilute standard state at 298.15 K while that for H<sub>2</sub>O is the ideal gas at 0 K. Note also that the final term is the excess Gibbs energy of the solution at  $m_r = 55.508 \text{ mol} \cdot \text{kg}^{-1}$ . Although the excess Gibbs energy is defined above, it is rewritten in detail as follows for any molality of NaCl

$$\begin{aligned} \frac{G^{\text{EX}}(T,P,m)}{n_2 RT} &= -(4A_{\phi}/b) \ln(1 + bm^{1/2}) + 2m\beta^{(0)} \\ &+ (4\beta^{(1)}/\alpha^2) [1 - (1 + \alpha m^{1/2}) \exp(-\alpha m^{1/2})] + m^2 C^{\phi} \end{aligned} \quad (A-8)$$

The virial coefficient parameters are functions of temperature and pressure as follows:

$$\begin{aligned}
 \beta^{(0)} = & z_{17}/T + z_{18} + z_{19}P + z_{20}P^2 + z_{21}P^3 + z_{22} \ln T \\
 & + (z_{23} + z_{24}P + z_{25}P^2 + z_{26}P^3)T + z_{27} + z_{28}P + z_{29}P^2)T^2 \\
 & + (z_{30} + z_{31}P + z_{32}P^2 + z_{33}P^3)/(T-227) \\
 & + (z_{34} + z_{35}P + z_{36}P^2 + z_{37}P^3)/(680-T), \tag{A-9}
 \end{aligned}$$

$$\beta^{(1)} = z_{38}/T + z_{39} + z_{40}T + z_{41}/(T-227), \tag{A-10}$$

$$\begin{aligned}
 C^\phi = & z_{42}/T + z_{43} + z_{44}P + z_{45} \ln T + (z_{46} + z_{47}P)T \\
 & + (z_{48} + z_{49}P)T^2 + (z_{50} + z_{51}P)/(T-227) \\
 & + (z_{52} + z_{53}P)/(680-T). \tag{A-11}
 \end{aligned}$$

In addition to a general fit for the range 273-573 K a limited fit was generated for the temperature range 273-358 K which requires fewer parameters but yields higher precision at low temperature. The two sets of parameters are given in Table A-1.

It should be noted that parameter  $z_5$  involves the entropy of aqueous NaCl which was taken to be  $13.88_6R$  at 298.15 K based on the absolute entropy of solid NaCl. The equation for  $H_2O$  also yields the entropy on an absolute basis.

One may now calculate volumes, enthalpies, entropies, heat capacities or other quantities by appropriate derivatives with respect to pressure or temperature. Equations for the osmotic and activity coefficients were given above. These equations, with the parameters in Table A-1 and with the properties of pure water, give a very general and accurate expression of the properties of aqueous NaCl from 273-573 K, 1-1000 bar, and 0-6 mol·kg<sup>-1</sup>. With high accuracy at saturation pressure but reduced accuracy at higher pressure, the molality range may be extended to saturation. Pitzer, et al., (1984) also note particular increases of uncertainty as the temperature approaches 573 K at certain pressures and compositions. They give extensive tables of the various quantities likely to be of interest as listed in Table 1 above.

Table A-1. Parameters  $z_i$  for Equations A-6 to A-10

$i$	low T value	high T value
1	-71659.531	-71637.203
2	2.3483335	2.2209012
3	$-8.3668484 \times 10^{-5}$	$-7.7991396 \times 10^{-5}$
4	$2.4018168 \times 10^{-9}$	$-4.8099272 \times 10^{-9}$
5	624.88208	624.68125
6	$-5.3697119 \times 10^{-4}$	$6.0159787 \times 10^{-4}$
7	$3.5126966 \times 10^{-7}$	$3.4069074 \times 10^{-7}$
8	0	$2.1962044 \times 10^{-11}$
9	-110.74702	-110.74702
10	0.038900801	0.039494473
11	$2.6973456 \times 10^{-6}$	$-6.5313475 \times 10^{-7}$
12	$-6.2746876 \times 10^{-10}$	$-6.4781894 \times 10^{-10}$
13	$-1.5267612 \times 10^{-5}$	$-1.5842012 \times 10^{-5}$
14	0	$3.2452006 \times 10^{-9}$
15	516.99706	516.99706
16	$-5.9960301 \times 10^{+6}$	$-5.9960301 \times 10^{+6}$
17	-656.81518	-656.81518
18	24.879183	24.869130
19	$-2.1552731 \times 10^{-5}$	$5.3812753 \times 10^{-5}$
20	$5.0166855 \times 10^{-8}$	$-5.5887470 \times 10^{-8}$
21	0	$6.5893263 \times 10^{-12}$
22	-4.4640952	-4.4640952
23	0.011087099	0.011109914
24	$-6.4479761 \times 10^{-8}$	$-2.6573399 \times 10^{-7}$
25	$-2.3234032 \times 10^{-10}$	$1.7460070 \times 10^{-10}$
26	0	$1.0462619 \times 10^{-14}$
27	$-5.2194871 \times 10^{-6}$	$-5.3070129 \times 10^{-6}$
28	$2.4445210 \times 10^{-10}$	$8.6340233 \times 10^{-10}$
29	$2.8527066 \times 10^{-13}$	$-4.1785962 \times 10^{-13}$
30	-1.5696231	-1.5793660
31	$2.2337864 \times 10^{-3}$	$2.2022821 \times 10^{-3}$
32	$-6.3933891 \times 10^{-7}$	$-1.3105503 \times 10^{-7}$
33	$4.5270573 \times 10^{-11}$	$-6.3813683 \times 10^{-11}$
34	5.4151933	9.7065780



Table A-1. (continued)

i	low T value	high T value
35	0	$-2.6860396 \times 10^{-2}$
36	0	$1.5344744 \times 10^{-5}$
37	0	$-3.2153983 \times 10^{-9}$
38	119.31966	119.31966
39	-0.48309327	-0.48309327
40	$1.4068095 \times 10^{-3}$	$1.4068095 \times 10^{-3}$
41	-4.2345814	-4.2345814
42	-6.1084589	-6.1084589
43	0.40743803	0.40217793
44	$-6.8152430 \times 10^{-6}$	$2.2902837 \times 10^{-5}$
45	-0.075354649	-0.75354649
46	$1.2609014 \times 10^{-4}$	$1.5317673 \times 10^{-4}$
47	$6.2480692 \times 10^{-8}$	$-9.0550901 \times 10^{-8}$
48	$1.8994373 \times 10^{-8}$	$-1.5386008 \times 10^{-8}$
49	$-1.0731284 \times 10^{-10}$	$8.6926600 \times 10^{-11}$
50	0.32136572	0.35310414
51	$-2.5382945 \times 10^{-4}$	$-4.3314252 \times 10^{-4}$
52	0	-0.091871455
53	0	$5.1904777 \times 10^{-4}$

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