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Author

Pitzer, K.S.

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IN STEAM

Kenneth S. Pitzer

August 1982

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The Thermodynamics of Sodium Chloride Solutions in Steam

Kenneth S. Pitzer

Department of Chemistry and Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

Abstract

Gas-phase data from mass spectrometry are used to calculate the Gibbs energy of hydration of Na^+ and Cl^- ions in steam. A similar hydration model for the ion pair NaCl is fitted to the experimental measurements of the solubility of NaCl in steam. The ionization constant calculated from these sources fits the directly measured values at 1073 K and densities above 0.3 g cm^{-3} . At lower temperatures reasonable curves interpolate between the calculated values for low density and the direct measurements at higher density. Other thermodynamic properties are calculated for Na^+ , Cl^- , and NaCl in steam. The partial molal heat capacity of the ions is very large in the range 700 to 1000 K; this arises from the enthalpy of dissociation of water from the hydrated ions. The Born equation is compared with these results. A practical application to steam turbine technology is also considered.

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Recently the writer¹ showed that the mass spectrometric measurements on the hydration equilibria for H_3O^+ and OH^- could be used to calculate the self-ionization in steam in the region above the critical temperature and at pressures up to maxima increasing from one or two hundred bar near T_c to a thousand bar near 1000 K. Other thermodynamic properties of ions in steam were also calculated.

In this paper similar methods are applied to the system $\text{NaCl-H}_2\text{O}$ in the same region of temperature and pressure. Kebarle and associates^{2,3} have measured the hydration equilibria of gaseous Na^+ and Cl^- . For this system there is the additional problem of the hydration of the NaCl ion-pair in steam. Reasonable estimates are made for these hydration equilibria for NaCl with guidance from experimental values for the solubility of solid NaCl in steam. Unfortunately there are large differences among the various experimental solubility data,⁴⁻⁹ but it is found that many data are reasonable on this theoretical basis while the others are not. Further experiments are very desirable concerning this solubility of NaCl in steam.

The ionization of NaCl in steam has been measured by Quist and Marshall¹⁰ at densities from 0.3 to about 0.8 g cm^{-3} over the temperature range 673 to 1073 K. The calculated ionization constants for lower densities are fully concordant with the measurements of Quist and Marshall.

Gaseous Hydration Equilibria

The thermodynamic properties of gaseous NaCl , Na^+ , and Cl^- are reasonably well-known. We adopt the values given in the JANAF tables¹¹ as follows:

The JANAF tables also give entropies and heat capacities and, finally, Gibbs energy values at various temperatures from which the equilibrium constants can be calculated.

$$K_1 = f_{\text{NaCl}} \quad (3)$$

$$K_2 = f_{\text{Na}^+} f_{\text{Cl}^-} / f_{\text{NaCl}} \quad (4)$$

Since these fugacities are all very small they can be approximated by the partial pressures, but we retain the symbols f_{Na^+} , etc. to distinguish these quantities from the partial pressures in the aqueous system. The enthalpy and Gibbs energy for reaction (1) is uncertain by about $0.5 \text{ kcal mol}^{-1}$; various sets of data are concordant but still leave this uncertainty. The electron affinity of Cl had been uncertain by one kcal or more but has now been measured quite accurately.^{12,13}

In the aqueous system there are successive hydration equilibria

with the successive equilibrium constants K_n^+ , K_n^- , and K_n^0 .

For our purpose we need the sum of the partial pressures of all of the hydrates of a given species. We write

$$\Sigma P_n^+ / P_{\text{Na}^+} = (S^+) = 1 + K_1^+ P_{\text{H}_2\text{O}} + K_1^+ K_2^+ P_{\text{H}_2\text{O}}^2 + \dots \quad (8)$$

$$\Sigma P_n^- / P_{\text{Cl}^-} = (S^-) = 1 + K_1^- P_{\text{H}_2\text{O}} + K_1^- K_2^- P_{\text{H}_2\text{O}}^2 + \dots \quad (9)$$

$$\Sigma P_n^0 / P_{\text{NaCl}} = (S^0) = 1 + K_1^0 P_{\text{H}_2\text{O}} + K_1^0 K_2^0 P_{\text{H}_2\text{O}}^2 + \dots \quad (10)$$

where the symbols (S+), etc., are convenient abbreviations. Also, the partial pressures of the unhydrated species are assumed to be equal to their fugacities.

For the ions Kebarle and associates^{2,3} have measured these hydration equilibrium constants at several temperatures in a mass spectrometer with a high-pressure ion source and report ΔH_n and ΔS_n for the successive reactions. Table I gives these results for the first four steps in each case together with the approximate mean temperature of measurement. While at low pressures only these first four hydrates are significant, we need a model for further hydration to extend calculations to higher pressures. For Na^+ , model A represents the experimental values² for the next two steps, 5 and 6, quite accurately and may be used as a basis for extrapolation. We expect, however, that the rate of decrease of $-\Delta H_n$ will diminish as n increases; consequently, we consider an alternate model B with the increment of $1.5 \text{ kcal mol}^{-1}$ decreased to $0.8 \text{ kcal mol}^{-1}$. This value of 0.8 was found to fit quite well for the case of highly hydrated H_3O^+ and OH^- ions.

For the Cl^- ion values are reported³ for only the first four stages of hydration and these are given in Table I. The enthalpies for the early stages are much smaller for Cl^- than for Na^+ as would be expected for the larger radius of the Cl^- ion. Also the increment in this case is much smaller, about $0.5 \text{ kcal mol}^{-1}$, and that value is assumed for further hydration.

The difference in results for models A and B for Na^+ gives a measure of the uncertainty arising from extrapolation to high degrees of hydration beyond the level of the directly measured stages.

Since we will be making calculations at temperatures much higher than those of mass spectrometric measurement, the ΔC_p for successive

hydration reactions should be considered. A hydration step converts 3 modes of translation and 3 of rotation into six low frequency vibrational modes in the larger cluster. The torsional modes, especially, will be quite anharmonic. Also one PV term will be lost. Hence, one expects ΔC_p to be $6(R+?) - 4R$ or substantially in excess of $2R$. For the earlier calculations on the hydration of H_3O^+ and OH^- , the value $3.5R$ was adopted after exploratory calculations with $3R$ and $4R$. The value $3.5R$ also seems most reasonable theoretically, and it was used in the present calculations.

There are no molecular-level data on hydrates of the ion pair Na^+Cl^- . One expects the first two or three molecules of water to attach to the Na^+ since the enthalpies for Na^+ are much greater than for Cl^- for the first few stages. But the presence, at greater distance, of the negative charge of the Cl^- will lower the energy of attachment to Na^+ of these first few molecules. Thus a model was set up for the hydration of Na^+Cl^- in which the decimal fractions in the ΔS_n and ΔH_n values for Na^+ were rounded off and then all $-\Delta H_n$ values were reduced by a constant amount.

The partial pressure of aqueous NaCl in equilibrium with the solid is given by

$$P_{NaCl,aq} = (f_{NaCl})(SO) \quad (11)$$

where f_{NaCl} is the fugacity or vapor pressure of anhydrous NaCl and (SO) is the sum over the relative pressures for the hydrated species defined in equation (10). Curves for $P_{NaCl,aq}$ as a function of temperature and total pressure were calculated for various enthalpy reductions in the model stated above and compared with the sets of experimental results of

Martynova,⁶ of Styrikovich, et al.,^{4,5} of Sourirajan and Kennedy⁸ and of Galobardes, et al.⁹ Reasonable agreement was obtained with all of the data except that of Sourirajan and Kennedy for $-\Delta H_n$ values reduced by $6.5 \text{ kcal mol}^{-1}$. The agreement was improved if the reduction for stages 4 and above was only $4.5 \text{ kcal mol}^{-1}$. The parameters on this basis are given in Table I.

These measurements of the solubility of sodium chloride in steam are very difficult and the uncertainties in the results are quite large. Figure 1, parts a, b, and c, compare the experimental data with the calculated curves. Figure 1a shows the data (except those of Sourirajan) for 450°C (723 K); all of the measurements agree quite well near 100 bar but there are considerable differences below 50 bar. Our model yields a curve midway between the values of Galobardes, et al., and the two Russian measurements. Qualitatively the curve must decrease in slope at sufficiently low steam pressure and eventually approach the pressure of unhydrated NaCl molecules. This feature was recognized by Styrikovich, Martynova, and Murgulina⁷ in their 1966 paper.

Figures 1b and 1c show the temperature dependence at 50 and 100 bar, respectively, and show the gross discrepancy between the measurements of Sourirajan and Kennedy⁸ from all others. At the lower temperatures one can fit the Sourirajan data fairly well with a model in which all $-\Delta H_n$ values are increased by $1.5 \text{ kcal mol}^{-1}$ from those listed in Table I. But at the highest temperature there is still a discrepancy of a factor of 30 from the modified model. Indeed the shape of the Sourirajan curves above 900 K implies an impossibly rapid change in the ΔH of hydration.

There are measurements by other investigators for the region of two liquid phases which occurs at higher pressures. The most recent work is

that of Parslod and Plattner¹⁴ who compare their results with those of others. These recent measurements agree with those of Khaibullin and Borisov,¹⁵ from the same laboratory as Martynova and Styrikovich, and disagree significantly with those of Sourirajan and Kennedy⁸ for this higher pressure region. Thus it seems clear that the evidence favors the model fitting the results of Martynova, of Styrikovich, et al., and of Galobardes, et al., and those parameters (given in Table I) were used in all further calculations. The details of this model are much less certain than those for Na^+ and Cl^- , and it will probably need revision when better experimental data are available. But it is physically plausible in relationship to the models for the hydration of Na^+ and Cl^- and it represents those experimental data which are internally consistent as well as is possible. Figure 1d shows the resulting vapor pressure of aqueous NaCl over a wide range of conditions.

Ionization Constant for NaCl in Steam

The ionization constant for gaseous NaCl in the absence of water K_2 is obtained from data in the JANAF tables. The ionization constant in the presence of steam is then

$$K_i = \frac{P_{\text{Na}^+, \text{aq}} P_{\text{Cl}^-, \text{aq}}}{P_{\text{NaCl}, \text{aq}}} = \frac{K_2 (S^+) (S^-)}{(S_0)} \quad (12)$$

The resulting curves for $\log K_i$ as a function of the density of the steam at several temperatures are shown in figure 2 along with the experimental values of Quist and Marshall.¹⁰ The pairs of calculated points are for model A (lower point) and model B (upper point). At 1073 K the calculated results fit very smoothly with the experimental values with the best curve much closer to model B than A. At lower temperatures the curves take an

S shape with a gradually steeper slope connecting the gas-like region of lower density with the liquid-like region of higher density. Below the critical temperature of water this would become a discontinuity with a gap in both $\log \rho$ and $\log K_i$ between the values for the saturated liquid and the saturated vapor. At the lower temperatures the calculations for the higher pressures become quite uncertain as indicated by a large difference between models A and B. In this region it is quite possible that the ions are even more hydrated than indicated for model B. Also the departure from the ideal gas law becomes substantial under these conditions. Thus there is considerable uncertainty in the interpolated portions of the curves on figure 2 for the lower temperatures.

Results and Discussion

There seems no need to present an extensive tabulation of the absolute values of various thermodynamic properties of Na^+ , Cl^- , and NaCl in steam since any value can easily be obtained as the sum of the absolute value for the anhydrous species in the standard state, as given in the JANAF tables, the correction to the desired pressure, and the change for hydration as calculated from the model defined in Table I. The change in Gibbs energy for hydration of Na^+ is

$$\Delta_h G/RT = -\ln(S^+) \quad (11)$$

with corresponding equations for Cl^- and NaCl . Direct calculation from the model is easy, but for convenience Table II gives an array of these $\Delta_h G$ values at the same temperatures as are used in the JANAF tables.

Enthalpies and entropies can be obtained from the temperature derivative of the Gibbs energies, but with decreased precision. A few values for 100 bar total pressure are given in Table III which also includes values for the mean hydration number $\langle n \rangle$.

One can relate the change in mean hydration number to the change in enthalpy. Thus $\text{Na}^+(\text{aq})$ loses just over one water from 800 to 900 K and the enthalpy change is 14 kcal mol^{-1} which corresponds to the $-\Delta H_n$ for the larger n values in Table I. (The effects of ΔC_p should be included in a more precise calculation.) This implies a heat capacity of about $70 R$ in the 800 to 900 K interval. This is a very large heat capacity.

Below the critical temperature of water, the partial molal heat capacities of ions are also large but negative. In very approximate terms one may view these large thermal effects in the following manner. Below T_c it is the hydrogen bonding between water molecules which is breaking up and this yields a large C_p for water. Since the water in the hydration shell around an ion is still tightly bound the difference is a negative heat capacity ascribed to the ion. But above T_c in the range we are considering, the water molecules in steam are separate gaseous molecules. It is now the hydration-shell molecules that are gradually being dissociated from the ion and their dissociation enthalpy contributes the large positive heat capacity ascribed to the ion in this range.

Figure 3 shows the Gibbs energy of hydration for the critical pressure, 221 bar, over a wide range of temperature. Also shown is the curve calculated from the Born equation.

$$-\Delta_h G = (e^2/8\pi\epsilon_0)(1 - 1/\epsilon)(1/R_+ + 1/R_-) \quad (12)$$

where R_+ and R_- are the radii of the spherical cavities in the dielectric which contain the positive and negative ions, ϵ is the dielectric constant or relative permittivity, ϵ_0 is the vacuum permittivity and e the protonic charge. The effective mean radius $R^* = 2(1/R_+ + 1/R_-)^{-1} = 1.86 \text{ \AA}$ is chosen to fit the Gibbs energy of hydration of $\text{Na}^+ + \text{Cl}^-$ at room temperature.

The dielectric constant is taken from Uematsu and Franck.¹⁶ The Born equation yields a qualitatively correct curve, but there is a large quantitative difference above the critical temperature.

Since the Born model assumes a continuous dielectric, one would not expect it to be successful in the high temperature range where there are only a few water molecules attached to each ion in the locations for strongest bonding.

Also we note that even in the liquid range at lower temperatures, where the Born equation fits a particular property fairly well, different effective radii are needed to fit different properties. Thus in comparison to the 1.86 Å needed to fit the Gibbs energy of hydration, one may mention the value of 3.27 Å chosen by Smith-Magowan and Wood¹⁷ to fit the heat capacity of aqueous NaCl in the range 500 to 600 K. To fit the partial molal volume of NaCl, Helgesen and Kirkham¹⁸ chose 1.81 Å which agrees rather closely with our 1.86 Å.

Application to Steam Turbine Technology

One practical problem to which these data are relevant is that of solid deposition in the low-pressure stages of steam turbines. This problem is discussed by Galombardes, et al.,⁹ who state that the important criterion is the solubility of NaCl in steam in the range 1-5 bar pressure and 400 to 450 K. Figure 1d shows the prediction of our model for the solubility (as $P_{\text{NaCl}}/P_{\text{H}_2\text{O}}$). In the range of interest this ratio is below 10^{-12} which is smaller than the value attainable by current technology for purification of boiler feed water. In this conclusion the present model agrees with the estimate of Galobardes, et al.

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TABLE I. Enthalpy and Entropy Changes for Successive Hydration of Na^+ , Cl^- , and Na^+Cl^-

n	T*/K	$\frac{-\Delta S^\circ_{T^*}}{\text{calK}^{-1}\text{mol}^{-1}}$	$\frac{-\Delta H^\circ_{T^*}}{\text{kcalmol}^{-1}}$	Model
(Na ⁺)				
1	700	21.5	24.0	
2	550	22.2	19.8	
3	450	21.9	15.8	
4+	350	25.0	13.8 - 1.5(n-4)	A
			13.8 - 0.8(n-4)	B
(Cl ⁻)				
1	400	16.5	13.1	
2	400	20.8	12.7	
3	350	23.2	11.7	
4+	330	25.8	11.1 - 0.5(n-4)	
(Na ⁺ Cl ⁻)				
1	500	22	17.5	
2	500	22	13.5	
3	500	22	9.5	
4+	500	25	9.5 - 0.8(n-4)	

TABLE II. Values of $-\Delta G/RT$ of Hydration
for Na^+ (Model B), Cl^- , and NaCl

P/bar	T/K	Na^+	Cl^-	NaCl
10	700	18.6	6.0 ₅	5.5
10	800	12.8	4.1	3.4
10	900	8.9	3.0	2.0 ₅
20	700	21.9	7.8 ₅	6.9
20	800	15.3	5.5 ₈	4.5 ₅
20	900	11.1	4.1 ₅	3.0
20	1000	8.2	3.2 ₅	2.0
20	1100	6.1	2.7	1.4
50	700	27.4	10.8	9.1
50	800	19.6	7.9	6.3 ₅
50	900	14.6	6.1 ₅	4.5 ₅
50	1000	11.2	5.0	3.3
50	1100	8.8	4.2	2.4 ₅
100	800	23.8	10.2	8.0
100	900	18.0	8.1	6.0
100	1000	14.1	6.7	4.6
100	1100	11.3	5.8	3.6
200	900	22.4	10.5	7.7
200	1000	17.8	8.8	6.1
200	1100	14.6	7.7	5.0
500	1000	24.5	12.6 ₅	8.6
500	1100	20.6	11.1	7.3
1000	1000	30.9	17.1	10.9
1000	1100	26.6	15.0	9.4 ₅

TABLE III. Enthalpies of Hydration and Entropies
(Absolute) at 100 Bar for Na^+ (Model B),
 Cl^- , and NaCl

	T/K			
	700	800	900	1000
$-\Delta_{\text{h}}H/RT (\text{Na}^+)$	76	56.5	42.5	33
$S/R (\text{Na}^+)$	-28	-17	- 9	- 2.5
$\langle n \rangle (\text{Na}^+)$	8.1	6.8	5.6	4.7
$-\Delta_{\text{h}}H/RT (\text{Cl}^-)$	33	21	15	11
$S/R (\text{Cl}^-)$	- 3	5	9.5	12
$\langle n \rangle (\text{Cl}^-)$	4.9	3.7	3.1	2.7
$-\Delta_{\text{h}}H/RT (\text{NaCl})$	26	19.5	15	12
$S/R (\text{NaCl})$	12	16	19	21
$\langle n \rangle (\text{NaCl})$	3.0	2.5	2.2	2.0

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Figure 1. The saturation vapor pressure of NaCl in steam: (a) as a function of P at 450°C (723 K), points from references: 6, solid circles; 4, open circles; 9, triangles; (b) as a function of T at 50 bar, points from references: 6, circles; 8, triangles; (c) as a function of T at 100 bar, points from references: 4, circles; 8, triangles. On all parts the curves are calculated from the models discussed in the text.

Figure 2. The ionization constant of NaCl in steam at several temperatures. The open symbols are calculated values: the solid symbols are measured values of Quist and Marshall. The vertical scale is offset for the various curves as indicated.

Figure 3. The Gibbs energy of hydration of $\text{Na}^+ + \text{Cl}^-$ at the critical pressure 221 bar. The dotted portion is interpolated between experimental values at low temperature and the present calculated values for high temperature. The dashed curve is for the Born equation. Also shown are mean hydration numbers for Na^+ and Cl^- with a separate scale on the right.

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