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Traceable Values for Activity and Osmotic Coefficients in Aqueous Sodium Chloride Solutions at Temperatures from 273.15 to 373.15 K up to the Saturated Solutions

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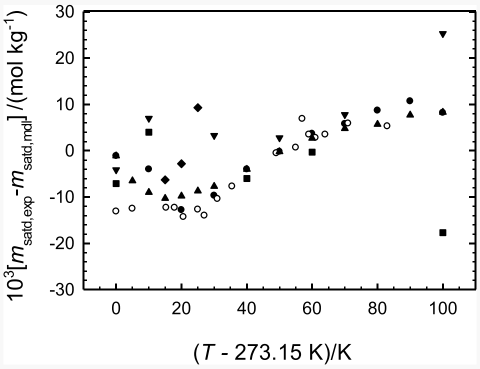
ABSTRACT: We present traceable three-parameter extended Hückel equations for the activity coefficient of sodium chloride and for the osmotic coefficient of water in aqueous NaCl solutions from 273.15 to 373.15 K. In this temperature range, our equations seem to apply within experimental error to all thermodynamic data available for these solutions up to the molality of the saturated solution. Our previous studies (*J. Chem. Eng. Data* **2017**, 62, 2617−2632 and **2019**, 64, 16−33) showed that, from 273.15 to 373.15 K, two-parameter Hückel equations can successfully explain the literature results of electrochemical, isopiestic, and cryoscopic measurements at least up to a molality of 0.2 mol·kg^{-1}. The model recommended in this study employs the values of our previous two-parameter model for the ion-size parameter in the original Debye−Hückel equation, *B*, and for the coefficient of the linear term with respect to the molality, b_1. In addition, it includes a quadratic term with respect to the molality with the coefficient b_2. Both b_1 and b_2 are quadratically dependent on temperature. With the introduction of b_2, our model is able to explain the existing vapor pressure, electrochemical, and solubility data from 273.15 to 373.15 K up to the saturated solution. A comparison with the most important literature values for the activity and osmotic coefficients revealed that the agreement is always at least satisfactory, but is best for temperatures below 363 K. On the basis of these results, our activity and osmotic coefficients are the most reliable values for these thermodynamic quantities so far. We propose this is true also for the values from 363 to 373 K.



■ INTRODUCTION

Sodium chloride is overwhelmingly the most abundant salt component in seawater. It plays a decisively important role in biological fluids and in many industrial solutions. Consequently, it is one the most important salt constituents existing in natural and manmade liquid systems. It is no surprise that the thermodynamic properties of NaCl in aqueous solutions have been carefully determined through several experimental procedures in various temperatures, pressures, and mixtures with water (see the extensive reviews by Pitzer et al.,[1] Clarke and Glew,[2] and Archer[3]). On this foundation of experimental findings for common electrolytes such as NaCl, theoretical models have been developed to aid in the interpretation of the existing data and allow for the estimation of thermodynamic properties in areas where data are lacking. Some models, such as the nonrandom two-liquid[4,5] and mean-spherical-approximation nonrandom two-liquid[6] ones take the excess Gibbs free energy as their starting point. A second family of models is based upon the equation of state and includes, for example, the perturbed-chain-statistical-associated-fluid-theory.[7,8] In the conductor-like-screening-model with segment-activity-coefficients approach the molecular surface area is subdivided into charged segments that interact with each other.[9] Recent studies have demonstrated that one can also use Monte Carlo and molecular dynamical modeling to calculate the activity and osmotic coefficients in NaCl solutions.[10−12]

Perhaps the most recognized approach for treating solutions of electrolytes such as NaCl is the Pitzer model,[13] introduced in 1973. While Pitzer's equations cover the thermodynamics of NaCl(aq) for a wide range of temperatures and pressures, in practice they are very complicated, consisting of multiple parameters that can depend on the fundamental variables of temperature, pressure, and molality. A similar complexity issue plagues many of the other models listed above. However, recent studies have demonstrated that at 298.15 K, the simple Hückel equation is as applicable as these multiparameter equations in the interpretation of the thermodynamic results of dilute solutions of pure electrolytes.[14,15]

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Table 1. Debye–Hückel Parameter α[a], the Vapor Pressure of Pure Water (p_1^*)[b], the Molar Volume of Liquid Water [$V_{\mathrm{m},1}^*(\mathrm{liq})$][b], and the Second Virial Coefficient of Water Vapor (β_1)[c] as Functions of Temperature T in the Range from 273.15 to 373.15 K

$(T - T_0)$[d]/K	$\alpha/(\mathrm{mol{\cdot}kg^{-1}})^{-1/2}$	p_1^*/Pa	$V_{\mathrm{m},1}^*(\mathrm{liq})\ /\mathrm{cm^3{\cdot}mol^{-1}}$	$\beta_1/\mathrm{cm^3{\cdot}mol^{-1}}$
0	1.1293	610.7	18.018	−2078
0.3	1.1301[e]			
5	1.1376	872.0	18.016	−1863
10	1.1462	1227.6	18.020	−1679
12.5	1.1505[e]			
15	1.1552	1705.1	18.031	−1520
20	1.1646	2338.4	18.048	−1382
25	1.1744	3168.6	18.068	−1262
30	1.1848	4245.1	18.095	−1156
35	1.1956	5626.4		
37.5	1.2011[e]	6458[f]	18.147[g]	−1021
40	1.2068	7381.2	18.156	−980
45	1.2186	9589.8		
50	1.2308	12345	18.239	−841
55	1.2436	15752		
60	1.2568	19933	18.323	−730
62.5	1.2636[e]	22361[f]	18.350[g]	−706
65	1.2704	2502.4		
70	1.2846	31177	18.425	−640
75	1.2992	38564	18.480	−601
80	1.3143	47375	18.538	−565
85	1.3299	57817		
87.5	1.3380[e]	63675[f]	18.627[g]	−518
90	1.3460	70120	18.662	−503
95	1.3626	84532		
100	1.3797	101325	18.798	−451

[a] Given by Archer and Wang (in Table 5).[38] [b] Given by Kell.[41] [c] Calculated from eq 5 (this equation is given in ref 40). [d] T_0 = 273.15 K. [e] Calculated from eq 6. [f] Calculated from eq 7. [g] Calculated from eq 8.

Our recent NaCl studies show that an extended version of the simple Hückel equation applies well to experimental data from various sources in the temperature range from 273.15 to 373.15 K.[16−19] With our best parametrization for the temperature dependence, the extended Hückel equation could predict all calorimetric data reported in the literature up to 373 K for dilute NaCl solutions, even though these data were not included in the parameter estimation. In the present study, we demonstrate that by extending our parametrization with a quadratic molality term, we can predict all the thermodynamic properties of NaCl solutions from 273.15 to 373.15 K at all temperatures up to the saturated solutions.

It is important to emphasize the fully traceable and transparent nature of the best parametrization presented here and in our previous studies,[16−19] in addition to its ability to predict experimental results. A critical reader can reproduce all calculations using the presented results with the appropriate literature data. This is not common in thermodynamic studies of electrolyte solutions, as the data often come from the isopiestic method. Owing to its comparative nature, this method requires knowledge of the thermodynamic activities of the reference electrolyte solution. However, the methods that provide activities for solutions of a pure electrolyte are not as accurate as the isopiestic method over wide ranges of molality, temperature, and pressure. To tackle this issue, we have previously determined traceable and highly accurate activity and osmotic coefficients for solutions of the common reference electrolytes NaCl and KCl at 298.15 K.[14] These values have been utilized in all our subsequent studies containing isopiestic data[16−34] including this one. Due to the abundance of theoretical models, we mainly compare our results against different types of experimental data and reserve alternative activity models for future publications. Finally, only equilibrium thermodynamic data reported at a constant or an almost constant temperature are considered in the present article, while future studies will report on the enthalpy and heat capacity results of NaCl solutions.

THEORY

General Equations for the Activity Quantities. In aqueous solutions of many salts at least up to an ionic strength (I_m) of 1 mol·kg^{-1}, the following extended Hückel equations can be used to predict the mean activity coefficient (γ) of the salt and the osmotic coefficient (ϕ) of water:[14,16−37]

$$\ln \gamma = -\frac{\alpha |z_+ z_-| \sqrt{I_\mathrm{m}}}{1 + B\sqrt{I_\mathrm{m}}} + b_1\left(\frac{m}{m^\circ}\right) + b_2\left(\frac{m}{m^\circ}\right)^2 \tag{1}$$

$$\varphi = 1 - \frac{\alpha |z_+ z_-|}{B^3 I_\mathrm{m}}\left[(1 + B\sqrt{I_\mathrm{m}}) - 2\ln(1 + B\sqrt{I_\mathrm{m}}) - \frac{1}{1 + B\sqrt{I_\mathrm{m}}}\right] + \frac{b_1}{2}\left(\frac{m}{m^\circ}\right) + \frac{2}{3}b_2\left(\frac{m}{m^\circ}\right)^2 \tag{2}$$

where for the standard Hückel equation the parameter b_2 is set equal to zero. In eqs 1 and 2, m is the molality, m° is 1 mol·kg^{-1}, z_+ and z_- are the charge numbers of the cation and anion, respectively, α is the Debye–Hückel parameter, and B, b_1, and b_2 are electrolyte dependent parameters. For temperatures from 273.15 to 373.15 K, the values of α at 101.325 kPa are given in Table 1. The values were taken from ref 38. For a uniunivalent electrolyte such as NaCl, $|z_+z_-| = 1$, $I_m = m$, and the osmotic coefficient is related to the activity of water (a_1, with subscript 1 is used here for the solvent) in pure solutions by the following thermodynamic identity

$$\ln a_1 = -2mM_1\varphi \tag{3}$$

where M_1 is the molar mass of water (= 0.018015 kg·mol^{-1}). The activity of water is associated with its vapor pressure over the solution (p_1) and that over pure water (p_1^*) through

$$\ln a_1 = \ln\left(\frac{p_1}{p_1^*}\right) + \frac{[\beta_1 - V_{m,1}^*(\text{liq})](p_1 - p_1^*)}{RT} \tag{4}$$

where T is the temperature in Kelvin, R is the gas constant, $V_{m,1}^*(\text{liq})$ is the molar volume of liquid water, and β_1 is the second virial coefficient of water vapor. This coefficient was calculated from the equation presented by Keyes et al.,[39] which was taken in the form used by Gibbard et al.[40] in the analysis of the vapor pressure data measured at several temperatures in NaCl solutions,

$$\frac{\beta_1}{\text{cm}^3\cdot\text{mol}^{-1}} = 34.0 - 47549\cdot\frac{10^{80870/(T/\text{K})^2}}{T/\text{K}} \tag{5}$$

The values used for β_1, $V_{m,1}^*(\text{liq})$, p_1^*, and α at various temperatures are given in Table 1. When available, we used the exact values from Archer and Wang[38] for α in eqs 1 and 2. Similarly, the exact values from Kell[41] for both $V_{m,1}^*(\text{liq})$ and p_1^* were utilized when possible in eq 4. When interpolation was needed, it was based on the equations presented in ref 19:

$$\frac{\alpha}{(\text{mol}\cdot\text{kg}^{-1})^{-1/2}} = 1.1296 + 1.550 \times 10^{-3}\left(\frac{T - T_0}{\text{K}}\right) + 9.5 \times 10^{-6}\left(\frac{T - T_0}{\text{K}}\right)^2 \tag{6}$$

$$\ln\left(\frac{p_1^*}{p^\text{o}}\right) = 23.02129 - 3611.77\left(\frac{\text{K}}{T}\right) - 253000\left(\frac{\text{K}}{T}\right)^2 \tag{7}$$

$$\frac{V_{m,1}^*(\text{liq})}{\text{cm}^3\cdot\text{mol}^{-1}} = 17.982 + 2.161 \times 10^{-3}\left(\frac{T - T_0}{\text{K}}\right) + 59.\ 6 \times 10^{-6}\left(\frac{T - T_0}{\text{K}}\right)^2 \tag{8}$$

where in eq 7 the symbol p^o is the unit of the pressure (i.e., p^o = 1 Pa) and in eqs 6 to 8 T_0 is equal to 273.15 K.

General Equations for the Solubility of a Uniunivalent Salt. The solubility product (K_{sp}) of a uniunivalent salt at a constant temperature has the form

$$K_{sp} = (\gamma_\text{satd}m_\text{satd}/m^\text{o})^2 \tag{9}$$

where the subscript "satd" refers to the saturated solution at each temperature. The solubility product is associated with the standard molar Gibbs energy of the dissolution reaction by the following thermodynamic identity

$$\Delta G_m^\text{o} = -RT\ln(K_{sp}) \tag{10}$$

This Gibbs energy can be obtained from the chemical potential of the salt in solutions ($\mu_{2,aq}$) and that as a solid ($\mu_{2,s}$) at the standard pressure by

$$\Delta G_m^\text{o} = \mu_{2,aq}^\text{o} - \mu_{2,s}^\text{o} \tag{11}$$

If the molar heat capacity of the salt at a constant pressure ($C_{m,s}$) is assumed to be constant at the temperatures considered, the standard molar enthalpy for a solid salt, $H_{m,2}^\text{o}(\text{s})$, has the following temperature dependence

$$H_{m,2}^\text{o}(\text{s}) = H_{m,2}^\text{o}(\text{s}, T_\text{ref}) + C_{m,s}(T - T_\text{ref}) \tag{12}$$

where T_ref is the thermodynamic reference temperature of 298.15 K. The enthalpy is connected to the Gibbs energy via

$$H = -T^2\frac{\partial\left(\frac{G}{T}\right)}{\partial T} \tag{13}$$

Hence, the standard molar reaction enthalpy ΔH_m^o is associated with the chemical potential of the salt in solutions ($\mu_{2,aq}$) and that as a solid ($\mu_{2,s}$) by the equation

$$\begin{aligned}\Delta H_m^\text{o} &= -T^2\frac{\partial\left(\frac{\Delta G_m^\text{o}}{T}\right)}{\partial T} = -T^2\frac{\partial\left(\frac{\mu_{2,aq}^\text{o} - \mu_{2,s}^\text{o}}{T}\right)}{\partial T} \\ &= -T^2\frac{\partial\left(\frac{\mu_{2,aq}^\text{o}}{T}\right)}{\partial T} + T^2\frac{\partial\left(\frac{\mu_{2,s}^\text{o}}{T}\right)}{\partial T}\end{aligned} \tag{14}$$

Thus,

$$\begin{aligned}\Delta H_m^\text{o} &= H_{m,2}^\infty(\text{real}) - H_{m,2}^\text{o}(\text{s}) \\ &= H_{m,2}^\infty(\text{real}) - H_{m,2}^\text{o}(\text{s}, T_\text{ref}) - C_{m,s}(T - T_\text{ref}) \\ &= [H_{m,2}^\infty(\text{real}) - H_{m,2}^\text{o}(\text{s}, T_\text{ref})] - C_{m,s}(T - T_\text{ref}) \\ &= H_{m,2}^\infty - C_{m,s}(T - T_\text{ref})\end{aligned} \tag{15}$$

where $H_{m,2}^\infty(\text{real})$ is the real molar enthalpy of salt at infinite dilution, $H_{m,2}^\text{o}(\text{s},T_\text{ref})$ is the nondeterminable absolute molar enthalpy of solid salt at T_ref, and $H_{m,2}^\infty = [H_{m,2}^\infty(\text{real}) - H_{m,2}^\infty(\text{s},T_\text{ref})]$ is the experimentally accessible partial molar enthalpy of salt in aqueous solution at infinite dilution.

RESULTS AND DISCUSSION

Parameter Estimation. For dilute NaCl solutions, we have observed in our previous studies that the constant value of 1.4 (mol·kg^{-1})$^{-1/2}$ generally applies for parameter B at all temperatures from 273 to 500 K.[14,16−19] In our most successful parametrization of the Hückel equation, the following quadratic equation was determined for parameter b_1 (see ref 17):

$$b_1 = 0.0077 + 3.1853 \times 10^{-3}\left(\frac{T - T_0}{\text{K}}\right) - 25.17 \times 10^{-6}\left(\frac{T - T_0}{\text{K}}\right)^2 \tag{16}$$

This equation was obtained from the following three values for $b_1(T)$: b_1 (273.15 K) = 0.0077 (determined in ref 16), b_1 (298.15 K) = 0.0716 (ref 14), and b_1 (348.15 K) = 0.105 (ref 17). With this parametrization, our Hückel equation can explain the existing thermodynamic data for dilute NaCl solutions within experimental error at least up to 0.2 mol·kg^{-1}

Table 2. Values of the Hückel Parameter b_2 in eqs 1 and 2 Obtained in the Present Study from Vapor Pressure Data as a Function of Temperature T

$(T - T_0)$[a]/K	b_1[b]	b_2(observed)	b_2(predicted)[c]	N[d]	ref
0	0.0077	0.0132	0.01328	20	43
15	0.0498	0.0083	0.00842	20	45
20	0.0613	0.0071	0.00706	10	42
25	0.0716	0.0058[e]	0.00585	10	40
25	0.0716	0.0059[f]	0.00585	15	42
30	0.0806	0.0048	0.00477	11	42
37.5	0.0918	0.0033	0.00340	5	40
50	0.1040	0.0018	0.00179	10	40
62.5	0.1086	0.0010	0.00103	5	40
75	0.1050	0.0010	0.00112	10	40
87.5	0.0937	0.0020	0.00204	5	40
100	0.0745	0.0039	0.00381	10	40

[a] T_0 = 273.15 K. [b] Calculated from eq 16. [c] Calculated from eq 17. [d] Number of points. [e] Determined from the data of Gibbard et al.[40] [f] Determined from the data of Olynyk and Gordon.[42]

in the temperature interval of (273, 383) K. For the more concentrated solutions considered in this study, we retained eq 16 for b_1 to preserve the excellent agreement with experimental results in dilute solutions. In addition, we extracted a new temperature dependent parameter b_2 from the existing vapor pressure data. As shown in eqs 1 and 2, this parameter multiplies the quadratic term with respect to the molality, which becomes significant in concentrated NaCl solutions. For each vapor pressure data set at a given temperature, the observed b_2 value was obtained by minimizing the square sum of pressure residuals. These b_2 values are reported in Table 2. Next, the resulting b_2 values at various temperatures were fitted to a quadratic equation with respect to the temperature. This equation has the form

$$b_2 = 0.01328 - 364.7 \times 10^{-6}\left(\frac{T - T_0}{\mathrm{K}}\right) + 2.7 \times 10^{-6}\left(\frac{T - T_0}{\mathrm{K}}\right)^2 \tag{17}$$

The standard deviation about the regression is 0.00011. To further validate the quality of our fit, eq 17 was used to obtain the predicted values for b_2 in Table 2. As shown in this table, at temperatures above 303.15 K, only the experimental vapor pressures from Gibbard et al.[40] were used in the estimation. At 298.15 K, we complemented the data from this source with the values from Olynyk and Gordon[42] whose vapor pressures we also used for temperatures 293.15 and 303.15 K. At 273.15 K, vapor pressures based on the osmotic coefficients of Platford[43]

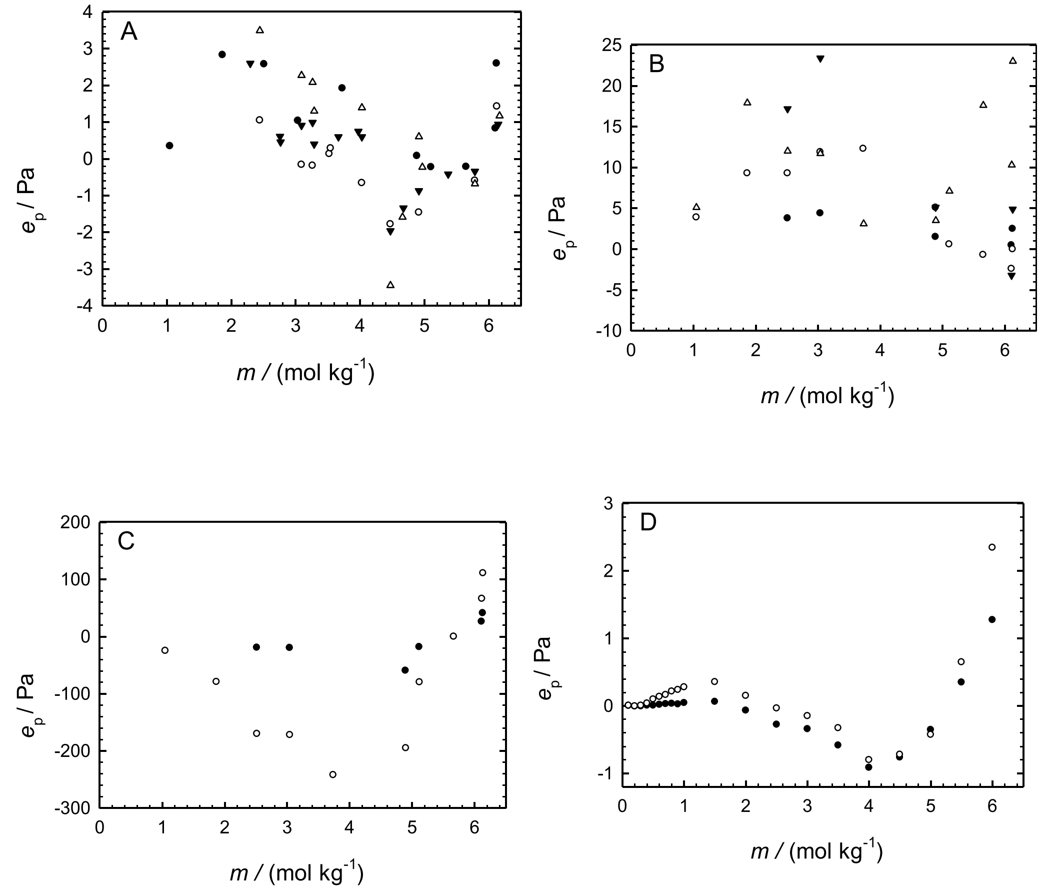

Figure 1. Plot of e_p (eq 18), the deviation between the literature value of the vapor pressure and that predicted by present parametrization, for NaCl solutions as a function of molality m. The vapor pressures were predicted using eqs 2, 3, and 4 with the present model. The literature values were obtained from the data of Gibbard et al.,[40] Olynyk and Gordon,[42] Platford,[43] and Childs and Platford.[45] Symbols for graph A: ●, T = 298.15 K, ref 40; ○, 293.15 K, ref 42; ▼, 298.15 K, ref 42; △, 303.15 K, ref 42. Symbols for graph B where the only the data from ref 40 were used: ●, T = 310.65 K; ○, 323.15 K; ▼, 335.65 K; △, 348.15 K. Symbols for graph C where only the data from ref 40 were used: ●, T = 360.65 K; ○, 373.15 K. Symbols for graph D: ●, ref 43, T = 273.15 K; ○, ref 45, 288.15 K.

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Table 3. Molality of the Saturated Sodium Chloride Solution (m_{satd}) and Solubility Product (K_{sp}) of This Salt as Functions of Temperature T (m^o = 1 mol·kg^{-1})

$(T-T_0)^a$/K	$m_{satd}(\text{IUPAC})^b/m^o$	m_{satd} (C&G)$^c/m^o$	γ(C&G)^{c,d}	K_{sp}(suggd)^e	K_{sp}(C&G)^c
0	6.0997	6.096	0.91090	31.41	30.83
5		6.099	0.93842		32.76
10	6.1123	6.106	0.96140	34.56	34.46
15		6.117	0.98026		35.96
20	6.1407	6.131	0.99537	37.51	37.24
25	6.1534	6.146	1.00707	38.68	38.31
30	6.1755	6.168	1.01567	39.87	39.25
40	6.2232	6.217	1.02458	41.67	40.56
50	6.2774	6.274	1.02390	42.66	41.27
60	6.3383	6.341	1.01503	42.77	41.43
70	6.4092	6.416	0.99921	42.12	41.11
80	6.4903	6.498	0.97751	40.74	40.35
90	6.5818	6.587	0.95063	38.76	39.21
100	6.6707	6.680	0.92038	36.03	37.80

[a] T_0 = 273.15 K. [b] The value is recommended in ref 49. [c] C&G refers to the value determined by Clarke and Glew[2] or calculated from their data. [d] The activity coefficient at the saturated solution. [e] The value calculated from the molality suggested by IUPAC using the present activity-coefficient model.

Table 4. Molality of the Saturated Sodium Chloride Solution (m_{satd}) and Solubility Product (K_{sp}) of This Salt as Functions of Temperature T Obtained by Using the Activity Coefficient Model Recommended Here (m^o = 1 mol·kg^{-1})

$(T-T_0)^a$/K	$[m_{satd}\ (\text{recd})/m^o]^b$	K_{sp}(recd)^c
0	6.097	31.36
5	6.105	33.03
10	6.115	34.62
15	6.127	36.12
20	6.141	37.51
25	6.157	38.77
30	6.175	39.88
35	6.196	40.83
40	6.220	41.60
45	6.246	42.19
50	6.274	42.58
55	6.305	42.78
60	6.338	42.78
65	6.373	42.57
70	6.411	42.16
75	6.450	41.57
80	6.492	40.78
85	6.535	39.82
90	6.579	38.71
95	6.624	37.44
100	6.671	36.05

[a] T_0 = 273.15 K. [b] Calculated iteratively by using eqs 9, 10, and 24. [c] Calculated from eq 24.

were employed. He determined the osmotic coefficients using an isopiestic method against urea solutions for which the osmotic coefficients of urea were obtained from the freezing-point data of Stokes.[44] Finally at 288.15 K, the vapor pressures of NaCl solutions were calculated from the osmotic coefficients of Childs and Platford.[45] Like Platford, they used the isopiestic method against urea solutions. In their case, the osmotic coefficients of urea at 288.15 K was taken from a table by Stokes[46] that was obtained from vapor pressure measurements at 298.15 K using appropriate enthalpy data.

To investigate the quality of our fit, the experimental vapor pressure data were predicted using our model, and the error plots are shown in Figure 1. The error is calculated from

$$e_p = p(\text{reported}) - p(\text{predicted}) \tag{18}$$

and presented as a function of molality. Graph A shows the results for 293.15, 298.15, and 303.15 K; graph B for 310.65, 323.15, 335.65, and 348.15 K; and graph C for 360.65 and 373.15 K. Finally, graph D gives the results obtained from the isopiestic data at 273.15 and 288.15 K. These results generally support our model well. Even though the errors remain small for the isopiestic results at low temperatures, the agreement is only satisfactory because of the trend evident in graph D. To account for the exponential increase of the vapor pressure with temperature, we also calculated the relative vapor pressure errors, where the e_p in eq 18 is divided by the vapor pressure of pure water at the temperature of interest. These errors are plotted in Figure S1 of Appendix A in the Supporting Information included in this article as a function of the salt molality. This figure will be discussed later. Finally, vapor pressure results are often reported using the osmotic coefficient as in Table S1 of Appendix B in Supporting Information, where we show the experimental osmotic coefficients from Gibbard et al.[40] together with the values from our model. The agreement in the table is always good except at 373.15 K where it is only satisfactory.

Model Comparison with Electrochemical Data. Then the full model presented in eqs 1 and 2 was tested with the amalgam cell data of Harned and Nims[47] who measured concentration cells of the type

$$\text{Ag(s)|AgCl(s)|NaCl(aq, } m_1\text{)|Na(Hg, } x\text{)|NaCl(aq, } m_2\text{)|AgCl(s)|Ag(s)} \tag{19}$$

where Na(Hg, x) is the sodium amalgam electrode and x refers to the mole fraction of sodium in the amalgam. The data of Harned and Nims consist of measurements at temperatures 273.45, 285.65, 288.15, 293.15, 298.15, 303.15, 310.65, and 313.15 K. In each set of experiments, both the temperature and the molality of the reference solution, m_1, were constant with m_1 = 0.1 mol·kg^{-1}. The molality of the tested solution (m_2) varied from one point to another in the range from 0.05 to 4.0

Table 5. New and Literature Values for the Partial Molar Enthalpy of Sodium Chloride at Infinite Dilution [(i.e., for $H_{m,2}^{\infty}$ and the Given Quantity is $H_{m,2}^{\infty}/(\text{J}\cdot\text{mol}^{-1})$] at Various Temperatures

$(T-T_0)$[a]/K	$H_{m,2}^{\infty}$ (new)[b]	$H_{m,2}^{\infty}$(eq 25)[c]	$H_{m,2}^{\infty}$ (ref2)[d]	$H_{m,2}^{\infty}$ (ref51)[e]	$H_{m,2}^{\infty}$ (ref52)[f]
0	5480	4530	6890	6720	5480
5	5370	4500	6090	5940	5150
10	5220	4450	5410	5270	4830
15	5030	4350	4820	4710	4500
20	4800	4230	4310	4230	4170
25	4520	4070	3860	3820	3850
30	4210	3870	3460		3520
35	3840	3640		3070	3190
40	3430	3370	2760		2868
45	2970	3060		2420	2540
50	2460	2710	2070		2220
55	1900	2320		1830	1890
60	1290	1890	1280		1560
65	630	1420		1160	1240
70	−90	910	210		910
75	−860	350		460	584
80	−1690	−260	−1330		260
85	−2570	−910		−220	−70
90	−3510	−1600	−3550		−400
95	−4520	−2350		−1030	−720
100	−5580	−3140	−6730		−1050

[a] T_0 = 273.15 K. [b] Obtained by using the present calculation method from the solubility data of IUPAC (eq 24). [c] Obtained by using the present calculation method from the solubility data of Clarke and Glew[2] (eq 25). [d] Literature values from Clarke and Glew.[2] [e] Literature values from Criss and Cobble[51] and the exact values for $(T-T_0)$/K are in this order 0.02, 5.00, 9.99, 15.00, 19.97, 25.00, 34.96, 45.00, 54.83, 64.86, 75.01, 84.98, and 95.18, see also footnote *a*. [f] Obtained by Hubert et al.[52] from their linear representation of molar standard solution enthalpy of NaCl versus temperature.

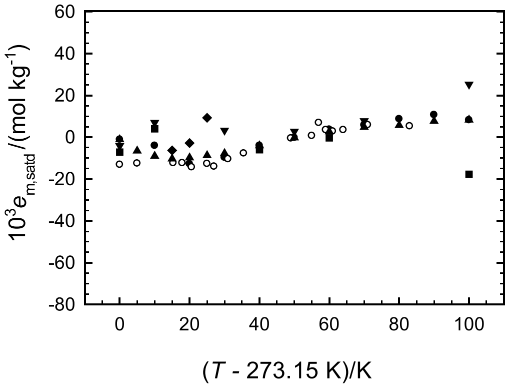

Figure 2. Plot of $e_{m,satd}$ (eq 26), the deviation between the literature value of the molality of the saturated solution and that predicted using the present model for the activity coefficient of the salt, in NaCl solutions as a function of temperature T. The saturated molalities were predicted by eqs 1, 9, 10, and 24. The literature values were obtained from the data of Küpper[54] (symbol ○), Flöttmann[55] (◆), Cornec and Krombach[57] (■), Nallet and Paris[60] (▼), Potter and Clynne[61] (●); and Clarke and Glew[2] (▲). All data except those from ref 2 were taken from ref 49.

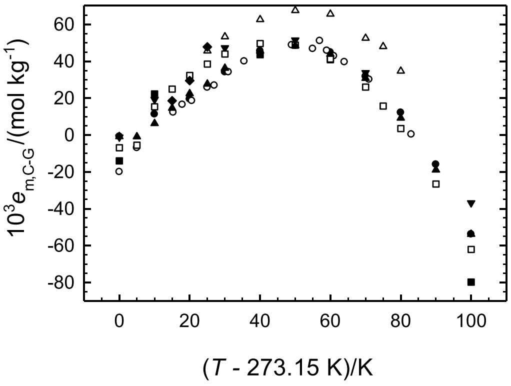

Figure 3. Plot of $e_{m,C-G}$ (eq 27), the deviation between the suggested value of the molality of the saturated solution and that predicted by the model obtained from the multiparameter equations of Clarke and Glew[2] for the activity coefficient of the salt, in NaCl solutions as a function of temperature T. The saturated molalities were predicted by eqs 1, 9, 10, and 25. The values used in testing were obtained from the data of Küpper[54] (symbol ○), Flöttmann[55] (◆), Cornec and Krombach[57] (■), eq 24 in the present study (□), Pinho and Macedo[53] (△), Nallet and Paris[60] (▼), Potter and Clynne[61] (●); Clarke and Glew[2] (▲). All data except those from refs 2 and 53 and from eq 24 were taken from ref 49.

mol·kg^{-1}. The cell potential difference (cpd = E) for cells of this kind can be expressed as

$$E = -\frac{2RT}{F}\ln\left(\frac{m_2}{m_1}\right) - \frac{2RT}{F}\ln\left(\frac{\gamma_2}{\gamma_1}\right) \tag{20}$$

where F is the Faraday constant. All data in the Harned and Nims' sets were predicted using eq 1 both with and without the b_2-parameter term for the activity coefficient. The cpd errors, defined by

$$e_{cpd} = E(\text{observed}) - E(\text{predicted}) \tag{21}$$

are provided in Appendix C of the Supporting Information. The results without the b_2-parameter are shown in graph A of Figure S2 and the ones with it are in graph B as a function of

Table 6. Recommended Activity Coefficients (γ) of Salt in Aqueous Sodium Chloride Solutions at Temperatures from 273.15 to 298.15 K as a Function of Molality m[a]

m/mol·kg^{-1}	$\gamma(0)$	$\gamma(5)$	$\gamma(10)$	$\gamma(15)$	$\gamma(20)$	$\gamma(25)$
0.20[b]	0.7341	0.7347	0.7350	0.7351	0.7349	0.7344
0.20	0.735	0.735	0.735	0.735	0.735	0.735
0.30	0.707	0.708	0.709	0.710	0.710	0.710
0.40	0.688	0.690	0.692	0.693	0.694	0.695
0.50	0.674	0.677	0.680	0.681	0.683	0.684
0.60	0.663	0.667	0.670	0.673	0.675	0.676
0.70	0.655	0.659	0.663	0.666	0.669	0.671
0.80	0.648	0.653	0.658	0.661	0.664	0.667
0.90	0.642	0.648	0.653	0.658	0.661	0.664
1.00	0.638	0.644	0.650	0.655	0.659	0.662
1.2	0.631	0.639	0.646	0.652	0.657	0.661
1.4	0.627	0.636	0.645	0.652	0.658	0.663
1.5	0.626	0.636	0.644	0.652	0.659	0.664
1.6	0.625	0.636	0.645	0.653	0.660	0.666
1.8	0.625	0.637	0.647	0.656	0.664	0.671
2.0	0.627	0.639	0.650	0.660	0.669	0.677
2.5	0.635	0.650	0.664	0.676	0.687	0.696
3.0	0.651	0.669	0.684	0.698	0.711	0.721
3.5	0.674	0.693	0.711	0.726	0.740	0.752
4.0	0.704	0.724	0.743	0.760	0.775	0.788
4.5	0.741	0.763	0.782	0.800	0.816	0.829
5.0	0.786	0.808	0.829	0.847	0.863	0.877
5.5	0.840	0.863	0.883	0.901	0.917	0.930
6.0	0.905	0.926	0.946	0.964	0.979	0.991

[a] The values have been calculated using the parametrization recommended here and the values in each column are given at temperature T expressed in parentheses as $(T - 273.15\ \mathrm{K})/\mathrm{K}$. [b] Recommended in ref 17.

Table 7. Recommended Activity Coefficients (γ) of Salt in Aqueous Sodium Chloride Solutions at Temperatures from 303.15 to 328.15 K as a Function of Molality m[a]

m/mol·kg^{-1}	$\gamma(30)$	$\gamma(35)$	$\gamma(40)$	$\gamma(45)$	$\gamma(50)$	$\gamma(55)$
0.20[b]	0.7336	0.7326	0.7313	0.7297	0.7278	0.7257
0.20	0.734	0.733	0.731	0.730	0.728	0.726
0.30	0.710	0.709	0.708	0.706	0.705	0.702
0.40	0.695	0.694	0.693	0.692	0.690	0.688
0.50	0.684	0.684	0.683	0.682	0.681	0.678
0.60	0.677	0.677	0.677	0.676	0.674	0.672
0.70	0.672	0.672	0.672	0.671	0.670	0.668
0.80	0.668	0.669	0.669	0.669	0.667	0.665
0.90	0.666	0.667	0.668	0.667	0.666	0.664
1.0	0.665	0.666	0.667	0.667	0.666	0.664
1.2	0.665	0.667	0.668	0.668	0.667	0.665
1.4	0.667	0.669	0.671	0.672	0.671	0.669
1.5	0.668	0.671	0.673	0.674	0.674	0.672
1.6	0.671	0.674	0.676	0.677	0.677	0.675
1.8	0.676	0.680	0.682	0.684	0.683	0.682
2.0	0.682	0.687	0.690	0.692	0.692	0.690
2.5	0.704	0.709	0.713	0.715	0.716	0.714
3.0	0.730	0.737	0.742	0.744	0.745	0.744
3.5	0.762	0.770	0.775	0.778	0.779	0.777
4.0	0.799	0.807	0.812	0.816	0.816	0.814
4.5	0.840	0.849	0.855	0.858	0.858	0.855
5.0	0.888	0.896	0.901	0.904	0.904	0.900
5.5	0.941	0.948	0.953	0.955	0.954	0.949
6.0	1.000	1.006	1.010	1.011	1.008	1.003

[a] The values have been calculated using the parametrization recommended here and the values in each column are given at temperature T expressed in parentheses as $(T - 273.15\ \mathrm{K})/\mathrm{K}$. [b] Recommended in ref 17.

Table 8. Recommended Activity Coefficients (γ) of Salt in Aqueous Sodium Chloride Solutions at Temperatures from 333.15 to 353.15 K as a Function of Molality m[a]

m/mol·kg^{-1}	$\gamma(60)$	$\gamma(65)$	$\gamma(70)$	$\gamma(75)$	$\gamma(80)$
0.20[b]	0.7232	0.7206	0.7176	0.7144	0.7109
0.20	0.723	0.721	0.718	0.714	0.711
0.30	0.700	0.697	0.694	0.690	0.686
0.40	0.685	0.682	0.679	0.675	0.670
0.50	0.676	0.672	0.669	0.664	0.660
0.60	0.669	0.666	0.662	0.657	0.652
0.70	0.665	0.662	0.657	0.653	0.647
0.80	0.662	0.659	0.655	0.650	0.644
0.90	0.661	0.657	0.653	0.648	0.642
1.0	0.661	0.657	0.652	0.647	0.641
1.2	0.662	0.658	0.654	0.648	0.641
1.4	0.666	0.662	0.657	0.651	0.644
1.5	0.669	0.665	0.659	0.653	0.646
1.6	0.672	0.668	0.662	0.656	0.648
1.8	0.679	0.674	0.669	0.662	0.653
2.0	0.687	0.682	0.676	0.669	0.660
2.5	0.711	0.706	0.699	0.691	0.681
3.0	0.740	0.735	0.727	0.717	0.706
3.5	0.773	0.767	0.758	0.748	0.735
4.0	0.810	0.803	0.794	0.782	0.768
4.5	0.850	0.843	0.832	0.819	0.804
5.0	0.894	0.886	0.874	0.860	0.844
5.5	0.942	0.933	0.920	0.905	0.887
6.0	0.994	0.983	0.969	0.953	0.934

[a] The values have been calculated using the parametrization recommended here and the values in each column are given at temperature T expressed in parentheses as $(T - 273.15\ \mathrm{K})/\mathrm{K}$. [b] Recommended in ref 17.

Table 9. Recommended Activity Coefficients (γ) of Salt in Aqueous Sodium Chloride Solutions at Temperatures from 358.15 to 373.15 K as a Function of Molality m[a]

m/mol·kg^{-1}	$\gamma(85)$	$\gamma(90)$	$\gamma(95)$	$\gamma(100)$
0.20[b]	0.7072	0.7032	0.6990	0.6945
0.20	0.707	0.703	0.699	0.695
0.30	0.682	0.677	0.672	0.667
0.40	0.666	0.660	0.655	0.649
0.50	0.655	0.649	0.643	0.636
0.60	0.647	0.641	0.634	0.627
0.70	0.641	0.635	0.628	0.620
0.80	0.638	0.631	0.623	0.615
0.90	0.635	0.628	0.620	0.611
1.0	0.634	0.626	0.618	0.609
1.2	0.633	0.625	0.616	0.605
1.4	0.635	0.626	0.616	0.605
1.5	0.637	0.627	0.617	0.605
1.6	0.639	0.629	0.618	0.606
1.8	0.644	0.633	0.621	0.608
2.0	0.650	0.639	0.626	0.612
2.5	0.669	0.656	0.641	0.626
3.0	0.693	0.678	0.662	0.644
3.5	0.721	0.704	0.686	0.666
4.0	0.752	0.734	0.714	0.693
4.5	0.787	0.767	0.746	0.722
5.0	0.825	0.804	0.781	0.756
5.5	0.867	0.844	0.820	0.794
6.0	0.912	0.889	0.863	0.836

[a] The values have been calculated using the parametrization recommended here and the values in each column are given at temperature T expressed in parentheses as $(T - 273.15\ \mathrm{K})/\mathrm{K}$. [b] Recommended in ref 19.

the molality of the tested solution, m_2. The simpler model in graph A applies well at all temperatures up to 1.5 mol·kg^{-1}, but only at 310.65 and 313.15 K do the full data agree accurately with the values predicted with this model. In contrast, in graph B almost all amalgam-cell data can be explained within 1 mV with the new Hückel parameters when parameter b_2 is included in the calculation. However, it should be borne in mind in the evaluation of these results that the amalgam cells are not comparable in accuracy with the best electrochemical cells.

Next, we tested the quality of our Hückel parameters against the galvanic cell data obtained from cells with a single electrolyte solution. Mussini et al.[48] measured solutions of NaCl using direct amalgam cells of the type

$$\mathrm{Na(Hg},\ x)|\mathrm{NaCl(aq},\ m)|\mathrm{AgCl(s)}|\mathrm{Ag(s)} \quad (22)$$

where x is the mole fraction of the alkali metal in the amalgam. These data include 23 series in which x is constant and the molality, m, varies: one at 283.15 K, seven series at 298.15 K, five series at 313.15 K, at 328.15 K, and at 343.15 K. As in our previous research with the simpler models (see ref 16), all these data were used in testing the new extended Hückel equations. The cpd for the cells of this kind is given by the following equation

$$E = E^\circ - \frac{2RT}{F}\ln\left(\frac{\gamma m}{m^\circ}\right) \quad (23)$$

where E° is the standard cpd and it depends on T and x. The error plots for these amalgam cell data are given in the four graphs of Figure S3 in Appendix C of the Supporting Information. Graph A gives the results for 298.15 K, graph B for 283.15 K and 313.15 K, graph C for 328.15 K, and graph D finally for 343.15 K. The error of each experimental point has been calculated from eq 21. The best value of E° was estimated for each mole fraction of amalgam and for each temperature, and these E° values are given in Table S2 of Appendix C. Clearly, there is no appreciable quality difference between the graphs in Figure S3, and the extended Hückel equation accurately predicts the data from these quite dilute solutions at all investigated temperatures.

Model Comparison with Solubility Data. The new extended Hückel equations were also tested against the solubility data recommended by IUPAC[49] for NaCl solutions. First, we determined the solubility product using eq 9 from the given saturated molalities and the activity coefficients obtained from eq 1. These calculations were done at 298.15 K and at each rounded Celsius temperature from 273.15 to 373.15 K in intervals of 10 K. The observed K_{sp} values are listed in Table 3. Next, we used eq 10 and the K_{sp} values to fit a quadratic equation with respect to the Celsius temperature using $\Delta G_m^\circ/T$ as the response variable. The resulting expression is

$$\frac{\Delta G_m^\circ/T}{(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})} = -28.64697 - 90.1930\times 10^{-3}\left(\frac{T-T_0}{\mathrm{K}}\right) + 786\times 10^{-6}\left(\frac{T-T_0}{\mathrm{K}}\right)^2 \quad (24)$$

and the standard deviation for this fit is 0.012. Finally, we used iterative calculations to predict the values for the saturated molality and the solubility product based on this fit. Table 4

Table 10. Recommended Osmotic Coefficients (ϕ) of Water in Aqueous Sodium Chloride Solutions at Temperatures from 273.15 to 298.15 K as a Function of Molality m[a]

m/mol·kg^{-1}	$\phi(0)$	$\phi(5)$	$\phi(10)$	$\phi(15)$	$\phi(20)$	$\phi(25)$
0.20[b]	0.9210	0.9219	0.9227	0.9234	0.9239	0.9242
0.20	0.921	0.922	0.923	0.924	0.924	0.924
0.30	0.916	0.918	0.919	0.920	0.921	0.922
0.40	0.914	0.916	0.918	0.920	0.921	0.922
0.50	0.913	0.915	0.918	0.920	0.922	0.924
0.60	0.912	0.916	0.919	0.922	0.924	0.926
0.70	0.913	0.917	0.921	0.924	0.927	0.929
0.80	0.914	0.919	0.923	0.926	0.930	0.932
0.90	0.915	0.921	0.925	0.929	0.933	0.936
1.00	0.917	0.923	0.928	0.933	0.937	0.940
1.2	0.921	0.928	0.934	0.940	0.945	0.949
1.4	0.927	0.935	0.942	0.948	0.953	0.958
1.5	0.930	0.938	0.945	0.952	0.958	0.963
1.6	0.933	0.942	0.949	0.956	0.963	0.968
1.8	0.940	0.950	0.958	0.966	0.972	0.978
2.0	0.948	0.958	0.967	0.975	0.982	0.989
2.5	0.972	0.983	0.993	1.002	1.010	1.017
3.0	0.999	1.011	1.022	1.031	1.039	1.047
3.5	1.031	1.043	1.054	1.063	1.072	1.079
4.0	1.067	1.079	1.089	1.098	1.106	1.113
4.5	1.109	1.119	1.128	1.136	1.143	1.149
5.0	1.154	1.162	1.170	1.176	1.182	1.186
5.5	1.204	1.210	1.215	1.219	1.223	1.226
6.0	1.258	1.261	1.263	1.265	1.267	1.268

[a] The values have been calculated using the parametrization recommended here and the values in each column are given at temperature T expressed in parentheses as $(T - 273.15\text{ K})/\text{K}$. [b] Recommended in ref 17.

Table 11. Recommended Osmotic Coefficients (ϕ) of Water in Aqueous Sodium Chloride Solutions at Temperatures from 303.15 to 328.15 K as a Function of Molality m[a]

m/mol·kg^{-1}	$\phi(30)$	$\phi(35)$	$\phi(40)$	$\phi(45)$	$\phi(50)$	$\phi(55)$
0.20[b]	0.9244	0.9244	0.9242	0.9239	0.9235	0.9228
0.20	0.925	0.924	0.924	0.924	0.924	0.923
0.30	0.922	0.923	0.923	0.923	0.922	0.922
0.40	0.923	0.924	0.924	0.924	0.924	0.923
0.50	0.925	0.926	0.926	0.927	0.927	0.926
0.60	0.928	0.929	0.930	0.930	0.930	0.930
0.70	0.931	0.933	0.934	0.934	0.934	0.934
0.80	0.935	0.937	0.938	0.939	0.939	0.939
0.90	0.939	0.941	0.942	0.943	0.944	0.944
1.0	0.943	0.945	0.947	0.948	0.949	0.949
1.2	0.952	0.955	0.957	0.959	0.960	0.960
1.4	0.962	0.965	0.968	0.970	0.971	0.971
1.5	0.967	0.971	0.973	0.975	0.976	0.977
1.6	0.972	0.976	0.979	0.981	0.982	0.982
1.8	0.983	0.987	0.990	0.992	0.994	0.994
2.0	0.994	0.998	1.002	1.004	1.006	1.006
2.5	1.023	1.027	1.031	1.034	1.036	1.036
3.0	1.053	1.058	1.062	1.065	1.067	1.067
3.5	1.085	1.090	1.094	1.096	1.098	1.098
4.0	1.118	1.123	1.126	1.129	1.130	1.130
4.5	1.154	1.157	1.160	1.162	1.163	1.162
5.0	1.190	1.193	1.195	1.196	1.196	1.195
5.5	1.228	1.230	1.230	1.230	1.229	1.228
6.0	1.268	1.268	1.267	1.265	1.263	1.261

[a] The values have been calculated using the parametrization recommended here and the values in each column are given at temperature T expressed in parentheses as $(T - 273.15\text{ K})/\text{K}$. [b] Recommended in ref 17.

Table 12. Recommended Osmotic Coefficients (ϕ) of Water in Aqueous Sodium Chloride Solutions at Temperatures from 333.15 to 353.15 K as a Function of Molality m[a]

m/mol·kg^{-1}	$\phi(60)$	$\phi(65)$	$\phi(70)$	$\phi(75)$	$\phi(80)$
0.20[b]	0.9221	0.9211	0.9200	0.9187	0.9173
0.20	0.922	0.921	0.920	0.919	0.917
0.30	0.921	0.920	0.919	0.917	0.916
0.40	0.922	0.921	0.920	0.918	0.917
0.50	0.925	0.924	0.923	0.921	0.919
0.60	0.929	0.928	0.927	0.925	0.922
0.70	0.933	0.932	0.931	0.929	0.926
0.80	0.938	0.937	0.935	0.933	0.931
0.90	0.943	0.942	0.940	0.938	0.935
1.0	0.948	0.947	0.946	0.943	0.940
1.2	0.959	0.958	0.956	0.954	0.951
1.4	0.971	0.969	0.967	0.965	0.961
1.5	0.976	0.975	0.973	0.970	0.967
1.6	0.982	0.981	0.979	0.976	0.972
1.8	0.994	0.993	0.990	0.987	0.983
2.0	1.006	1.004	1.002	0.999	0.995
2.5	1.036	1.034	1.032	1.028	1.024
3.0	1.067	1.065	1.062	1.058	1.053
3.5	1.098	1.096	1.093	1.089	1.083
4.0	1.129	1.127	1.124	1.119	1.114
4.5	1.161	1.158	1.155	1.150	1.145
5.0	1.193	1.190	1.186	1.181	1.176
5.5	1.225	1.222	1.218	1.213	1.207
6.0	1.258	1.254	1.250	1.245	1.239

[a] The values have been calculated using the parametrization recommended here and the values in each column are given at temperature T expressed in parentheses as $(T - 273.15\ \text{K})/\text{K}$. [b] Recommended in ref 17.

Table 13. Recommended Osmotic Coefficients (ϕ) of Water in Aqueous Sodium Solutions at Temperatures from 358.15 to 373.15 K as a Function of Molality m[a]

m/mol·kg^{-1}	$\phi(85)$	$\phi(90)$	$\phi(95)$	$\phi(100)$
0.20[b]	0.9157	0.9140	0.9121	0.9100
0.20	0.916	0.914	0.912	0.910
0.30	0.914	0.912	0.909	0.907
0.40	0.914	0.912	0.909	0.906
0.50	0.917	0.914	0.911	0.907
0.60	0.920	0.917	0.913	0.910
0.70	0.924	0.920	0.916	0.912
0.80	0.928	0.924	0.920	0.916
0.90	0.932	0.928	0.924	0.919
1.0	0.937	0.933	0.928	0.923
1.2	0.947	0.942	0.937	0.931
1.4	0.957	0.952	0.946	0.940
1.5	0.962	0.957	0.951	0.945
1.6	0.968	0.962	0.956	0.949
1.8	0.979	0.973	0.966	0.959
2.0	0.990	0.984	0.977	0.969
2.5	1.018	1.011	1.004	0.995
3.0	1.047	1.040	1.032	1.022
3.5	1.077	1.069	1.061	1.051
4.0	1.107	1.099	1.091	1.081
4.5	1.138	1.130	1.121	1.112
5.0	1.169	1.162	1.153	1.144
5.5	1.201	1.194	1.186	1.177
6.0	1.233	1.227	1.220	1.212

[a] The values have been calculated using the parametrization recommended here and the values in each column are given at temperature T expressed in parentheses as $(T - 273.15\ \text{K})/\text{K}$. [b] Recommended in ref 19.

reports these values both for the data used in the estimation and for the omitted temperatures in intervals of 5 K.

In addition to the IUPAC values, Clarke and Glew[2] also presented solubilities and activity coefficients for saturated NaCl solutions based on their multiparameter equations. These values are collected in Table 3 and were used to further test our model. The equation obtained from their data for quantity $\Delta G_\text{m}^\text{o}/T$ is

$$\frac{\Delta G_\text{m}^\text{o}/T}{(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})} = -28.68118 - 77.498 \times 10^{-3}\left(\frac{T - T_0}{\text{K}}\right) + 635 \times 10^{-6}\left(\frac{T - T_0}{\text{K}}\right)^2 \qquad (25)$$

The standard deviation for this fit is 0.092, which is almost nine times larger than that obtained for eq 24. Thus, the simple quadratic equation with respect to the temperature for the molar standard Gibbs energy of dissolution might better predict the experimental IUPAC results when combined with our activity data than the activity coefficients and saturated molalities of Clarke and Glew.

To validate our model further, we also used the fitted eqs 24 and 25 to obtain partial molar enthalpies of NaCl at infinite dilution from eqs 14 and 15 at various temperatures. In these calculations, we used an average molar heat capacity of 50 J·K^{-1}·mol^{-1} for solid NaCl in the temperature range of 273−373 K. This was based on the data by Archer.[50] The resulting $H_{\text{m},2}^{\infty}$ values are given in Table 5. This table further includes the experimental enthalpies determined by Criss and Cobble[51] and the multiparameter-equation values suggested by Clarke and Glew.[2] The final column lists the values from Hubert et al.,[52] who obtained a linear representation for the standard molar solution enthalpy as a function of temperature based on their own solution-enthalpy data at 298, 318, and 333 K. However, a linear relationship is not theoretically feasible because it requires that the heat capacity of aqueous NaCl remains constant at all temperatures. This contradicts the experimental results. According to Table 5, the new enthalpies agree semiquantitatively with the literature values up to 373 K. There is no appreciable difference between eq 24 and eq 25, which was based on the results of Clarke and Glew,[2] in the ability to predict the experimental data. Although the present parametrization seems to do slightly better at high temperatures, one should note that the accuracy of the experimental enthalpy values is usually not good in this temperature region. Furthermore, the accuracy of the infinite-dilution-enthalpy values determined from the properties of saturated solutions is likely not high. We observe, for example, that the heat capacities of NaCl at infinite dilution that result from the present parametrization are often very far from the literature values.

Finally, we conducted broad comparisons of our new solubility values with the most important experimental ones. For completeness, the m_satd values from ref 2 were included in these tests. Most experimental values were taken from the critical IUPAC review of ref 49, which was complemented by data from Pinho and Macedo.[53] The considered review data originates from refs 54 to 61. The details and the results are presented in Table S3 of Appendix D in the Supporting Information. It shows that the suggested solubility at each temperature supports our extended Hückel equation very well. This is also evident in the two graphs of Figure S4 in Appendix D, where the molality error of the saturated solution is shown as a function of the temperature. This error is calculated from

$$e_{\mathrm{m,satd}} = m_{\mathrm{satd}}(\text{observed}) - m_{\mathrm{satd}}(\text{predicted using eq 24}) \tag{26}$$

Graph A in Figure S4 shows the results for the more precise data sets, and graph B shows the results for the rest of the sets.

The m_{satd} values we obtained from the multiparameter equations of Clarke and Glew[2] were also compared to the literature values of graph A in Figure S4 of Appendix D in the Supporting Information. To facilitate this comparison, the values of this graph are reshown in Figure 2 in the main text on a slightly different scale. In contrast, Figure 3 shows the molality errors of the saturated solution calculated from

$$e_{\mathrm{m,C-G}} = m_{\mathrm{satd}}(\text{observed}) - m_{\mathrm{satd}}(\text{predicted using eq25}) \tag{27}$$

as a function of the temperature. In addition to the literature data used in Figure 2, Figure 3 includes the recommended m_{satd} values from eq 24 (see, e.g., Table 4) and the more recent data from Pinho and Macedo[53] that were considered in graph B of Figure S4 in Appendix D. The numerical details of the calculations associated with eq 25 are presented in Table S4 of Appendix E. Comparison of the results in Figures 2 and 3 in the main article and those in Tables S3 and S4 in the Supporting Information, together with the difference in the standard deviations of these equations observed above, verify that eq 24 is superior to eq 25. Additionally, the suggested solubilities in Figure 3 do not support eq 25 very well even though all errors are quite small. This seems to imply that our activity coefficients are more reliable, and the saturated molalities from IUPAC recommendations[49] are of higher accuracy than those of Clarke and Glew.[2]

Model Comparison with Pre-existing Activity and Osmotic Coefficients. In addition to the vapor pressure, electrochemical, and solubility comparisons, we also studied how our new activity and osmotic coefficients differ from the existing literature values for these quantities. The results from the comparison with activity and osmotic coefficients obtained from the general multiparameter equations of both Pitzer et al.[1] and Clarke and Glew[2] are reported in Figures S5 and S6 in Appendix F of the Supporting Information, respectively. For the activity-coefficient comparison with ref 2, also the results of the saturated solution at each temperature have been included in Figure S5. The saturated molalities of that study[2] can be found in Table 3 of the present study. To align this activity-coefficient comparison with how experimental results are reported, we have calculated the deviation from

$$e_{\mathrm{cpd}} = -\frac{2RT}{F}\ln\left(\frac{\gamma_{\mathrm{recd}}}{\gamma_{\mathrm{lit}}}\right) \tag{28}$$

where γ_{recd} is the value obtained from our eq 1, and γ_{lit} is the corresponding value from the literature. In this way, any deviations are closely associated with the errors of the cell potential difference measured using the direct amalgam cells, that is, of the type shown in eq 22. Graph A of Figure S5 illustrates the errors in interval (273.15, 293.15) K, graph B in interval (298.15, 323.15) K, and graph C in interval (333.15, 373.15) K. Only for the temperatures 363.15 and 373.15 K in graph C are the errors considerably larger than the experimental ones (see, for example, Figures S2 and S3 in Appendix C of the Supporting Information).

Analogously to the activity coefficient case, we used relative vapor pressure deviations to make the osmotic-coefficient comparison relatable to experimental findings. These vapor pressure deviations were defined by

$$e_{\mathrm{p}}/p_1^* = \frac{p(\text{recd}) - p(\text{lit})}{p_1^*} \tag{29}$$

where the recommended vapor pressures were calculated from the new extended-Hückel-equation model and the literature ones from the reported osmotic coefficients. Our recommended vapor pressures at rounded molalities can be found in Tables S5, S6, and S7 in Appendix G of the Supporting Information. The deviations are shown in three graphs of Figure S6 in Appendix F. In graph A, only the errors for molalities larger than or equal to 2 mol·kg^{-1} are included up to 293.15 K because all relative errors up to this limiting value are very small. At the higher temperatures of graphs B and C, this threshold molality was set to 1 mol·kg^{-1}.

To make easier the comparison between the relative vapor pressure deviations in Figure S6 and the experimental errors, one should contrast these results with Figure S1 in Appendix A. In the two graphs of this figure, the corresponding relative deviations are presented for the experimental data introduced in Table 2 for the parameter estimation of b_2. Graph A in this figure shows the results from 293.15 to 323.15 K, and graph B shows the rest of the results. The agreement between the new osmotic coefficients and those obtained using the multiparameter equations[1,2] seems to be within experimental error up to the saturated solutions at least in the range from 273 to 353 K. As in the case for the activity coefficients at 363.15 K and especially at 373.15 K, the agreement is not as good. However, the solubility data at these temperatures strongly supports our model: As shown in Tables 3 and 4, the IUPAC solubility values of NaCl are 6.5818 mol·kg^{-1} at 363.15 K, and 6.6707 mol·kg^{-1} at 373.15 K, while the extended Hückel model predicts the values of 6.579 and 6.671 mol·kg^{-1}, respectively. Therefore, we believe that our new extended Hückel equations apply well up to the saturated solutions at all considered temperatures.

Besides the multiparameter results of Pitzer et al.[1] and Clarke and Glew,[2] we also compared our new nonideality values with the rest of the available literature data. Nine sources of data were included in our discussion: the values originating from vapor-pressure data by Gibbard et al.,[40] the text-book data from Harned and Owen[62] and from Robinson and Stokes,[63] our previous values,[14] and the values based on enthalpy data by Ensor and Anderson,[64] Messikomer and Wood,[65] and Mayrath and Wood.[66] We also included the values calculated mainly from boiling-point-elevation data by Smith[67] and Smith and Hirtle.[68] In the data by Wood et al.,[65,66] the osmotic coefficient deviation of $\phi(T) - \phi(T_{\mathrm{ref}})$ is reported as a function of the molality at various temperatures. Thus, the $\phi(T_{\mathrm{ref}})$ values need to be known to extract the real osmotic coefficients from these deviations. We employed our eq 2 at $T_{\mathrm{ref}} = 298.15$ K, to obtain these values for each molality.

Figures S7 and S8 in Appendix F compare our new nonideality values against the literature ones detailed in the preceding paragraph. The four graphs of Figure S7 show the activity-coefficient results, while the osmotic-coefficient results are in Figure S8. The temperature ranges of the graphs of these figures are provided in Appendix F. The results in Figure S7 support the new activity coefficients well except in the temperature range from 303.15 to 323.25 K in graph B and at 373.15 K in graph D. In Figure S8, the agreement is even better for the osmotic coefficients, and significant deviations are seen only in graph D at 373.15 K. On the basis of the experimental evidence supporting our model, we think that the new activity or osmotic coefficients are more reliable also in these slightly contradicting cases.

Recommended Activity and Osmotic Coefficients. The figures and tables in the present study demonstrate that our extended Hückel equation applies well to the experimental data for NaCl solutions at each temperature from 273 to 373 K and up to the saturated solution. Previously, traceable and transparent activity and osmotic coefficients were tabulated in refs 17 and 19 using eqs 1 and 2 with $b_2 = 0$ up to 0.2 mol·kg^{-1} in all these temperatures. We now continue these tables up to the saturated solutions in this temperature range. The activity coefficients of NaCl are given at rounded molalities up to 6.0 mol·kg^{-1} in Tables 6, 7, 8, and 9 between the limits of (273.15, 298.15) K, (303.15, 328.15) K, (333.15, 353.15) K, and (358.15, 373.15) K, respectively. Tables 10−13 give corresponding values for the osmotic coefficients of water.

For comparison with our previous highly accurate activity coefficient data, we have included in Tables 6−9 the activity coefficients at molality 0.2 mol·kg^{-1} from our previous tables for dilute solutions (see Tables 8−10 in ref 17 and Table 5 in ref 19). Analogous values are provided for the osmotic coefficients in Tables 10−13 (see Tables 11−13 in ref 17 and Table 6 in ref 19). The agreement between these values at 0.2 mol·kg^{-1} is consistently excellent. Consequently, the new extended-Hückel-equation model also applies to the molalities equal to or less than 0.2 mol·kg^{-1}, and the results are practically the same as those obtained in refs 17 and 19 with the simpler parametrization.

In one of our earlier studies, we reported activity and osmotic coefficients similar to those in Tables 6 and 10 from 273.15 to 298.15 K but based on a slightly different model (see Tables 8 and 10 in ref 16). For completeness, we represent these fully traceable values here in Tables S8 and S9 in Appendix H of the Supporting Information. The values obtained by the present method and those in Tables S8 and S9 for this molality range differ only slightly from each other. To emphasize that the differences remain small, we also report the galvanic cell deviation from eq 28 and the vapor pressure deviation from eq 29 at 1.0 mol·kg^{-1} in Tables S8 and S9, respectively. The absolute galvanic-cell deviations between the recommended activity coefficients and the values reported in Table S8 are all below 0.7 mV. The vapor-pressure deviations between the recommended osmotic coefficients and the values in Table S9 are below 1.2 Pa.

The influence of the accuracy of parameter values for the activity and osmotic coefficient up to a NaCl molality of 1 mol·kg^{-1} has been investigated in Tables 16 and 17 of ref 16, respectively, where the confidence intervals at the significance level of 0.95 are given for these quantities. Above that molality and the standard temperature of 298.15 K, the evaluation of the accuracy becomes challenging due to the lack of reliable high-accuracy data from which the experimental quantities can be extracted. Consequently, we report our recommended values for these quantities using three digits (i.e., within ±0.001), but the last digit at higher molalities and temperatures is probably not fully certain.

CONCLUSIONS

We have proposed three-parameter extended Hückel equations for the activity coefficient of sodium chloride and for the osmotic coefficient of water in aqueous NaCl solutions. The models and chemicals considered in this study are summarized in the chemical sample table of Table 14. Our extensive test calculations indicate that the new equations apply within experimental error to all available thermodynamic data up to the saturated molalities in the temperature range from 273.15 to 373.15 K. In addition to the terms of the Debye−Hückel model, our approach includes linear and quadratic terms with respect to the molality. The coefficients of these terms depend quadratically on the temperature, while the ion-size parameter of the Debye−Hückel model is constant. We have used our equations to tabulate recommended activity coefficients, osmotic coefficients, and vapor pressures for the more concentrated NaCl solutions from 273.15 to 373.15 K. These likely represent the most accurate values currently available in the literature.

Table 14. Chemical Compounds and Models

chemical name	chemical formula	CARN	model
water	H_2O	7732-18-5	eq 2[a]
sodium chloride	NaCl	7440-23-5	eq 1[a]

[a] For the osmotic coefficients of water and the activity coefficients of sodium chloride in aqueous NaCl solutions, we have presented three-parameter Hückel models of eqs 1 and 2. The quadratic temperature dependences of the parameters b_1 and b_2 in these equations are given in eqs 16 and 17, respectively. Parameter B does not depend on the temperature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.0c00402.

> Relative vapor pressure errors from the data used in the parameter estimation for the extended-Hückel-equation model recommended for NaCl solutions; osmotic coefficient errors obtained using the extended-Hückel-equation model recommended for NaCl solutions from the vapor pressure data of Gibbard et al.; results of the tests of the extended-Hückel-equation model recommended for NaCl solutions with the electrochemical data and with the solubility data; results of the tests of the Pitzer-equation model from Clarke and Glew for NaCl solutions with the solubility data; results of the comparison of the present activity and osmotic coefficients to those suggested in the literature for NaCl solutions; recommended value for the vapor pressure of aqueous NaCl solutions at various temperatures; our previously recommended traceable values for the activity and osmotic coefficients for aqueous NaCl solutions in the temperature range from 273.15 to 298.15 K (PDF)

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Pitzer, K. S.; Peiper, J. C.; Busey, R. H. Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data* **1984**, *13*, 1−102.

(2) Clarke, E. C. W.; Glew, D. N. Evaluation of the thermodynamic functions for aqueous sodium chloride from equilibrium and calorimetric measurements below 154 °C. *J. Phys. Chem. Ref. Data* **1985**, *14*, 489−610.

(3) Archer, D. G. Thermodynamic properties of the NaCl + H_2O system. II. Thermodynamic properties of NaCl(aq), $NaCl{\cdot}2H_2O$(cr), and phase equilibria. *J. Phys. Chem. Ref. Data* **1992**, *21*, 793−829.

(4) Chen, C.-C.; Britt, H. I.; Boston, J. F.; Evans, L. B. Local composition model for excess Gibbs energy of electrolyte systems. Part I. Single solvent, single completely dissociated electrolyte systems. *AIChE J.* **1982**, *28*, 588−596.

(5) Chen, C.-C.; Evans, L. B. A local composition model for the excess Gibbs energy of aqueous electrolyte systems. *AIChE J.* **1986**, *32*, 444−454.

(6) Papaiconomou, N.; Simonin, J.-P.; Bernard, O.; Kunz, W. MSA-NRTL model for the description of the thermodynamic properties of electrolyte solutions. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4435−4443.

(7) Cameretti, L. F.; Sadowski, G.; Mollerup, J. M. Modeling of aqueous electrolyte solutions with perturbed-chain statistical associated fluid theory. *Ind. Eng. Chem. Res.* **2005**, *44*, 3355−3362.

(8) Held, C.; Cameretti, L. F.; Sadowski, G. Modeling of aqueous electrolyte solutions. Part 1. Fully dissociated electrolytes. *Fluid Phase Equilib.* **2008**, *270*, 87−96.

(9) Wang, S.; Song, Y.; Chen, C.-C. Extension of COSMO-SAC solvation model for electrolytes. *Ind. Eng. Chem. Res.* **2011**, *50*, 176−187.

(10) Abbas, Z.; Ahlberg, E. Activity coefficients of concentrated salt solutions: A Monte Carlo investigation. *J. Solution Chem.* **2019**, *48*, 1222−1243.

(11) Mester, Z.; Panagiotopoulos, A. Z. Mean ionic activity coefficients in aqueous NaCl solutions from molecular dynamics simulations. *J. Chem. Phys.* **2015**, *142* (4), 044507.

(12) Mester, Z.; Panagiotopoulos, A. Z. Temperature-dependent solubilities and mean ionic activity coefficients of alkali halides in water from molecular dynamics simulations. *J. Chem. Phys.* **2015**, *143* (4), 044505.

(13) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **1973**, *77*, 268−277.

(14) Partanen, J. I.; Covington, A. K. Re-evaluation of the thermodynamic activity quantities in aqueous sodium and potassium chloride solutions at 25 °C. *J. Chem. Eng. Data* **2009**, *54*, 208−219.

(15) Rowland, D.; May, P. M. Thermodynamics of strong aqueous electrolyte solutions at t = 25 °C described by the Hückel equations. *J. Chem. Eng. Data* **2014**, *59*, 2030−2039.

(16) Partanen, J. I. Mean activity coefficients and osmotic coefficients in dilute aqueous sodium or potassium chloride solutions at temperatures from (0 to 70) °C. *J. Chem. Eng. Data* **2016**, *61*, 286−306.

(17) Partanen, J. I.; Partanen, L. J.; Vahteristo, K. P. Traceable thermodynamic quantities for dilute aqueous sodium chloride solutions at temperatures from (0 to 80) °C. Part 1. Activity coefficient, osmotic coefficient, and the quantities associated with the partial molar enthalpy. *J. Chem. Eng. Data* **2017**, *62*, 2617−2632.

(18) Partanen, J. I.; Partanen, L. J.; Vahteristo, K. P. Traceable thermodynamic quantities for dilute aqueous sodium chloride solutions at temperatures from (0 to 80) °C. Part 2. The quantities associated with the partial molar heat capacity. *J. Chem. Eng. Data* **2017**, *62*, 4215−4227.

(19) Partanen, J. I.; Partanen, L. J.; Vahteristo, K. P. Traceable thermodynamic quantities for dilute aqueous NaCl solutions at temperatures from (353.15 to 383.15) K and for dilute aqueous KCl solutions from (273.15 to 383.15) K. *J. Chem. Eng. Data* **2019**, *64*, 16−33.

(20) Partanen, J. I. Re-evaluation of the thermodynamic activity quantities in aqueous lithium chloride solutions at 25 °C up to a molality of 6.0 $mol{\cdot}kg^{-1}$. *J. Chem. Eng. Data* **2009**, *54*, 882−889.

(21) Partanen, J. I. Re-evaluation of the thermodynamic activity quantities in aqueous rubidium and cesium chloride solutions at 25 °C. *J. Chem. Eng. Data* **2010**, *55*, 249−257.

(22) Partanen, J. I. Re-evaluation of the thermodynamic activity quantities in aqueous solutions of silver nitrate, alkali metal fluorides and nitrites, and dihydrogen phosphate, dihydrogen arsenate, and thiocyanate salts with sodium and potassium ions at 25 °C. *J. Chem. Eng. Data* **2011**, *56*, 2044−2062.

(23) Partanen, J. I. Re-evaluation of the thermodynamic activity quantities in aqueous alkali metal bromide solutions at 25 °C. *J. Chem. Eng. Data* **2010**, *55*, 2202−2213.

(24) Partanen, J. I. Re-evaluation of the thermodynamic activity quantities in aqueous alkali metal iodide solutions at 25 °C. *J. Chem. Eng. Data* **2010**, *55*, 3708−3719.

(25) Partanen, J. I. Re-evaluation of the thermodynamic activity quantities in aqueous alkali metal nitrate solutions at T = 298.15 K. *J. Chem. Thermodyn.* **2010**, *42*, 1485−1493.

(26) Partanen, J. I.; Covington, A. K. Re-evaluation of the thermodynamic activity quantities in aqueous solutions of uni-univalent alkali metal salts of aliphatic carboxylic acids and thallium acetate at 25 °C. *J. Chem. Eng. Data* **2011**, *56*, 4524−4543.

(27) Partanen, J. I. Mean activity coefficients and osmotic coefficients in aqueous solutions of salts of ammonium ions with univalent anions at 25 °C. *J. Chem. Eng. Data* **2012**, *57*, 2654−2666.

(28) Partanen, J. I. Re-evaluation of the thermodynamic activity quantities in pure aqueous solutions of chlorate, perchlorate, and bromate salts of lithium, sodium or potassium ions at 298.15 K. *J. Solution Chem.* **2012**, *41*, 271−293.

(29) Partanen, J. I. Traceable mean activity coefficients and osmotic coefficients in aqueous calcium chloride solutions at 25 °C up to a molality of 3.0 $mol{\cdot}kg^{-1}$. *J. Chem. Eng. Data* **2012**, *57*, 3247−3257.

(30) Partanen, J. I.; Makkonen, E. K.; Vahteristo, K. P. Re-evaluation of activity coefficients in dilute aqueous hydrobromic and hydriodic acid solutions at temperatures from 0 to 60 °C. *J. Solution Chem.* **2013**, *42*, 190−210.

(31) Partanen, J. I. Traceable mean activity coefficients and osmotic coefficients in aqueous magnesium chloride solutions at T = 298.15 K up to a molality of 3.0 $mol{\cdot}kg^{-1}$. *J. Chem. Thermodyn.* **2013**, *66*, 65−70.

(32) Partanen, J. I. Re-evaluation of the mean activity coefficients of strontium chloride in dilute aqueous solutions from (10 to 60) °C and at 25 °C up to the saturated solution where the molality is 3.520 $mol{\cdot}kg^{-1}$. *J. Chem. Eng. Data* **2013**, *58*, 2738−2747.

(33) Partanen, J. I. Traceable mean activity coefficients of barium chloride in dilute aqueous solutions from (273 to 333) K and at T = 298.15 K up to the saturated solution where the molality is 1.7884 $mol{\cdot}kg^{-1}$. *J. Chem. Thermodyn.* **2014**, *75*, 128−135.

(34) Partanen, J. I. Traceable activity and osmotic coefficients in pure aqueous solutions of alkaline earth metal bromides and iodides at 25 °C. *J. Chem. Eng. Data* **2014**, *59*, 2530−2540.

(35) Partanen, J. I.; Juusola, P. M.; Vahteristo, K. P.; de Mendonça, A. J. G. Re-evaluation of the activity coefficients of aqueous hydrochloric acid solutions up to a molality of 16.0 mol·kg^{-1} using the Hückel and Pitzer equations at temperatures from 0 to 50 °C. *J. Solution Chem.* **2007**, *36*, 39−59.

(36) Partanen, J. I.; Partanen, L. J.; Vahteristo, K. P. Thermodynamically traceable calorimetric results for dilute aqueous potassium chloride solutions at temperatures from (273.15 to 373.15) K. Part 1. The quantities associated with the partial molar enthalpy. *J. Chem. Eng. Data* **2019**, *64*, 2519−2535.

(37) Partanen, J. I.; Partanen, L. J.; Vahteristo, K. P. Thermodynamically traceable calorimetric results for dilute aqueous potassium chloride solutions at temperatures from 273.15 to 373.15 K. Part 2. The quantities associated with the partial molar heat capacity. *J. Chem. Eng. Data* **2019**, *64*, 3971−3982.

(38) Archer, D. G.; Wang, P. The dielectric constant of water and Debye−Hückel limiting law slopes. *J. Phys. Chem. Ref. Data* **1990**, *19*, 371−411.

(39) Keyes, F. G.; Smith, L. B.; Gerry, H. T. The specific volume of steam in the saturated and superheated condition together with derived values of the enthalpy, entropy, heat capacity and Joule Thomson coefficients. Part IV. Steam research program. *Proc. Am. Acad. Arts Sci.* **1936**, *70*, 319−364.

(40) Gibbard, H. F., Jr.; Scatchard, G.; Rousseau, R. A.; Creek, J. L. Liquid-vapor equilibrium of aqueous sodium chloride, from 298 to 373 K and from 1 to 6 mol·kg^{-1}, and related properties. *J. Chem. Eng. Data* **1974**, *19*, 281−288.

(41) Kell, G. S. Density, thermal expansivity, and compressibility of liquid water from 0° to 150 °C: correlations and tables for atmospheric pressure and saturation reviewed and expressed on 1968 temperature scale. *J. Chem. Eng. Data* **1975**, *20*, 97−105.

(42) Olynyk, P.; Gordon, A. R. The vapor pressure of aqueous solutions of sodium chloride at 20, 25 and 30 °C for concentrations from 2 molal to saturation. *J. Am. Chem. Soc.* **1943**, *65*, 224−226.

(43) Platford, R. F. Osmotic coefficients of aqueous solutions of seven compounds at 0 °C. *J. Chem. Eng. Data* **1973**, *18*, 215−217.

(44) Stokes, R. H. Osmotic coefficients of concentrated aqueous urea solutions from fzeezing-point measurements. *J. Phys. Chem.* **1966**, *70*, 1199−1203.

(45) Childs, C. W.; Platford, R. F. Excess free energies of mixing at temperatures below 25°. Isopiestic measurements on the systems H_2O-NaCl-Na_2SO_4 and H_2O-NaCl-$MgSO_4$. *Aust. J. Chem.* **1971**, *24*, 2487−2491.

(46) Stokes, R. H. Thermodynamics of aqueous urea solutions. *Aust. J. Chem.* **1967**, *20*, 2087−2100.

(47) Harned, H. S.; Nims, L. F. The thermodynamic properties of aqueous sodium chloride solutions from 0 to 40°. *J. Am. Chem. Soc.* **1932**, *54*, 423−432.

(48) Mussini, T.; Maina, A.; Pagella, A. Standard potentials of sodium amalgam electrode at various temperatures, with related thermodynamic functions. *J. Chem. Thermodyn.* **1971**, 3, 281−288.

(49) Cohen-Adad, R., Lorimer, J. W. Eds. *Alkali metal and ammonium chlorides in water and heavy water (binary systems). 2. Sodium chloride*; Solubility Data Series 47; International Union of Pure and Applied Chemistry; Pergamon Press, 1991; pp 64−209.

(50) Archer, D. G. Thermodynamic properties of the NaCl + H_2O system. I. Thermodynamic properties of NaCl(cr). *J. Phys. Chem. Ref. Data* **1992**, *21*, 1−21.

(51) Criss, C. M.; Cobble, J. W. The thermodynamic properties of high temperature aqueous solutions. I. Standard partial molal heat capacities of sodium chloride and barium chloride from 0 to 100 °. *J. Am. Chem. Soc.* **1961**, *83*, 3223−3228.

(52) Hubert, N.; Solimando, R.; Pere, A.; Schuffenecker, L. Dissolution enthalpy of NaCl in water at 25 °C, 45 and 60 °C. Determination of Pitzer's parameters of the {H_2O−NaCl} system and the molar dissolution enthalpy at infinite dilution of NaCl in water between 25 and 100 °C. *Thermochim. Acta* **1997**, *294*, 157−163.

(53) Pinho, S. P.; Macedo, E. A. Solubility of NaCl, NaBr, and KCl in water, methanol, ethanol, and their mixed solvents. *J. Chem. Eng. Data* **2005**, *50*, 29−32.

(54) Küpper, A. Sistema reciproco. Agua - cloruro de sodio - sulfato de magnesio − cloruro de magnesio - sulfato de sodio. *Caliche* **1927**, *8*, 467−487.

(55) Flöttmann, Fr. Über Löslichkeitsgleichgewichte. *Anal. Bioanal. Chem.* **1928**, *73*, 1−39.

(56) Chrétien, A. Etude du systeme quaternaire. Eau, nitrate de sodium, chlorure de sodium, sulfate de sodium. *Ann. Chem. (Paris)* **1929**, *12*, 9−155.

(57) Cornec, E.; Krombach, H. Equilibres entre le chlorure de potassium, le chlorure de sodium et l'eau depuis − 23° jusqu'a + 190°. *Ann. Chem. (Paris)* **1932**, *18*, 5−31.

(58) Osokoreva, N. A.; Opikhtina, M. A.; Shioket, A. N.; Plaksina, E. F.; Zaslavskii, A. I.; Kurnakova, N. S.; Manoeva, D. P. Soljanye ravnovesija v sisteme NaCl−KCl−$MgCl_2$−H_2O. *Tr. Gos. Inst. Prikl. Khim.* **1932**, *16*, 24−47.

(59) Jarlykoff, M. M. Der Gleichgewichtszustand der Löslichkeit der Systeme KCl−H_2O−NH_4Cl und NaCl−H_2O−NH_4Cl. *Zhur. Prikl. Khim. (Leningrad)* **1935**, *7*, 902−905.

(60) Nallet, A.; Paris, R. A. Etude des equilibres de solubilite dans l'eau des chlorures et chlorates de sodium et de potassium. *Bull. Soc. Chem. F.* **1955**, *94*, 488−497.

(61) Potter, R. W., II; Clynne, M. A. Solubility of highly soluble salts in aqueous media. Part 1. NaCl, KCl, $CaCl_2$, Na_2SO_4, and K_2SO_4 solubilities to 100 °C. *J. Res. U. S. Geol. Surv.* **1978**, *6*, 701−705.

(62) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, 3rd ed.; Reinhold Publishing Corporation: New York, 1958; p 726.

(63) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths Scientific Publications: London, 1959; p 476.

(64) Ensor, D. D.; Anderson, H. L. Heats of dilution of NaCl: temperature dependence. *J. Chem. Eng. Data* **1973**, *18*, 205−212.

(65) Messikomer, E. E.; Wood, R. H. The enthalpy of dilution of aqueous sodium chloride at 298.15 to 373.15 K, measured with a flow calorimeter. *J. Chem. Thermodyn.* **1975**, *7*, 119−130.

(66) Mayrath, J. E.; Wood, R. H. Enthalpy of dilution of aqueous sodium chloride at 348.15 to 472.95 K measured with a flow calorimeter. *J. Chem. Thermodyn.* **1982**, *14*, 15−26.

(67) Smith, R. P. The boiling point elevation. II. Sodium chloride 0.05 to 1.0 M and 60 to 100°. *J. Am. Chem. Soc.* **1939**, *61*, 500−503.

(68) Smith, R. P.; Hirtle, D. S. The boiling point elevation. III. Sodium chloride 1.0 to 4.0 M and 60 to 100 °C. *J. Am. Chem. Soc.* **1939**, *61*, 1123−1126.