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Isopiestic Investigation of the Osmotic and Activity Coefficients of Aqueous NaBr and the Solubility of $NaBr{\cdot}2H_2O(cr)$ at 298.15 K: Thermodynamic Properties of the NaBr + H_2O System over Wide Ranges of Temperature and Pressure

Joseph A. Rard*

Earth Sciences Division, Environmental Programs Directorate, Lawrence Livermore National Laboratory,
University of California, Livermore, California 94550

Donald G. Archer

Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology,
Gaithersburg, Maryland 20899

Isopiestic vapor-pressure measurements have been performed for aqueous solutions of well-characterized high-purity NaBr from 1.9551 to 9.4778 $mol{\cdot}kg^{-1}$ at 298.15 K; the highest five molalities correspond to supersaturated concentrations. Solubilities have also been determined by this method. A few equilibrations were made between solutions of NaCl and H_2SO_4 to refine the osmotic coefficients of H_2SO_4 at high molalities. These isopiestic results for NaBr have been combined with other experimental thermodynamic quantities (vapor pressures, activity coefficients, solubilities, freezing temperatures, and volumetric and calorimetric measurements) to yield revised parameters for an extended form of Pitzer's equation applicable over wide ranges of molality, temperature, and pressure. It was not possible to obtain a complete consistency between the experimental results for either the NaBr + H_2O system or the NaCl + H_2O system with entropies from the *CODATA Key Values for Thermodynamics.*

Introduction

Archer (*1*) has published a comprehensive critical evaluation of the thermodynamic properties of aqueous NaBr solutions and of NaBr(cr) and $NaBr{\cdot}2H_2O(cr)$ over the entire experimental temperature and pressure ranges. The solution properties examined by him were mean molal activity coefficients, vapor pressures (both isopiestic and direct pressure measurements), enthalpies of dilution, heat capacities, densities, adiabatic compressibilities, and solubilities, and for the solid phases enthalpies of solution, heat capacities, and entropy, and the decomposition pressures of $NaBr{\cdot}2H_2O(cr)$. Archer was able to represent accurately these thermodynamic properties with a pressure- and temperature-dependent version of Pitzer's equations (*2*), provided the third virial coefficient was assigned an ionic strength dependence similar to that normally used for the second virial coefficient. The approximate temperature and pressure ranges of validity of the parameters reported by Archer for solution properties are, respectively, 260–600 K and from the vapor pressures of the solutions to 150 MPa.

Although much of the thermodynamic data for aqueous NaBr and solid NaBr and $NaBr{\cdot}2H_2O$ are thermodynamically consistent, some individual data sets and some of the individual properties were found by Archer to be quite incompatible (*1*). In particular, he noted the existence of an inconsistency among standard thermodynamic values given in the *NBS Tables* (*3*), the available solubilities and enthalpies of solution of NaBr(cr), and the *CODATA Key Values for Thermodynamics* (*4*). One part of this problem is obvious from the nearly 5-fold variation of −0.22 to −1.026 $kJ{\cdot}mol^{-1}$ in the reported standard enthalpies of solution of NaBr(cr) at 298.15 K and 0.1 MPa, as can be seen in his Table 6 (*1*). Archer explained this variation as most probably due to those enthalpies of solution actually being measured for partially hydrated samples with variable water content, rather than for truly anhydrous samples of NaBr.

Archer (*1*) also commented on an alternative possibility of "... substantial [systematic] errors in the isopiestic molality determinations for 298.15 K, 0.1 MPa and molalities greater than 4 $mol{\cdot}kg^{-1}$." Indeed, his plots of the residuals of the experimental osmotic coefficients at 298.15 K from his least-squares equation show considerable variation between the different studies even after the obviously erroneous vapor pressure measurements of Pearce *et al.* (*5*) are eliminated. Different sets of isopiestic data at these high molalities show discrepancies of from 0.01 to more than 0.02 in the osmotic coefficients, or 0.8–1.7%. Rard and Platford (*6*) noted that for very favorable systems osmotic coefficients from different isopiestic studies can agree to 0.2–0.3% or better.

Inasmuch as the published isopiestic data show variations 4–6 times larger than the accuracy this method is capable of, and because of inconsistencies between some sets of thermodynamic data as noted above, vapor pressures were measured by the isopiestic method for aqueous NaBr solutions at 298.15 K. These new measurements extend into the supersaturated molality region, for which there are no previous results.

Experimental Section

Preparation of Stock Solutions and Impurity Analyses. Stock solutions of aqueous NaBr, NaCl, $CaCl_2$, and H_2SO_4 were prepared for the experiments as described below, where the last three were used as isopiestic reference standards. Water for these solutions was tap water that had been purified first by ion exchange and then by distillation.

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A concentrated stock solution of NaBr was prepared by dissolving Aldrich "99.99$^+$%" NaBr (lot number 12730JX) in purified water. This percentage is presumably mass percent. Dissolution of the anhydrous NaBr was fairly slow since it was supplied in the form of hard lumps. The resulting solution had a slight milky appearance and exhibited a distinct Tyndall cone. It was filtered with a (prewashed) Nalgene 0.2 μm polycarbonate membrane filtering unit to yield a clear colorless solution with no Tyndall cone. No attempt was made to purify the NaBr by recrystallization, since, as emphasized by Archer (*1*), this enriches the chloride content. The impurity content of this NaBr as reported by the supplier is 20 ppm Li, 10 ppm Mg, and 2 ppm Al, presumably in ppm by mass. No analysis was reported for the chloride content, which is the most common anionic impurity in bromide salts.

This NaBr was analyzed for impurities at Livermore using direct current arc optical emission spectroscopy (DCAOES) for cations and ion chromatography (IC) for anions. Impurities detected by DCAOES, in mass fractions, are 3×10^{-4} K, 1×10^{-5} each of Mg, Al, and Li, 1×10^{-6} Ca, $\leq 3 \times 10^{-6}$ Si, and $\leq 1 \times 10^{-6}$ Cu; the chloride mass fraction from IC is 1.9×10^{-4}. The cationic impurity present in largest amount was potassium, which was also not reported by the supplier. Using the IUPAC recommended "1989" atomic masses for these elements (*7*) and the observed impurity concentrations indicates the Aldrich "99.99$^+$%" NaBr is essentially equivalent to a mixture of 99.866 mol % NaBr, 0.055 mol % NaCl, and 0.079 mol % KBr, with an effective molar mass of 102.882 g·mol^{-1}.

The NaCl stock solution had been prepared by mass from oven-dried "Baker Analyzed" NaCl and purified water. The $CaCl_2$ stock solution is identical to stock solution no. 2 described previously (*8*), and the H_2SO_4 stock solution is identical to the one used for isopiestic measurements for aqueous Na_2SO_4 + H_2SO_4 mixtures at high H_2SO_4 mole fractions (*9*).

A sample of this NaCl stock solution was analyzed for impurities at Livermore using IC for fluoride and sulfate ions, and inductively-coupled plasma atomic emission spectroscopy (ICPAES) and inductively-coupled plasma mass spectrometry (ICPMS) for cations and other anions. This solution was thus found to contain (in grams of impurity per liter of solution) 5.5×10^{-3} F and 4.3×10^{-2} SO_4^{2-} by IC; 1.1×10^{-4} Sr and 3×10^{-5} Li by ICPMS; and 2×10^{-3} Ca, 3×10^{-4} Mg, 2×10^{-3} Si, 6×10^{-3} S, and 3.4×10^{-2} K by ICPAES. Other impurities such as Al, Fe, Br, NO_3^-, NO_2^-, and HPO_4^{2-} were not detected. Even after adjustment for the mass differences between sulfur reported as S in the ICPAES analysis and reported as SO_4^{2-} in the IC analysis, the IC value is slightly more than twice as large. Having no reason to prefer one result over the other, the average of the sulfur analyses was used in subsequent calculations.

These impurity concentrations (g·L^{-1}) were converted into a "dry mass" basis of grams of impurity per gram of total dry solid by using the mass fraction of salt in the stock solution from dehydration analysis and the experimental solution density as given below. The concentration of potassium found is about a factor of 4 larger than reported by the supplier, and that of sulfur is more than 30 times larger. These impurity concentrations indicate that the "Baker Analyzed" NaCl is essentially equivalent to (not counting water) a mixture of 99.9415 mol % NaCl, 0.0316 mol % KCl, 0.0105 mol % NaF, 0.0115 mol % Na_2SO_4, and 0.005 mol % other impurities, with an effective molar mass of 58.456_6 g·mol^{-1}. The alkali metal halides comprise 72 mol % of the total impurities.

The $CaCl_2$ stock solution was prepared from Mallinckrodt Primary Standard $CaCO_3$ (lot number DKH) and aqueous HCl; impurity concentrations for this $CaCO_3$ as reported by the supplier are 0.005% Ba, 0.001% heavy metals (reported as Pb), 0.001% each of Fe and SiO_2, 0.01% each of Mg and K, 0.0026% Na, 0.1% Sr, 0.005% SO_4^{2-}, and 0.0015% F. A sample of the $CaCO_3$ was analyzed by DCAOES at Livermore and found to contain actually (in mass fractions) 5×10^{-4} Sr, 1×10^{-4} Ba, 3×10^{-5} each of Na, Fe, and Mg, 2×10^{-5} each of Si, Al, and Mn, and 1×10^{-6} each of Li and Cu. Twenty-four other elements were examined for but not found. The "$CaCl_2$" was thus 99.885 mol % $CaCl_2$, 0.057 mol % $SrCl_2$, 0.013 mol % NaCl, 0.012 mol % $MgCl_2$, 0.007 mol % each of $BaCl_2$, SiO_2, and, $AlCl_3$, and 0.012 mol % other impurities. Since the $CaCl_2$ is fairly pure, and because 2/3 of the impurities are the chemically similar alkaline-earth-metal chlorides, its isopiestic behavior should be nearly identical to that of pure $CaCl_2$.

Molality Analyses of Stock Solutions. The molality of the $CaCl_2$ stock solution was determined gravimetrically by conversion of samples to anhydrous $CaSO_4$, and two separate analyses were in excellent agreement. For the H_2SO_4 stock solution, the molality analysis was done by using mass titration of four samples with a standardized NaOH solution and with phenolphthalein as indicator. More detailed descriptions of the methods and results for these two stock solutions can be found in earlier papers (*8, 9*).

Analysis of the NaCl stock solution was done by evaporation of three samples to dryness on a hot plate, followed by further drying of these samples in a furnace at 773 K. Dehydration at 773 K was found to be optimum for achieving essentially complete drying of NaCl. On the basis of test experiments with stock solutions prepared from vacuum-fused NaCl and water, systematic errors in the calculated molality from neglect of residual moisture are $\leq 0.01\%$ at this temperature. Lower temperatures than 773 K do not yield completely anhydrous material (e.g., 0.10–0.16 mass % residual moisture for samples dried at 473 K). Drying temperatures of 823 K and above (in the presence of air) gave a slow mass decrease with time, presumably from decomposition of the NaCl by loss of chloride. Samples of NaCl heated at 773 K sometimes show a very slight mass decrease with time, in which case masses obtained after 1 d of heating give the most reliable results.

Dehydration analysis of the NaCl stock solution yielded a molality of 2.9243 ± 0.0008 mol·kg^{-1} using the effective molar mass of 58.456_6 g·mol^{-1}. Here and elsewhere the uncertainty limits are 1 σ_{n-1} standard deviation.

As a check on the dehydration results, the density of the NaCl stock solution was measured at 298.15 ± 0.005 K and that value was used for back-calculation of the molality. The experimental density of 1.10348 g·cm^{-3} was determined using a 30.865 cm^3 single-stem pycnometer, based upon an assumed water density of 0.997 045 g·cm^{-3}. This experimental density is uncertain by about 3×10^{-5} g·cm^{-3}. By using the equations given by Archer (*10*), the molality of the NaCl stock solution was calculated to be 2.9297 mol·kg^{-1}, with an uncertainty of about 0.2%. Although this value is 0.185% above the values obtained from the dehydration analyses, it does agree within experimental error. The stock molality calculated from the density equation was expected to be slightly high because inadequate drying of NaCl was done in some of the density studies.

Dehydration of triplicate samples was also used for determination of the NaBr stock solution molality, and

Table 1. Dehydration Results for Analysis of NaBr Stock Solution

T/K[a]	$m(T)$[b]/(mol·kg^{-1})	ln{$m(T)/m°$}	T/K[a]	$m(T)$[b]/(mol·kg^{-1})	ln{$m(T)/m°$}
473.15	$6.6696_3 \pm 0.0010_3$	1.8975_6	623.15	$6.6662_7 \pm 0.0015_3$	1.8970_6
523.15	$6.6677_4 \pm 0.0011_8$	1.8972_8	673.15	decreasing	
573.15	$6.6669_5 \pm 0.0009_6$	1.8971_6			

[a] Temperature of furnace used for dehydration analysis. Although the two figures past the decimal point are not significant, they were obtained from conversion of the Celsius temperatures to kelvin and were retained for least-squares fits. [b] Value of the apparent molality calculated by assuming the residues from evaporation of stock solution samples were anhydrous NaBr. These are the molalities that would be calculated if the presence of residual moisture was not known or was neglected. The reported values are the average molalities and standard deviations (σ_{n-1}) from the mean for four to six weighings at each temperature.

again the calculated molality varied slightly with dehydration temperature due to progressive loss of small amounts of water still present in the solid phase. These samples were weighed on four to six separate days at each temperature, and no decrease in mass was observed with time for any temperature from 473 to 623 K. The calculated molality was thus independent of the duration of heating in this temperature region, and depended only on temperature. These molalities also seem to approach a limiting value at the higher temperatures as more of the residual moisture is driven off. However, heating the residues to 673 K or higher resulted in a steady decrease of their masses with time at constant temperature, apparently due to partial decomposition with loss of bromide. The rate of decrease in the calculated (apparent) molality was about 0.0005 mol·kg^{-1}·d^{-1} at 673 K and 0.0022 mol·kg^{-1}·d^{-1} at 773 K.

This interpretation of the gradual loss of mass with time as being due to loss of bromide is consistent with the observation of Jervis *et al.* (*11*): "Any procedure which yields the dihydrate, *e.g.*, recrystallization from aqueous solution, will in our experience yield on heating a slightly basic product even if heating takes place in an atmosphere of HBr."

Table 1 contains the calculated apparent molalities of the NaBr stock solution as a function of the dehydration temperature, and Figure 1 is a plot of these results. The apparent molality is essentially an exponential function of some power of the temperature up to 623 K. That is,

$$m(T) = m_0 \exp\{-Af(T)\} \tag{1}$$

where m_0 is the limiting value of the molality at high temperatures (i.e., the molality obtained if the solid phase were actually completely anhydrous NaBr) and $f(T)$ is some function of the absolute temperature T. The logarithmic equivalent of this equation is

$$\ln\{m(T)/m°\} = \ln\{m_0/m°\} - Af(T) \tag{2}$$

where $m°$ denotes the unit molality of 1 mol·kg^{-1}.

Test calculations with functions of the type $f(T) = T^x$ with $x > 0$ gave poor quality fits, whereas fits with $x \leq -1$ were of much better quality. A series of least-squares fits were performed with $x = -1.0, -1.5, ..., -6.5$, and -7.0. The optimum representation occurred with $x = -5.5$, $m_0 = 6.6653_8$ mol·kg^{-1}, $A = 3.25293 \times 10^{11}$ K$^{5.5}$, and a correlation coefficient of 0.99888. This function $T^{-5.5}$ is used as the abscissa in the lower plot of Figure 1. However, all fits with $x = -2.5$ through -7.0 had correlation coefficients of 0.99 or greater, and their corresponding values of m_0 were averaged to yield the recommended value of $m_0 = 6.6647_7 \pm 0.0009_9$ mol·kg^{-1} for the molality of the NaBr stock solution.

The above results indicate that if dehydration analysis is used to determine the molality of a NaBr solution, then 623 K is the "best" temperature for drying. However, the calculated molality will be about 0.02–0.03% too high from residual moisture. If greater accuracy is required, then the procedure in the preceding paragraphs can be used.

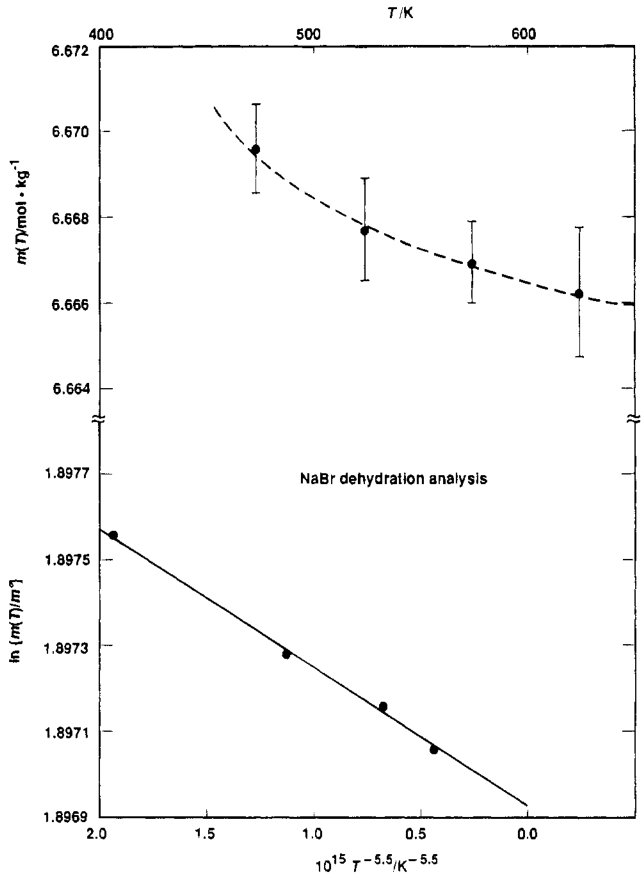

Figure 1. Variation of the apparent molality of the NaBr stock solution with the temperature T used for the dehydration analysis: (top curve) plot of $m(T)$ as a function of the furnace temperature; the curve connecting the points is merely to illustrate the general trend; (bottom curve) plot of ln{$m(T)/m°$} as a function of $T^{-5.5}$; the curve connecting the points is the corresponding least-squares curve.

To check this molality of NaBr, the stock solution density was measured at 298.15 ± 0.005 K and that value was used for back-calculation of the molality. The observed density is 1.41989 ± 0.00003 g·cm^{-3} for duplicate measurements using two separate single-stem pycnometers. By using the equations given by Archer (*1*), the NaBr stock solution molality was calculated to be 6.6638 ± 0.0014 mol·kg^{-1}. The stock solution molality used in subsequent calculations, $6.6644_5 \pm 0.0008_1$ mol·kg^{-1}, is the statistically-weighted average of this density-based value with the dehydration result from two paragraphs above.

Two further but unsuccessful attempts were made to analyze the molality of the NaBr stock solution. In the first attempt samples were evaporated to dryness two separate times with an excess of concentrated HCl to displace bromide, but the conversion was incomplete and varied from sample to sample. In the second attempt, nitric acid was used to oxidize the bromide ions to bromine, which was than evaporated away by heating. When an attempt was made to decompose the nitrate ions thermally, the resulting sodium oxide/hydroxide reacted chemically with the porcelain crucibles and some of it sublimed out of the crucibles.

Isopiestic Measurements. Isopiestic measurements were performed at 298.15 ± 0.005 K (IPTS-68) in the same stainless steel isopiestic chambers described elsewhere *(12)*, using sample cups of tantalum metal. Corrosion tests were performed prior to these experiments, in which concentrated solutions and, in some cases, wet crystals of various bromide salts were placed in a spare sample cup or on a slab of tantalum metal for several months. In only a single instance was corrosion observed; this involved a saturated solution and crystals of potassium bromide in the presence of air. Corrosion was obvious because the KBr solution and crystals turned from colorless to orange-brown. Tantalum metal is quite resistant to corrosion by the great majority of aqueous electrolytes because of an inert and self-healing surface coating of Ta_2O_5.

Isopiestic experiments were done in the standard manner *(6)* with all weights being converted to masses. Above about 3.6 mol·kg^{-1} in NaBr, equilibrium periods were generally 6−8 d with a few being longer. Below that molality the equilibration periods were gradually increased, reaching a maximum of about 5 weeks by the lowest molalities. Aqueous NaCl was used as the reference standard at lower molalities, and H_2SO_4 and $CaCl_2$ were used at higher molalities.

After every experiment the NaBr solutions were carefully examined, and in no case was there a color change indicative of corrosion. A number of equilibrations were performed with each set of samples. In general, for experiments with aqueous NaCl as the reference standard, these samples were diluted during the subsequent equilibrations. In contrast, for experiments with aqueous H_2SO_4 and $CaCl_2$ as reference standards, the concentrations were generally increased during subsequent equilibrations. However, in four of the five series of experiments, the general direction of molality changes was reversed once or twice, and results after these changes agreed well with previous measurements for those same samples. That is, significant hysteresis was absent from the isopiestic molality ratios.

As further checks, the samples of NaBr were periodically replaced with fresh ones and experiments were done in which the equilibrium molalities for the new samples overlapped those for the previous samples. In no case was there a shift in the isopiestic molality ratios that would indicate chemical reactions or sample decomposition. We therefore conclude that there is no error in the isopiestic molality ratios from these sources.

Tables 2 and 3 contain the experimental isopiestic molalities. The experiments were done with two samples of each electrolyte, and in all but two cases the reported results are average molalities and average deviations from the mean values. In the majority of experiments the average deviations were less than 0.05% of the molality and were usually only a few hundredths of a percent. In only one experiment did the average deviation exceed 0.1% for one of the electrolytes.

Table 2. Isopiestic Molalities of Aqueous NaBr with NaCl Reference Standards and Osmotic Coefficients of NaBr at 298.15 K

m(NaCl)/(mol·kg^{-1})	m(NaBr)/(mol·kg^{-1})	ϕ*(NaCl)[a]	ϕ(NaBr)
Series 1[b]			
5.7045 ± 0.0002[c]	5.3647 ± 0.0018[c]	1.2461	1.3250
6.0686 ± 0.0012	5.6946 ± 0.0006	1.2749	1.3586
5.9135 ± 0.0018	5.5546 ± 0.0020	1.2626	1.3442
5.6256 ± 0.0014	5.2890 ± 0.0002	1.2400	1.3189
5.5695 ± 0.0000	5.2376 ± 0.0020	1.2356	1.3139
5.4043 ± 0.0003	5.0874 ± 0.0015	1.2228	1.2990
5.2432 ± 0.0003	4.9374 ± 0.0008	1.2103	1.2853
5.0954 ± 0.0010	4.8040 ± 0.0001	1.1990	1.2717
5.1261 ± 0.0008	4.8321 ± 0.0000	1.2014	1.2745
4.9250 ± 0.0005	4.6459 ± 0.0009	1.1861	1.2574
4.7747 ± 0.0002	4.5069 ± 0.0003	1.1747	1.2445
5.0603 ± 0.0004	4.7704 ± 0.0002	1.1963	1.2690
Series 2			
4.9581 ± 0.0006	4.6753 ± 0.0032	1.1886	1.2605
4.6688 ± 0.0019	4.4033 ± 0.0018	1.1668	1.2372
4.5577 ± 0.0008	4.3035 ± 0.0008	1.1585	1.2269
4.3445 ± 0.0023	4.1070 ± 0.0006	1.1427	1.2088
4.2083 ± 0.0016	3.9801 ± 0.0008	1.1328	1.1977
4.0367 ± 0.0014	3.8205 ± 0.0030	1.1204	1.1838
3.8688 ± 0.0018	3.6656 ± 0.0005	1.1083	1.1697
3.7398 ± 0.0026	3.5426 ± 0.0007	1.0992	1.1604
3.5861 ± 0.0024	3.4008 ± 0.0002	1.0884	1.1477
3.8653 ± 0.0002	3.6606 ± 0.0020	1.1081	1.1701
3.4110 ± 0.0007	3.2410 ± 0.0000	1.0763	1.1328
3.2780 ± 0.0014	3.1170 ± 0.0009	1.0673	1.1224
Series 3			
3.3617 ± 0.0003	3.1985 ± 0.0012	1.0730	1.1277
3.2327 ± 0.0023	3.0773 ± 0.0024	1.0642	1.1179
3.0828 ± 0.0019	2.9384 ± 0.0016	1.0541	1.1059
2.9221 ± 0.0003	2.7890 ± 0.0006	1.0435	1.0933
2.5027 ± 0.0002	2.3978 ± 0.0008	1.0168	1.0613
2.2055 ± 0.0012	2.1183 ± 0.0007	0.9988	1.0399
2.0285 ± 0.0011	1.9551 ± 0.0021	0.9885	1.0256

[a] Osmotic coefficients of the NaCl reference standard solutions were calculated from the equation of Archer *(10)*. [b] The same samples of NaCl were used for all three series of experiments, but fresh samples of NaBr were weighed for each series. [c] Reported values are the average molalities from duplicate samples, along with the average deviation from the mean. Results are reported (from top to bottom in this table) in the actual order that they were measured.

Experiments were continued into the supersaturated molality region until spontaneous crystallization occurred in the NaBr solutions, but it was only possible to go about 0.3 mol·kg^{-1} above saturation. Crystallization occurred in one of the samples during one supersaturated solution experiment, so the reported molality of NaBr is for a single sample.

The isopiestic chambers were degassed with a vacuum pump prior to starting each equilibration, since this increases the rate at which isopiestic equilibrium is reached *(6)*. However, we had one incident in which water leaked into the vacuum line; this caused incomplete degassing and a slight loss in accuracy for the experiment with a NaBr molality of 6.6711 mol·kg^{-1}. Because the isopiestic molality ratios of NaBr to reference standards still agreed to within 0.2% of those for the other experiments, that experiment was retained in the table but was given no weight in the least-squares treatment.

Crystals of $NaBr \cdot 2H_2O$ for the solubility experiments were grown by evaporating a sample of the stock solution in a desiccator until crystallization occurred. The resulting crystals were small, colorless, and transparent. They were aged for over a month at room temperature before the solubility experiments were started, to allow for crystal growth.

Solubilities were determined with the isopiestic method as described earlier *(12)*. Five equilibrations were done with different equilibration periods. Values are given in Table 3 and vary from 9.1701 ± 0.0018 to 9.1907 ± 0.0004 mol·kg^{-1}. This variation of 0.22% between the solubility values is larger than usual for the isopiestic method *(12)*,

Table 3. Isopiestic Molalities of Aqueous NaBr with H_2SO_4 and $CaCl_2$ Reference Standards, Osmotic Coefficients of NaBr, and Intercomparison of Isopiestic Reference Standards at 298.15 K

$m(H_2SO_4)/(mol{\cdot}kg^{-1})$	$m(CaCl_2)/(mol{\cdot}kg^{-1})$	$m(NaBr)/(mol{\cdot}kg^{-1})$	$\phi^*(H_2SO_4)$[a]	$\phi(NaBr)$
		Series 4[b]		
4.1025 ± 0.0015[c]	2.8172 ± 0.0003[c]	5.3866 ± 0.0005[c]	1.1652	1.3311
4.1923 ± 0.0018	2.8744 ± 0.0002	5.5207 ± 0.0002	1.1795	1.3435
4.2815 ± 0.0013	2.9312 ± 0.0003	5.6520 ± 0.0001	1.1936	1.3563
4.3719 ± 0.0008	2.9884 ± 0.0002	5.7865 ± 0.0002	1.2079	1.3689
4.4601 ± 0.0004	3.0438 ± 0.0002	5.9161 ± 0.0004	1.2218	1.3817
4.5881 ± 0.0010	3.1238 ± 0.0004	6.1073 ± 0.0015	1.2418	1.3994
4.6729 ± 0.0017	3.1773 ± 0.0001	6.2353 ± 0.0014	1.2549	1.4107
4.7733 ± 0.0004	3.2395 ± 0.0001	6.3837 ± 0.0023	1.2704	1.4249
4.8727 ± 0.0011	3.3014 ± 0.0001	6.5334 ± 0.0013	1.2856	1.4382
4.9781 ± 0.0011	3.3660 ± 0.0004	6.6897 ± 0.0014	1.3014	1.4526
5.0630 ± 0.0017	3.4184 ± 0.0007	6.8159 ± 0.0009	1.3141	1.4642
4.9698 ± 0.0014	3.3604 ± 0.0002	6.6711 ± 0.0007	1.3002	1.4529
		Series 5		
5.1212 ± 0.0013	3.4548 ± 0.0001	6.9045 ± 0.0005	1.3227	1.4716
5.0082 ± 0.0021	3.3862 ± 0.0001	6.7357 ± 0.0017	1.3060	1.4566
5.1807 ± 0.0010	3.4927 ± 0.0001	6.9951 ± 0.0006	1.3314	1.4791
5.3156 ± 0.0015	3.5746 ± 0.0003	7.1975 ± 0.0006	1.3509	1.4965
5.4521 ± 0.0015	3.6582 ± 0.0001	7.4061 ± 0.0002	1.3703	1.5131
5.5507 ± 0.0015	3.7168 ± 0.0011	7.5495 ± 0.0002	1.3840	1.5264
5.6692 ± 0.0012	3.7888 ± 0.0002	7.7315 ± 0.0009	1.4002	1.5401
5.7946 ± 0.0014	3.8643 ± 0.0001	7.9223 ± 0.0006	1.4170	1.5547
5.9061 ± 0.0021	3.9305 ± 0.0004	8.0927 ± 0.0013	1.4317	1.5673
5.9961 ± 0.0024	3.9842 ± 0.0002	8.2290 ± 0.0011	1.4432	1.5774
6.0940 ± 0.0016	4.0433 ± 0.0004	8.3856 ± 0.0007	1.4568_5	1.5881
6.1959 ± 0.0029	4.1029 ± 0.0002	8.5361 ± 0.0018	1.4706	1.6012
6.3410 ± 0.0039	4.1874 ± 0.0001	8.7605 ± 0.0010	1.4901	1.6178
6.4453 ± 0.0029	4.2497 ± 0.0006	8.9211 ± 0.0025	1.5039	1.6298
6.5499 ± 0.0032	4.3111 ± 0.0000	9.0857 ± 0.0006	1.5176	1.6411
6.6657 ± 0.0018	4.3787 ± 0.0005	9.2643 ± 0.0007	1.5326	1.6541
6.7204 ± 0.0021	4.4110 ± 0.0005	9.3530 ± 0.0007	1.5396	1.6594
6.8014 ± 0.0033	4.4579 ± 0.0005	9.4778 ± 0.0029	1.5499	1.6684
6.6066 ± 0.0037	4.3439 ± 0.0004	9.1701 ± 0.0018[d]	1.5250	1.6480
6.6142 ± 0.0030	4.3495 ± 0.0007	9.1867 ± 0.0005[e]	1.5259_5	1.6480
6.6105 ± 0.0028	4.3479 ± 0.0000	9.1796 ± 0.0015[f]	1.5255	1.6478
6.6167 ± 0.0026	4.3509 ± 0.0005	9.1907 ± 0.0004[g]	1.5263	1.6482
6.6142 ± 0.0020	4.3495 ± 0.0007	9.1867 ± 0.0005[h]	1.5259_5	1.6480
6.7459 ± 0.0034	4.4270 ± 0.0006	9.3951 ± 0.0014	1.5429	1.6617
6.7179 ± 0.0045	4.4104 ± 0.0004	9.3503[i]	1.5393	1.6589
		Intercomparison of Reference Standards		
4.4197 ± 0.0032	3.0200 ± 0.0019	6.2496[i,j]	(1.2154)[k]	(1.2893)[l]
4.2431 ± 0.0020	2.9045 ± 0.0028	5.9682 ± 0.0015[j]	(1.1880)[k]	(1.2669)[l]
4.0255 ± 0.0011	2.7682 ± 0.0001	5.6114 ± 0.0006[j]	(1.1513)[k]	(1.2389)[l]
4.0669 ± 0.0018	2.7946 ± 0.0005	5.6798 ± 0.0013[j]	(1.1584)[k]	(1.2442)[l]

[a] Although both H_2SO_4 and $CaCl_2$ were used as isopiestic reference standards, calculations of ϕ of NaBr were based solely upon the H_2SO_4 results. This is because the ϕ^* values of H_2SO_4 are more thoroughly and accurately characterized than those of $CaCl_2$. Osmotic coefficients of H_2SO_4 solutions above 6 mol·kg^{-1} were taken from Rard *et al.* (*18*) as revised slightly by Rard and Platford (*6*). Below 6 mol·kg^{-1} they are from the equation of Clegg *et al.* (*17*). [b] The same samples of H_2SO_4 and $CaCl_2$ were used for both series of measurements, but fresh samples of NaBr were weighed out for each series. [c] Reported values are the average molalities from duplicate samples, along with the average deviation from the mean. Results are reported (from top to bottom in this table) in the actual order that they were measured. [d] Solubility determination with 7-d equilibration. [e] Solubility determination with 9-d equilibration. [f] Solubility determination with 13-d equilibration. [g] Solubility determination with 8-d equilibration. [h] Solubility determination with 16-d equilibration. [i] Single sample owing to crystallization in the replicate sample. [j] Between these equilibrations and the previous one given in this table, the NaBr samples were discarded and the remaining samples were used for several equilibrations involving only H_2SO_4 and $CaCl_2$. Those results will be published elsewhere. Fresh samples of the NaCl stock solution were then added for these four equilibrations. Reported molalites are those of NaCl and not of NaBr. [k] Experimental osmotic coefficients of H_2SO_4 as calculated from the H_2SO_4 and NaCl isopiestic molalities using the activity equation of Archer for NaCl (*10*). These values were included by Clegg *et al.* (*17*) in their critical review. [l] Osmotic coefficients of NaCl were calculated using the activity equation of Archer (*10*).

but there is no obvious trend with the order in which the experiments were performed or with the length of the equilibration. Solubility determinations with 9- and 16-d equilibrations gave essentially identical results, whereas the other results are slightly higher or lower.

The initial solubility determination in Table 3 may possibly be slightly low if the solid phase has not yet become the pure dihydrate. Thus, the recommended value for the solubility from the present study is the average of the last four determinations, $9.1859_2 \pm 0.0043_6$ mol·kg^{-1}, where this σ_{n-1} standard deviation is statistical only. Including the uncertainty in the stock solution molality gives a total uncertainty of ± 0.0055 mol·kg^{-1}. The solubility recommended by Linke (*13*) of 9.193 mol·kg^{-1} is 0.077% higher than the present determination and is in good agreement. That literature value was based upon a graphical smoothing of the results at various temperatures from 12 studies published between 1862 to 1942.

Linke (*13*) tabulated the results from a number of independent solubility determinations at 298.15 K from which were calculated solubilities of 8.939, 9.092, 9.120, 9.127, 9.149, 9.175, 9.189, and 9.267 mol·kg^{-1}; this is a considerable variation. It is obvious that many of these solubilities are significantly in error because, for example, of allowing insufficient time for the solutions to become saturated (which would give low values if saturation was approached "from below"), because of use of low purity NaBr, or because of inaccurate molality analyses (which would yield slightly high results if the molality was determined by dehydration).

Several equilibrations were done to intercompare the three reference standards at higher molalities in order to refine their osmotic coefficients. These are also included in Table 3. The NaCl-to-H_2SO_4 isopiestic molality ratio is 0.1−0.2% below those reported by Rard (*14*) and Rard and Miller (*15*) and within 0.1% of that of Robinson (*16*).

Calculation of Osmotic Coefficients

Molal ("practical") osmotic coefficients of the aqueous NaBr solutions were calculated by using the fundamental equation for isopiestic equilibrium:

$$\phi = \nu^* m^* \phi^* / \nu m \tag{3}$$

where m is the equilibrium molality of NaBr, m^* is the molality of a reference standard solution in isopiestic equilibrium with the NaBr, ϕ^* is the molal osmotic coefficient of that isopiestic reference standard, and ν and ν^* are the stoichiometric ionization numbers of NaBr and reference standards, respectively ($\nu = \nu^* = 2$ for NaBr and NaCl; $\nu^* = 3$ for H_2SO_4 and $CaCl_2$).

Values of ϕ^* of NaCl solutions at 298.15 K were computed from the equation given in the comprehensive critical evaluation of Archer (*10*); for H_2SO_4 the ϕ^* values were computed from the extended Pitzer equation used in the critical evaluation of Clegg *et al.* (*17*) for molalities up to 6 mol·kg^{-1}, and with the equation of Rard *et al.* (*18*) at higher molalities. These two equations for ϕ^* of H_2SO_4 differ by only 0.0003 at 6 mol·kg^{-1}; however, $(\partial\phi^*/\partial m)_{T,p}$ is different at this molality so some differences in slope result when the equations for that reference standard are changed. The $CaCl_2$ isopiestic molalities were not used in evaluating ϕ of NaBr; instead the H_2SO_4-to-$CaCl_2$ molality ratio will be used to refine the ϕ^* of $CaCl_2$ at some future time. Values of ϕ and ϕ^* are given in Tables 2 and 3 along with the experimental isopiestic molalities. Although these results were measured at 298.15 K on the International Practical Temperature Scale of 1968, they differ insignificantly from values at 298.15 K on the International Temperature Scale of 1990.

Three isopiestic experiments of Table 3 with H_2SO_4 as the reference standard overlapped in molality range with the higher-molality results of Table 2 with NaCl as the reference standard. Osmotic coefficients of NaBr with H_2SO_4 as the reference standard are parallel to and about 0.17% above those with NaCl as the reference standard. Given that available osmotic coefficients for H_2SO_4 exhibit variations of about ±0.3% in this molality range (*17*), the offset is within the combined uncertainties of the reference standards.

Treatment of the Thermodynamic Data

Description of Data Representation. The principle reason for undertaking the current work was to better elucidate the thermodynamic properties of NaBr(aq) and to try to resolve the incompatibilities of the different types of experimental results that were described previously (*1*). To use the present results to achieve these goals, the database of thermodynamic results described in ref 1 was refitted after incorporation of our new osmotic coefficients, as well as the additional results described below.

Because the model used here is similar to that used previously (*1*), only a brief description is given here. We have used Pitzer's ion-interaction model, with inclusion of an ionic strength dependence of the third virial coefficient, to represent the experimental results. The fitted equation for the excess Gibbs energy for an arbitrary valence type is

$$\frac{G^{E}}{n_{w}RT} = -4IA_{\phi}\ln(1 + bI^{1/2})/b + 2\nu_{M}\nu_{X}(m^{2}B_{MX} + m^{3}\nu_{M}z_{M}C_{MX}) \tag{4}$$

where

$$B_{MX} = \beta_{MX}^{(0)} + 2\beta_{MX}^{(1)}[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]/(\alpha^{2}I) \tag{4a}$$

and

$$C_{MX} = C_{MX}^{(0)} + 4C_{MX}^{(1)}[6 - (6 + 6\alpha_{2}I^{1/2} + 3\alpha_{2}^{2}I + \alpha_{2}^{3}I^{3/2})\exp(-\alpha_{2}I^{1/2})]/(\alpha_{2}^{4}I^{2}) \tag{4b}$$

$\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $C_{MX}^{(0)}$, and $C_{MX}^{(1)}$ are adjustable parameters (ion-interaction parameters) that are dependent on temperature and pressure, z_M and z_X are the charges of the cation and the anion, respectively, α and b were chosen to be constants with the values 2.0 and 1.2 kg$^{1/2}$·mol$^{-1/2}$, respectively, ν_M and ν_X are the stoichiometric numbers of cations and anions formed upon dissociation, and n_w is the number of kilograms of water. A_ϕ is the Debye−Hückel coefficient for the osmotic coefficient. The Debye−Hückel coefficients used in the present work were calculated from the equation of state for water from Hill (*19*) and the dielectric-constant equation from Archer and Wang (*20*). The value of α_2 used in the fitted equation was 1.7 kg$^{1/2}$·mol$^{-1/2}$. This value gave a good representation of experimental free energy and enthalpy results. However, it is different from the value of 2.5 kg$^{1/2}$·mol$^{-1/2}$ that gave good representations for NaCl(aq) and for Na_2SO_4(aq) (*10*) and which was also the value used by Clegg *et al.* (*17*) for H_2SO_4(aq).

The excess Gibbs energy, G^E, is related to the Gibbs energy of the solution, G, as

$$G^{E} = G - n_{1}G^{\circ}_{m,1} - n_{2}G^{\circ}_{m,2} + RT\nu n_{2}\{1 - \ln(m/m^{\circ})\} \tag{5}$$

where n_1 and n_2 are the number of moles of solvent and solute, respectively, m is the stoichiometric molality, ν is the number of ions formed upon complete dissociation of the electrolyte, and m° is 1.0 mol·kg^{-1}. The standard-state molar Gibbs energies for solvent and solute are $G^{\circ}_{m,1}$ and $G^{\circ}_{m,2}$, respectively. The standard states were chosen to be pure liquid for the solvent and the hypothetical 1 mol·kg^{-1} ideal solution for the solute at the temperature and pressure of interest, rather than at the temperature of interest and an arbitrary pressure.

Appropriate differentiation of eq 4 leads to the osmotic coefficient, ϕ, and the stoichiometric activity coefficient, $\gamma_\pm$:

$$\phi - 1 = -|z_{M}z_{X}|A_{\phi}\frac{I^{1/2}}{1 + bI^{1/2}} + m\frac{2\nu_{M}\nu_{X}}{\nu}(\beta_{MX}^{(0)} + \beta_{MX}^{(1)}\exp(-\alpha I^{1/2})) + m^{2}\frac{4\nu_{M}^{2}\nu_{X}z_{M}}{\nu}(C_{MX}^{(0)} + C_{MX}^{(1)}\exp(-\alpha_{2}I^{1/2})) \tag{6}$$

$$\ln \gamma_{\pm} = -|z_M z_X| A_\phi \left(\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right) + m \frac{2\nu_M \nu_X}{\nu} \left\{ 2\beta_{MX}^{(0)} + \frac{2\beta_{MX}^{(1)}}{\alpha^2 I} \left[1 - \left(1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2} \right) \exp(-\alpha I^{1/2}) \right] \right\} + m^2 \frac{2\nu_M{}^2 \nu_X z_M}{\nu} \{ 3C_{MX}^{(0)} + 4C_{MX}^{(1)}[6 - (6 + 6\alpha_2 I^{1/2} + 3\alpha_2{}^2 I + \alpha_2{}^3 I^{3/2} - \alpha_2{}^4 I^2/2) \exp(-\alpha_2 I^{1/2})]/(\alpha_2{}^4 I^2) \} \quad (7)$$

The osmotic coefficient is related to the activity of water as $\phi = (-\ln a_w)(M_1 \nu m)^{-1}$, where M_1 is the molar mass of the solvent. The relative apparent molar enthalpy, L_ϕ, is

$$L_\phi = \nu |z_M z_X| A_H \ln(1 + bI^{1/2})/2b - 2\nu_M \nu_X R T^2 (m B_{MX}^L + m^2 \nu_M z_M C_{MX}^L) \quad (8)$$

where

$$B_{MX}^L = \left(\frac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_p + 2 \left(\frac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_p [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})]/\alpha^2 I \quad (9)$$

$$C_{MX}^L = \left(\frac{\partial C_{MX}^{(0)}}{\partial T} \right)_p + 4 \left(\frac{\partial C_{MX}^{(1)}}{\partial T} \right)_p [6 - (6 + 6\alpha_2 I^{1/2} + 3\alpha_2{}^2 I + \alpha_2{}^3 I^{3/2}) \exp(-\alpha_2 I^{1/2})]/(\alpha_2{}^4 I^2) \quad (10)$$

and where A_H is the Debye–Hückel coefficient for apparent molar enthalpy. The constant-pressure apparent molar heat capacity, $C_{p,\phi}$, is

$$C_{p,\phi} = C^\circ{}_{p,m,2} + \nu |z_M z_X| A_C \ln(1 + bI^{1/2})/2b - 2\nu_M \nu_X R T^2 (m B_{MX}^C + m^2 \nu_M z_M C_{MX}^C) \quad (11)$$

where

$$B_{MX}^C = \left(\frac{\partial^2 \beta_{MX}^{(0)}}{\partial T^2} \right)_p + \frac{2}{T} \left(\frac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_p + 2 \left\{ \left(\frac{\partial^2 \beta_{MX}^{(1)}}{\partial T^2} \right)_p + \frac{2}{T} \left(\frac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_p \right\} [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})]/\alpha^2 I \quad (12)$$

$$C_{MX}^C = \left(\frac{\partial^2 C_{MX}^{(0)}}{\partial T^2} \right)_p + \frac{2}{T} \left(\frac{\partial C_{MX}^{(0)}}{\partial T} \right)_p + 4 \left\{ \left(\frac{\partial^2 C_{MX}^{(1)}}{\partial T^2} \right)_p + \frac{2}{T} \left(\frac{\partial C_{MX}^{(1)}}{\partial T} \right)_p \right\} [6 - (6 + 6\alpha_2 I^{1/2} + 3\alpha_2{}^2 I + \alpha_2{}^3 I^{3/2}) \exp(-\alpha_2 I^{1/2})]/(\alpha_2{}^4 I^2) \quad (13)$$

and where A_C is the Debye–Hückel coefficient for apparent molar heat capacity and $C^\circ{}_{p,m,2}$ is the standard-state molar heat capacity of the solute. As before (*1*), a reference molality was used in the fitting equations to avoid representation of the extreme temperature and pressure dependences of the usual ideal-solution standard state. In these terms, the apparent molar volume is represented with the equation

$$V_\phi + v_w/n_r = V(m_r)/n_r + \nu |z_M z_X| A_V \ln\{(1 + bI^{1/2})/(1 + bI_r{}^{1/2})\}/2b + 2\nu_M \nu_X R T \{(m - m_r) B_{MX}^V + (m^2 - m_r{}^2) \nu_M z_M C_{MX}^V\} \quad (14)$$

where

$$B_{MX}^V = \left(\frac{\partial \beta_{MX}^{(0)}}{\partial p} \right)_T + 2 \left(\frac{\partial \beta_{MX}^{(1)}}{\partial p} \right)_T [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})]/\alpha^2 I \quad (15)$$

$$C_{MX}^V = \left(\frac{\partial C_{MX}^{(0)}}{\partial p} \right)_T + 4 \left(\frac{\partial C_{MX}^{(1)}}{\partial p} \right)_T [6 - (6 + 6\alpha_2 I^{1/2} + 3\alpha_2{}^2 I + \alpha_2{}^3 I^{3/2}) \exp(-\alpha_2 I^{1/2})]/(\alpha_2{}^4 I^2) \quad (16)$$

and where v_w is the volume of 1 kg of water, $V(m_r)$ is the volume of a quantity of solution of molality m_r which contains 1 kg of water, and n_r is the number of moles of solute in this quantity of solution. In the present work m_r was chosen to be 6 mol·kg^{-1}. Equations similar to eq 14 may be written for the other apparent molar properties. The analogous equation for apparent molar heat capacity is

$$C_{p,\phi} + c_{p,w}/n_r = C_p(m_r)/n_r + \nu |z_M z_X| A_C \ln\{(1 + bI^{1/2})/(1 + bI_r{}^{1/2})\}/2b - 2\nu_M \nu_X R T^2 \{(m - m_r) B_{MX}^C + (m^2 - m_r{}^2) \nu_M z_M C_{MX}^C\} \quad (17)$$

where $C_p(m_r)$ is the heat capacity of a quantity of solution containing 1 kg of solvent at the desired temperature and pressure and $c_{p,w}$ is the heat capacity of 1 kg of water. The pressure dependence of $C_p(m_r)/n_r$ is contained in $V(m_r)/n_r$, and so the only additional variable parameters introduced are those that describe the behavior of $C_p(m_r)/n_r$ along an isobar. This isobar was chosen to be 0.1 MPa; $C_p(m_r)/n_r$ along this 0.1 MPa isobar will be referred to as $C_{p,p_r}(m_r)/n_r$.

The partial molar Gibbs energy of the solute in its standard state at temperature T and pressure p, $G^\circ{}_{m,2,T,p}$, may be written in terms of the above equations as

$$G^\circ{}_{m,2,T,p} = G^\circ{}_{m,2,T_r,p_r} + \frac{n_1 G^\circ{}_{m,1,T_r,p_r} - n_1 G^\circ{}_{m,1,T,p}}{n_r} + \frac{G^E{}_{T_r,p_r,m_r} - G^E{}_{T,p,m_r}}{n_r} - (T - T_r)\left(S^\circ{}_{2,m,T_r,p_r} + \frac{n_1 S^\circ{}_{1,m,T_r,p_r}}{n_r} + \frac{S^E{}_{T_r,p_r,m_r}}{n_r} \right) - T \int_{T_r}^{T} \frac{1}{T^2} \int_{T_r}^{T} \{C_{p,p_r}(m_r)/n_r\} \, dT \, dT + \int_{p_r}^{p} \{V(m_r)/n_r\} \, dp \quad (18)$$

where

$$S^E{}_{T_r,p_r} = -\left(\frac{\partial G^E{}_{T,p_r}}{\partial T} \right)_p \quad (19)$$

The equations describing the solubility of the anhydrous and dihydrate solid phases are

$$\Delta_{sol} G^\circ{}_{anhydrous} = G^\circ{}_{m,2} - G^\circ{}_{m,cr,anhydrous} = -2RT \ln(m_s \gamma_{\pm,s}/m^\circ) \quad (20)$$

and

$$\Delta_{sol} G^\circ{}_{dihydrate} = G^\circ{}_{m,2} + 2G^\circ{}_{m,1} - G^\circ{}_{m,cr,dihydrate} = -2RT \ln(m_s \gamma_{\pm,s}/m^\circ) - 2RT \ln a_{w,s} \quad (21)$$

where $G^\circ{}_{m,2}$, $G^\circ{}_{m,1}$, and $G^\circ{}_{m,cr,i}$ are the molar Gibbs energies for the solute, the pure liquid water, and the ith crystal phase all at a given T and p, respectively, $\Delta_{sol} G^\circ{}_i$ is the standard-state molar Gibbs energy for the solution process of the ith crystal phase and m_s, $\gamma_{\pm,s}$, and $a_{w,s}$ are the saturation molality, the mean stoichiometric activity coefficient for the solute at saturation, and the activity of water for the saturation molality, respectively. Of course, $G^\circ_{m,2}$, $G^\circ_{m,1}$, and $G^\circ_{m,cr,i}$ cannot be evaluated, and so eqs 20 and 21 were rewritten as

$$\Delta_{sol}G^\circ_{anhydrous,T} = \Delta_{sol}G^\circ_{anhydrous,T_r} + \{G^\circ_{m,2,T} - G^\circ_{m,2,T_r}\} - \{G^\circ_{m,cr,anhydrous,T} - G^\circ_{m,cr,anhydrous,T_r}\} = -2RT\ln(m_s\gamma_{\pm,s}/m^\circ) \quad (22)$$

and

$$\Delta_{sol}G^\circ_{dihydrate,T} = \Delta_{sol}G^\circ_{dihydrate,T_r} + \{G^\circ_{m,2,T} - G^\circ_{m,2,T_r}\} - \{G^\circ_{m,cr,dihydrate,T} - G^\circ_{m,cr,dihydrate,T_r}\} + 2\{G^\circ_{m,1,T} - G^\circ_{m,1,T_r}\} = -2RT\ln(m_s\gamma_{\pm,s}/m^\circ) - 2RT\ln a_{w,s} \quad (23)$$

The first braced terms of eqs 22 and 23 were obtained from eq 18, the second braced term of eq 22 was obtained from ref 1, and the third braced term of eq 23 was obtained from the equation of Hill (*19*). The second braced term of eq 23 was expressed as

$$\{G^\circ_{m,cr,dihydrate,T} - G^\circ_{m,cr,dihydrate,T_r}\} = -(T - T_r)S^\circ_{m,cr,dihydrate,T_r,p_r} + C^\circ_{p,m,dihydrate,T_r,p_r}\{(T - T_r) - T\ln(T/T_r)\} \quad (24)$$

where $C^\circ_{p,m,dihydrate,T_r,p_r} = 138\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ is the estimated molar heat capacity of the dihydrate crystal at 298.15 K and 0.1 MPa (*1*). Solubility measurements were included in the global data fit. The two Gibbs energies of solution at the reference temperature, T_r, and reference pressure, p_r, were treated as adjustable parameters, as were $S^\circ_{m,cr,dihydrate,T_r,p_r}$ and S°_{2,m,T_r,p_r}. In addition, the experimental solubility results make some contribution to the determination of the parameters for the excess Gibbs energy for the solution through eq 18.

For the dehydration (decomposition) reaction

$$\mathrm{NaBr{\cdot}2H_2O(cr) = NaBr(cr) + 2H_2O(g)} \quad (25)$$

the standard Gibbs energy of reaction for 298.15 K and 0.1 MPa, per mole of H_2O, is

$$\Delta_{dec}G^\circ_{m,T_r,p_r} = (\Delta_f G^\circ_{anhydrous,T_r,p_r} + 2\Delta_f G^\circ_{H_2O(g),T_r,p_r} - \Delta_f G^\circ_{dihydrate,T_r,p_r})/2 \quad (26)$$

where $\Delta_f G^\circ_{anhydrous,T_r,p_r}$ and $\Delta_f G^\circ_{dihydrate,T_r,p_r}$ are the standard-state Gibbs energies of formation of the anhydrous and dihydrated sodium bromide phases at T_r and p_r. The standard-state Gibbs energy of formation of $H_2O(g)$ at T_r and p_r, $\Delta_f G^\circ_{H_2O(g),T_r,p_r}$, was taken from Cox *et al.* (*4*). At any given temperature, the standard Gibbs energy of decomposition, $\Delta_{dec}G^\circ_{m,T,p_r}$, is

$$\Delta_{dec}G^\circ_{m,T,p_r} = \Delta_{dec}G^\circ_{m,T_r,p_r} + (S^\circ_{m,H_2O(g),T_r,p_r} + 0.5S^\circ_{m,anhydrous,T_r,p_r} - 0.5S^\circ_{m,dihydrate,T_r,p_r})(T_r - T) + \int_{T_r}^{T}(C^\circ_{p,m,H_2O(g),p_r} + 0.5C^\circ_{p,m,anhydrous,p_r} - 0.5C^\circ_{p,m,dihydrate,p_r})\,dT - T\int_{T_r}^{T}\{(C^\circ_{p,m,H_2O(g),p_r} + 0.5C^\circ_{p,m,anhydrous,p_r} - 0.5C^\circ_{p,m,dihydrate,p_r})/T\}\,dT \quad (27)$$

again per mole of water. The heat capacities and entropies for eq 27 have been referred to previously. The vapor pressure of water over the dihydrated solid, from 283.15 to 323.75 K, was included in the global data fit.

The adjustable parameters $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $C^{(0)}_{MX}$, and $C^{(1)}_{MX}$ were assumed to be linear combinations of functions of temperature and solvent density as

$$\beta^{(0)}_{MX} = f(1,\varrho_w,T)/m^\circ \quad (28)$$

$$\beta^{(1)}_{MX} = f(2,\varrho_w,T)/m^\circ \quad (29)$$

$$C^{(0)}_{MX} = f(3,\varrho_w,T)/(m^\circ)^2 \quad (30)$$

$$C^{(1)}_{MX} = f(4,\varrho_w,T)/(m^\circ)^2 \quad (31)$$

where

$$f(i,\varrho_w,T) = [b_{i,1} + 10^{-2}b_{i,2}(T - T_r)/T^\circ + 10^{-5}b_{i,3}\{(T - T_r)/T^\circ\}^2 + 10^2 b_{i,4}T^\circ/(T - 225\ \mathrm{K}) + 10b_{i,5}T^\circ/(680\ \mathrm{K} - T) + 10^3 b_{i,6}T^\circ/T + 10^{-7}b_{i,7}\{(T - T_r)/T^\circ\}^3 + 10b_{i,8}\varrho_w/\varrho^\circ + 10^{-3}b_{i,9}\varrho_w T/(\varrho^\circ T^\circ) + 10^{-5}b_{i,10}\varrho_w T^2/(\varrho^\circ T^{\circ 2}) + 10^3 b_{i,11}\varrho_w T^\circ/\{\varrho^\circ(T - 225\ \mathrm{K})\} + 10b_{i,12}\varrho_w T^\circ/\{(680\ \mathrm{K} - T)\varrho^\circ\} + 10b_{i,13}\varrho_w^{\ 2}/\varrho^{\circ 2} + 10^{-3}b_{i,14}\varrho_w^{\ 2}T/(T^\circ\varrho^{\circ 2}) + 10^2 b_{i,15}\varrho_w^{\ 2}T^\circ/\{\varrho^{\circ 2}(T - 225\ \mathrm{K})\} + 10^{-1}b_{i,16}\varrho_w^{\ 3}/\varrho^{\circ 3} + 10^6 b_{i,17}\{T^\circ/(T - 225\ \mathrm{K})\}^3 + 10b_{i,18}\varrho_w^{\ 2}T^\circ/\{(680\ \mathrm{K} - T)\varrho^{\circ 2}\}] \quad (32)$$

and where T° is 1.0 K, ϱ° is 1.0 $\mathrm{g{\cdot}cm^{-3}}$, m° is 1.0 $\mathrm{mol{\cdot}kg^{-1}}$, and T_r = 298.15 K. $V(m_r)/n_r$ and $C_p(m_r)/n_r$ were taken as functions of T and p as

$$V(m_r)/n_r = [b_{5,1} + b_{5,2}T/(3 \times 10^3 T^\circ) + b_{5,3}\{T/(300\ T^\circ)\}^2 + 10^{-2}b_{5,4}\{T/(300\ T^\circ)\}^3 + 10^{-3}b_{5,5}pT/(p^\circ 300\ T^\circ) + 10^{-4}b_{5,6}pT^2/\{p^\circ(300\ T^\circ)^2\} + 10^{-4}b_{5,7}pT^3/\{p^\circ(300\ T^\circ)^3\} + 10^{-7}b_{5,8}(p/p^\circ)^2 + 10^{-4}b_{5,9}p^2T/(p^{\circ 2}300\ T^\circ) + 10^{-7}b_{5,10}p^2T^2/\{p^{\circ 2}(300\ T^\circ)^2\}]V^\circ \quad (33)$$

and

$$C_{p,p_r}(m_r)/n_r = [b_{6,1} + 10^{-2}b_{6,2}T/T^\circ + 10^{-5}b_{6,3}(T/T^\circ)^2]C_p^\circ \quad (34)$$

where V° is 1.0 $\mathrm{cm^3{\cdot}mol^{-1}}$, C_p° is 1.0 $\mathrm{kJ{\cdot}mol^{-1}{\cdot}K^{-1}}$, and p° is 1.0 MPa. The weighting factors for the experimental results were calculated from an estimated square root of variance for each data set which is given in Tables 4 and 5. The least-squares estimated parameters are given in Table 6. Note that not all of the $b_{i,j}$ parameters were required to accurately represent the available experimental data.

Results of Data Representation. A summary of the agreement of the data representation with the experimental values is given in Tables 4 and 5. The present least-squares estimated model parameters represent all of the results that had been fitted previously (*1*) with approximately the same root-mean-square (rms) deviations as before, with the following exceptions. The recent 604.4 K volumetric results of Majer *et al.* (*41*) were included in the

Table 4. Literature Sources for the Volumetric Properties of NaBr(aq)

ref	temp/K	pressure/MPa	molality/(mol·kg^{-1})	n	type	σ_{exp}	σ_{fit}
21	298.15	0.1	m_s	2	ϱ_s/ϱ_w	550×10^{-6}	1274×10^{-6} [c]
22	298.15	0.1	0.006–1.0	9	ϱ_s/ϱ_w	40×10^{-6}	24×10^{-6} [d]
23	298.15	0.1	0.16–6.65	40	Δ_{dil}/V_ϕ	0.05–0.015	0.014 [e]
24	298.15	0.1	0.1–0.47	6	ϱ_s/ϱ_w	50×10^{-6}	19×10^{-6} [c]
25	298.15	0.1	0.06–0.54	10	$\varrho_s - \varrho_w$	5×10^{-6}, 0.1%	36×10^{-6} [f]
26	298.15	0.1	0.05–1.8	15	V_ϕ	0.1–0.02	0.027 [g]
27	298.15	0.1	0.03–1.0	17	$\varrho_s - \varrho_w$	5×10^{-6}, 0.1%	18×10^{-6} [f]
28	298.15	0.1	0.68–8.38	6	ϱ_s/ϱ_w	400×10^{-6}	522×10^{-6} [c]
29	298.15	0.1	0.1–1.0	10	$\varrho_s - \varrho_w$	5×10^{-6}, 0.1%	26×10^{-6} [f]
30	298.15	0.1	0.35–4.36	8	ϱ_s	400×10^{-6}	191×10^{-6} [c]
31	273.15–343.34	0.1	0.28–6.65	20	ϱ_s/ϱ_w	40×10^{-6}	104×10^{-6} [c]
32	273.15–365.10	0.1	m_s	14	ϱ_s/ϱ_w	1.0×10^{-3}	1.4×10^{-3} [c]
33	298.15–318.15	0.1	1.2–5.2	10	ϱ_s/ϱ_w	40×10^{-6}	72×10^{-6} [h]
34, 35	298.15–358.15	0.1–100	0.5–7.74	175	ϱ_s/ϱ_w	40×10^{-6}	53×10^{-6} [c]
36	298–573	a–100	0.20–7.95	341	v_s	$(3-5) \times 10^{-3}$	3.1×10^{-3} [i]
37	293.15–363.15	0.1	0.10–6.48	36	ϱ_s	$(0.2-2.0) \times 10^{-3}$	0.64×10^{-3} [c]
38	288.15–328.15	0.1	0.05–8.0	81	ϱ_s/ϱ_w	0.1%	215×10^{-6} [j]
39	298.15	0.1–40	0.05–4.97	40	$\varrho_s - \varrho_w$	b	790×10^{-6} [c]
40	321.6–549.8	a–32	0.05–3.03	174	$\varrho_s - \varrho_w$	k	780×10^{-6} [c]
41	604.4 K	18–38	0.005–3.0	84	$\varrho_s - \varrho_w$	l	1.2×10^{-3} [c]

[a] The lowest pressure for the data set changed with the experimental temperature. [b] These points were given an insignificant weight in the least-squares procedure. [c] Units are g·cm^{-3}. [d] Units are g·cm^{-3}. The lowest molality point was given an insignificant weight in the least-squares procedure, but it has been included in σ_{fit}. [e] Units are cm^3·mol^{-1}. Dilutions from 6.65 mol·kg^{-1}, $\sigma_{exp} = 0.05$ cm^3·mol^{-1}; dilutions from 2.11 and 1.84 mol·kg^{-1}, $\sigma_{exp} = 0.015$ cm^3·mol^{-1}; dilutions from 1.22 mol·kg^{-1}, $\sigma_{exp} = 0.018$ cm^3·mol^{-1}. [f] Units are g·cm^{-3}. Data were weighted as the larger of 5×10^{-6} cm^3·mol^{-1} or 0.1% of $\varrho_s - \varrho_w$. [g] Units are cm^3·mol^{-1}. Expected uncertainties ranged from 0.1 cm^3·mol^{-1} for 0.05 mol·kg^{-1} to 0.02 cm^3·mol^{-1} for 0.6 mol·kg^{-1} and larger. Only smoothed results were reported in this paper. [h] Units are g·cm^{-3}, lowest molality for 298.15 K given an insignificant weight in the least-squares procedure; σ_{fit} does not contain the residual for this point. [i] Units are cm^3·g^{-1}. Results for temperatures less than 373.15 K, $\sigma_{exp} = 3000 \times 10^{-6}$ cm^3·g^{-1}; $\sigma_{exp} = 5000 \times 10^{-6}$ cm^3·g^{-1} for temperatures greater than 373.15 K. [j] Units are g·cm^{-3}. Data were weighted as $\sigma_{exp} = 0.1\%$ of $\varrho_s - \varrho_w$. [k] Weighted according to twice the σ_{exp} given in ref 40. [l] Weighted according to the σ_{exp} given in ref 41. Data were also reported for temperatures to 725.5 K, which is outside the range of validity of our model.

present representation. In order to obtain a good representation of these new results, it was necessary to approximately double the error assigned to Majer *et al.*'s (*40*) earlier volumetric results (which spanned the temperature range of 322–550 K). This change in the weighting of the earlier results resulted in a representation of the 604.4 K results that was approximately half of the authors' claimed uncertainty in those results. Increasing the error assigned to Majer *et al.*'s (*40*) $\varrho_s - \varrho_w$ also resulted in improved agreement of the fitted equation and the volumetric results of Egorov *et al.* (*36*) and also of Mayrath and Wood's (*63*) enthalpies of dilution. Because the agreement of the fitted equation with the heat capacities from White *et al.* (*68*) remained the same as before (*1*), and because of the thermodynamic relations that relate the enthalpies of dilution near the saturation pressure to the heat capacities at 17 MPa, the improved representation of the enthalpies of dilution can be attributed to more accurate values of the temperature dependence of the volumetric properties generated from the present representation than those calculated from the previous equations (*1*). This improved agreement between calculated and experimental enthalpies and heat capacities indicates that Majer *et al.*'s (*40*) claimed uncertainties may be too small by a factor of 2–3.

Agreement of the present osmotic coefficients, as well as other osmotic coefficients, with the fitted equation is shown in Figure 2. The systematic differences of the values obtained with NaCl(aq) and with H_2SO_4(aq) standards can be seen in the figure. This difference falls within the claimed uncertainties for the fitted equation for H_2SO_4(aq). Additional terms could have been added to the fitted equation for NaBr(aq) to eliminate the slight systematic behavior observed for the residuals corresponding to the current results. However, because the systematic behavior falls entirely within the estimated uncertainty of the osmotic coefficients of the reference substance, elimination of the apparently systematic behavior seemed pointless. The one anomalously high point from Table 3 with H_2SO_4(aq) standard (weighted zero) had problems with degassing of the solution.

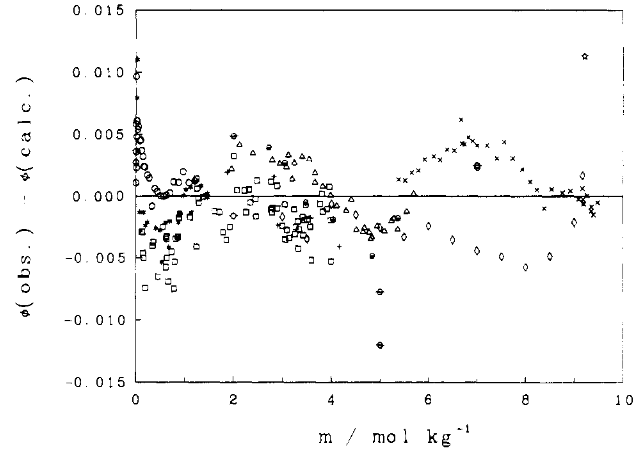

Figure 2. Differences of osmotic coefficients from the fitted equations: ○, ref 46; ∗, ref 47; □, refs 48 and 49; ◇, ref 52; ☆, ref 50; +, ref 53; ●, ref 54; ⊖, ref 56; △, present values with NaCl(aq) as reference; ×, present values with H_2SO_4(aq) as reference.

Results for osmotic coefficients of NaBr(aq) with H_2SO_4(aq) as standard, Table 3, and with $CaCl_2$(aq) as standard (*52*), are in fair agreement around 5 mol·kg^{-1} and in complete agreement around 9 mol·kg^{-1} as illustrated in Figure 2. However, results from these two studies diverge somewhat at intermediate molalities, reaching a maximum difference of 0.008 in ϕ or 0.55%. This difference is probably just within the combined experimental uncertainties from both studies. Makarov *et al.* (*52*) gave only smoothed results and not actual experimental data, so it will not be possible to recalculate their osmotic coefficients when values for the osmotic coefficients of the $CaCl_2$(aq) standard become more refined.

Table 5. Literature Sources for the Activity and Thermal Properties of NaBr(aq)

ref	temp/K	pressure/MPa	molality/(mol·kg^{-1})	n	type[b]	σ_{exp}	σ_{fit}
42	298.15	0.1	0.03−3.02	9	$\ln(\gamma_2/\gamma_1)$	[c]	0.0066
43	298.15	0.1	0.2−4.0	9	$\ln(\gamma_2/\gamma_1)$	[c]	0.0071
44	273.15−313.15	0.1	0.2−4.0	99	$\ln(\gamma_2/\gamma_1)$	[c]	0.0097
45	298.15	0.1	0.005−0.2	6	$\ln(\gamma_\pm)$	[c]	0.017
46	T_{fus}	0.1	0.0008−1.20	31	$\Delta_{fus}T$	[d]	0.0046[e]
47	T_{fus}	0.1	0.008−1.47	26	$\Delta_{fus}T$	[d]	0.0035[e]
48, 49	298.15	[a]	0.12−3.99	74	ϕ	0.005	0.0031[e]
50	298.15	[a]	m_s	1	ϕ	0.010	0.011[e]
51	298.15	[a]	2.8−8.9	16	ϕ	[c]	0.018[e]
52	298.15	[a]	3.0−9.17	14	ϕ	0.007	0.0034[e]
53	298.15	[a]	1.9−4.2	5	ϕ	0.003	0.0025[e]
54	298.15	[a]	2.7−5.4	6	ϕ	0.003	0.0030[e]
Table 2	298.15	[a]	2.0−5.4	31	ϕ	0.002	0.0025[e]
Table 3	298.15	[a]	5.4−9.5	36	ϕ	0.003	0.0025[e]
5	298.15	[a]	0.1−9.13	23	$p_s - p_w$	[c]	0.050[e]
55	293.45−353.15	[a]	m_s	6	$p_s - p_w$	[c]	0.045[e]
56	272.7−362.1	[a]	2.0−7.0	46	$p_s - p_w$	[f]	0.0048[e]
57	423.15−573.15	[a]	0.72−8.69	32	$p_s - p_w$	[c]	0.068[e]
58	298.15	0.1	0.0002−0.1	36	$\Delta_{dil}L_\phi$	0.004	0.005[g]
59	298.15	0.1	0.0017−9.004	9	$\Delta_{dil}L_\phi$	0.030	0.050[g]
60	298.15	0.1	0.9−1.5	23	$\Delta_{dil}L_\phi$	0.00025	0.00025[g]
61	298.15	0.1	0.15−3.0	10	$\Delta_{dil}L_\phi$	0.009	0.007[g]
62	303.15	0.1	0.26−1.08	7	$\Delta_{dil}L_\phi$	0.005	0.006[g]
63	373.15	0.2	0.03−8.0	8	$\Delta_{dil}L_\phi$	0.005−0.010	0.013[g]
63	423.65	0.5	0.04−8.1	11	$\Delta_{dil}L_\phi$	0.005−0.010	0.013[g]
63	472.95	1.6	0.03−8.1	9	$\Delta_{dil}L_\phi$	0.015	0.034[g]
64	298.15	0.1	1.1−9.1	2	$\Delta_{dil}L_\phi$	0.020	0.016[g]
64	298.15	0.1	1−8.6	15	$\Delta_{sol}H_m$	0.020	0.021[g]
59	298.15	0.1	0.03−0.06	6	$\Delta_{sol}H_m$	0.020	0.013[g]
65	283.15−348.15	0.1	0.38	4	$\Delta_{sol}H_m$	0.050	0.038[g]
66	298.15	0.1	0.05−1.0	7	$C_{p,\phi}$	0.012	0.0062[i]
27	298.15	0.1	0.028−1.0	17	$C_{p,\phi}$	0.004	0.0014[i]
67	278.15−358.15	0.1	0.09−7.6	40	$C_{p,\phi}$	0.012−0.002	0.0027[i]
68	306.15−350.30	17.0−17.8	0.05−3.0	66	$c_{p,s}/c_{p,w}$	[j]	0.008[h]
68	400.92−500.9	17.4−17.8	0.05−3.0	72	$c_{p,s}/c_{p,w}$	[j]	0.008[h]
68	551.90−602.74	17.4−17.6	0.05−3.0	59	$c_{p,s}/c_{p,w}$	[j]	0.137[k]
69	283.15−323.75	[a]		18	p_{dec}	0.013	0.017[l]
69	283.15−373.15	[a]	m_s	13	$p_s - p_w$	[m]	0.020[e]
13	249.35−253.15	[a]	m_s	2	$m_s(NaBr{\cdot}2H_2O)$	0.60	0.23[g]
13	263.15−324.15	[a]	m_s	10	$m_s(NaBr{\cdot}2H_2O)$	0.020	0.028[g]
13	324.15−523.15	[a]	m_s	6	$m_s(NaBr)$	[n]	0.071[g]
70	270.0−323.3	[a]	m_s	6	$m_s(NaBr{\cdot}2H_2O)$	0.020	0.025[g]
70	327.05−444.35	[a]	m_s	6	$m_s(NaBr)$	[n]	0.053[g]
this work	298.15	[a]	m_s	5	$m_s(NaBr{\cdot}2H_2O)$	0.007	0.020[g]

[a] The pressures for the data set changed with the experimental conditions. [b] $p_s - p_w$ refers to the difference in vapor pressure between the solution and solvent; p_{dec} is the vapor pressure of water in equilibrium with $NaBr{\cdot}2H_2O$. [c] These points were given an insignificant weight in the least-squares procedure. [d] Values of σ_{exp} were calculated as the uncertainty in the osmotic coefficient due to the uncertainty of 0.003 K for ref 47, or the uncertainties given for ref 46, respectively, or 0.003, whichever was larger. [e] σ_i in terms of osmotic coefficient. Only smoothed results were reported in ref 52. [f] Values of σ_{exp} were calculated as the uncertainty in the osmotic coefficient due to an uncertainty of 3×10^{-6} MPa or 0.005, whichever was larger. [g] Units are kJ·mol^{-1} for enthalpies of dilution and solution and for Gibbs energies of solution. [h] Units are kJ·K^{-1}·mol^{-1}. [i] Units are kJ·K^{-1}·mol^{-1}. These values were assigned weighting factors based on 0.3 of σ_{exp}. [j] Values of σ_{exp} were calculated from the uncertainties given in ref 68; these values vary with temperature and molality; σ_{fit} are given in terms of apparent molar heat capacity, kJ·K^{-1}·mol^{-1}. [k] Units are kJ·K^{-1}·mol^{-1}. The three values for 577.87 K and 0.0498 mol·kg^{-1} were not included in the fit or in σ_{fit}. [l] Units are kPa. [m] The vapor pressure of saturated solutions at 10 K intervals, and at 298.15 K, were taken from ref 69. Iterations were performed to arrive at a set of saturation molalities corresponding to these temperatures. Values of σ_{exp} were calculated from ref 69's estimated uncertainties of pressure of 0.013 kPa for $T \le 348.15$ K and 0.13 kPa for $T > 348.15$ K. The weighted rms deviation for this data set was 1.3. [n] Values of σ_{exp} were assigned to be 0.018 and 0.050 kJ·mol^{-1} for $T < 375$ K and $T > 375$ K, respectively.

Voigt *et al.* (*71*) determined isopiestic molalities of NaBr(aq) relative to $CaCl_2$(aq) at 373.45 K. Unfortunately, the osmotic coefficients of $CaCl_2$(aq) solutions greater than about 4 mol·kg^{-1}, for near 373 K, are not sufficiently well known presently to make these results useful to the current work. For example, both Ananthaswamy and Atkinson (*72*) and Garvin *et al.* (*73*) have fitted nearly the same experimental results for $CaCl_2$(aq), with Garvin *et al.*'s representation being tied into the Staples and Nuttall (*74*) analysis at 298.15 K. For 373.15 K and for 6 mol·kg^{-1}, they gave values of ϕ for $CaCl_2$(aq) of 2.194 and 2.315; for 5 mol·kg^{-1} they (*72, 73*) gave values of ϕ of 2.030 and 2.105, all respectively. Additionally, Garvin *et al.* estimated the uncertainty of ϕ of 5 mol·kg^{-1} $CaCl_2$(aq) as ±0.12 at 373.15 K. This inaccuracy in ϕ for $CaCl_2$(aq) corresponds to an inaccuracy in the higher concentrations of NaBr(aq) of approximately ±0.08−0.1 in ϕ at 10 mol·kg^{-1} for 373.45 K.

Figure 3 shows osmotic coefficients for $CaCl_2$(aq) calculated from Voigt *et al.*'s isopiestic molalities and the present model for NaBr(aq). Also shown are values from Garvin *et al.* and from Ananthaswamy and Atkinson. There is very little data influencing their two models for $CaCl_2$(aq) for large molalities and near 373 K; thus, both models agree with the experimental values within uncertainties representative of the experimental results considered in those two studies, although the results obtained here do agree better with those of Ananthaswamy and Atkinson. Al-

Table 6. Least-Squares Estimated Parameters for the Model

param	value	param	value	param	value[a]
$b_{1,1}$	1.658 737 872 331 97	$b_{2,1}$	−0.106 093 723 848 69	$b_{3,1}$	−0.067 203 471 673 133 1
$b_{1,2}$	−0.114 442 250 388 50	$b_{2,2}$	0.461 734 113 946 13	$b_{3,2}$	0.009 094 234 573 510 45
$b_{1,3}$		$b_{2,3}$		$b_{3,3}$	−0.010 366 400 310 992 3
$b_{1,4}$	−0.872 062 807 541 74	$b_{2,4}$		$b_{3,4}$	0.085 562 841 090 770 4
$b_{1,5}$		$b_{2,5}$		$b_{3,5}$	
$b_{1,6}$		$b_{2,6}$		$b_{3,6}$	
$b_{1,7}$		$b_{2,7}$		$b_{3,7}$	
$b_{1,8}$	−0.366 577 542 580 66	$b_{2,8}$	0.136 734 425 318 34	$b_{3,8}$	0.007 881 825 928 003 96
$b_{1,9}$		$b_{2,9}$	−3.081 372 372 041 51	$b_{3,9}$	
$b_{1,10}$	0.109 032 483 763 21	$b_{2,10}$		$b_{3,10}$	
$b_{1,11}$	0.126 778 747 050 68	$b_{2,11}$		$b_{3,11}$	−0.012 530 234 779 625 7
$b_{1,12}$	−4.154 173 369 652 82	$b_{2,12}$		$b_{3,12}$	0.158 661 593 265 32
$b_{1,13}$	0.333 591 649 865 64	$b_{2,13}$		$b_{3,13}$	
$b_{1,14}$		$b_{2,14}$		$b_{3,14}$	−0.075 984 007 126 119 0
$b_{1,15}$	−0.455 529 511 955 14	$b_{2,15}$		$b_{3,15}$	0.043 059 498 024 776 8
$b_{1,16}$	−11.533 416 270 196 10	$b_{2,16}$		$b_{3,16}$	
$b_{1,17}$		$b_{2,17}$	−0.001 890 434 067 121 76	$b_{3,17}$	
$b_{1,18}$	2.717 328 730 754 08	$b_{2,18}$	−3.122 673 677 774 13	$b_{3,18}$	
$b_{4,1}$	0.677 990 633 407 70	$b_{6,1}$	0.862 361 409 470 26	$\Delta_{sol}G^\circ{}_{anhydrous,T_r,p_r}$	−16.99325 ± 0.021 kJ·mol^{-1}
$b_{4,2}$	−0.163 934 168 447 85	$b_{6,2}$	−0.060 115 155 684 161 8	$\Delta_{sol}G^\circ{}_{dihydrate,T_r,p_r}$	−11.89051 ± 0.014 kJ·mol^{-1}
$b_{4,3}$	0.027 746 922 477 510 9	$b_{6,3}$	0.062 473 748 855 707 2	$S^\circ{}_{m,cr,dihydrate,T_r,p_r}$	178.8547 ± 0.55 J·K^{-1}·mol^{-1}
$b_{4,4}$	0.069 621 034 838 030 4			$S^\circ{}_{m,NaBr(aq),T_r,p_r}$	141.7973 ± 0.076 J·K^{-1}·mol^{-1}
$b_{4,5}$	4.048 135 464 405 73				
$b_{4,6}$	−0.297 826 621 924 33	$b_{5,1}$	0.172 640 126 346 49		
$b_{4,7}$		$b_{5,2}$	0.225 677 252 189 34		
$b_{4,8}$		$b_{5,3}$	−0.007 507 310 213 212 91		
$b_{4,9}$		$b_{5,4}$	0.712 787 744 919 78		
$b_{4,10}$		$b_{5,5}$	−0.132 306 981 637 70		
$b_{4,11}$		$b_{5,6}$	1.337 252 495 175 11		
$b_{4,12}$		$b_{5,7}$	−0.564 346 824 678 79		
$b_{4,13}$		$b_{5,8}$	−0.681 378 743 471 43		
$b_{4,14}$		$b_{5,9}$	0.001 156 458 354 823 36		
$b_{4,15}$		$b_{5,10}$	0.000 098 547 435 416 365 1		
$b_{4,16}$					
$b_{4,17}$	0.000 847 780 118 249 427				
$b_{4,18}$					

[a] The ± values are 95% confidence intervals within the global data representation. The calculated value of $m_{s,dihydrate,T_r,p_r}$ was 9.191 mol·kg^{-1}. The listed uncertainty for $S^\circ{}_{m,NaBr(aq),T_r,p_r}$ does not include the uncertainty in $S^\circ{}_{m,NaBr(cr),T_r,p_r}$. See text for details.

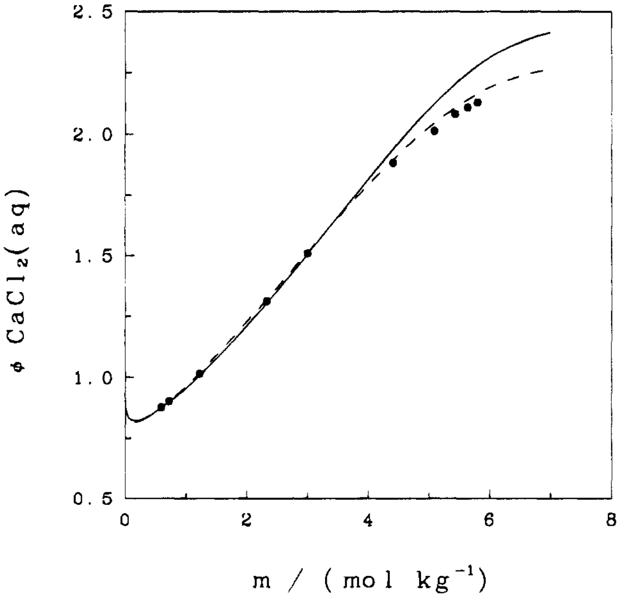

Figure 3. Osmotic coefficients for $CaCl_2$(aq) for 373.45 K. The symbols are values calculated from the isopiestic ratios of NaBr(aq) to $CaCl_2$(aq) from ref 71. The solid line is the calculated osmotic coefficient from ref 73. The dashed line is the calculated osmotic coefficient from ref 72.

though Voigt *et al.*'s isopiestic molalities were not useful for the present work, because of the lack of accurate values for the reference system, they might now be useful in the determination of the thermodynamic properties of $CaCl_2$(aq), using the present values for NaBr(aq). However, in such an application it must be recognized that a small extrapolation of the current values is required and thus will affect the weighting assigned to the $CaCl_2$(aq) values at the largest molalities.

Apelblat (*75*) has recently measured the vapor pressure of saturated solutions of NaBr(aq) from 284.43 to 311.52 K with a Servo Med AB dual-probe evaporimeter. Apelblat stated that his vapor pressures were determined "with a sensitivity of about 0.007 kPa" but gave no other statement of accuracy or precision other than stating the thermal stability of his cell was better than ±0.005 K and the samples were equilibrated for at least 2−3 h. No description was given of how the vapor pressures are actually measured. Figure 4 compares Apelblat's vapor pressures with two other sets of vapor pressures for saturated solutions that were determined in the 1930s (*69, 76*), as well as values calculated from our fitted model. Values from the fitted model are determined primarily from the isopiestic values at 298.15 K, enthalpies of dilution, heat capacities, and solubility measurements, and are not significantly levered by the direct vapor pressure measurements (*69*) included in the fit. The two earlier sets of measurements are in fairly good agreement with the fitted model and also agree with each other within approximately 0.03 kPa, but differ by up to 0.1 kPa from Apelblat's values which also show large deviations from the fitted model.

Apelblat (*75*) reported that interpolation of his results to 298.15 K yielded $\phi = 1.656$ for an assumed saturated solution molality of 9.191 mol·kg^{-1}, which agrees to near 0.5% with our value of 1.648 from Table 3. However, there also seems to be a systematic component to the differences of Apelblat's vapor pressures from other experimental

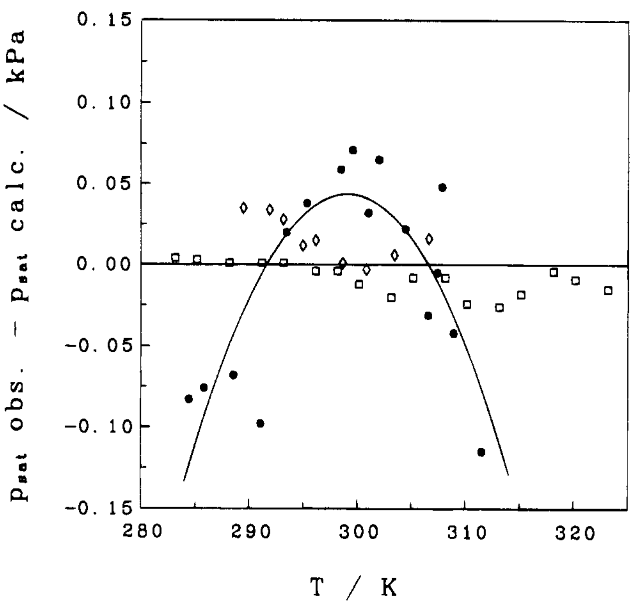

Figure 4. Differences of experimental values of the vapor pressure of solute-saturated NaBr(aq) from the fitted model: □, ref 69; ◇, ref 76; ●, ref 75. The solid line is a quadratic representation of the differences of ref 75 from the fitted model.

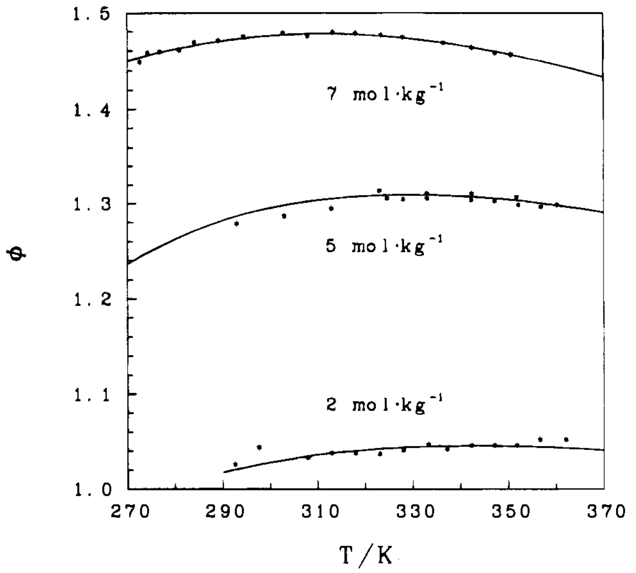

Figure 5. Comparison of osmotic coefficients calculated from the vapor pressures of Jakli and VanHook (*56*) with the fitted model.

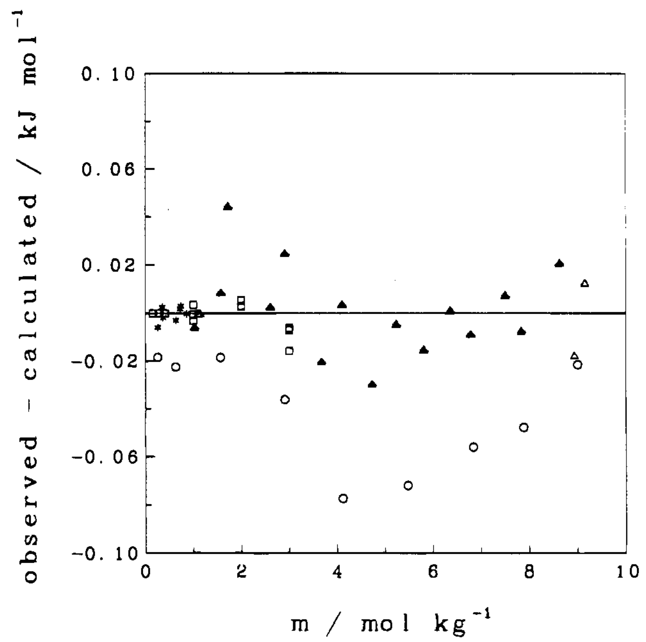

Figure 6. Differences of the 298.15 K enthalpies of solution and enthalpies of dilution from the fitted function: ○, ΔL_ϕ from ref 59; □, ΔL_ϕ from ref 61; ▲, $\Delta_{sol}H_m$ from ref 64; $*$, ΔL_ϕ (303.15 K) from ref 62; △, ΔL_ϕ from ref 64.

values for saturated solutions as evidenced by the quadratic dependence of the residuals for his measurements against temperature; see Figure 4. Apelblat's measurements are somewhat high at his intermediate temperatures but are significantly low at higher and lower temperatures. Because the deviations of Apelblat's results from other data and from the present fitted model have this unusual temperature dependence, the discrepancies seem to be too large to attribute to impurities in the NaBr(cr) and may be an artifact of the experimental method. The discrepancy could arise from other sources, for example, lack of attainment of equilibrium for either the true liquid−solid or the liquid−gas equilibrium. In any case, the discrepancies are such that these results were not included in the fitted database.

Patil *et al.* (*77*) have recently measured vapor pressures for NaBr(aq) for temperatures from 303.15 to 343.15 K and for 2−8 mol·kg^{-1}. These values agree with the fitted equation within ±0.01−0.05 kPa, with the exception of their 7.981 mol·kg^{-1} solution; values for which disagree by up to 0.14 kPa. These measurements were also not of sufficient accuracy to include in the fitted database. A contributing factor to the imprecision was their fairly large uncertainty of 0.35% for solution molalities.

Figure 5 is a comparison of the direct vapor pressure measurements from Jakli and Van Hook (*56*) with the fitted model. Agreement is good, especially at 7 mol·kg^{-1}, and is improved over that of the earlier model (*1*).

Incorporation of enthalpy of solution results, now possible because of the treatment of S°_{2,m,T_r,p_r} as a variable parameter, resulted in a different weighting and representation of the 298.15 K enthalpy results. The concentration dependence of the enthalpy of solution results from Wüst and Lange (*64*) showed better agreement with the Wood *et al.* (*61*) enthalpies of dilution than with the Wallace (*59*) enthalpies of dilution. Comparison of all of these results with the present model is shown in Figure 6.

The temperature and molality for the NaBr(cr) + NaBr·2H$_2$O(cr) + NaBr(aq) + H$_2$O(g) invariant equilibria calculated from the model, 323.98 K and 11.38 mol·kg^{-1}, are in good agreement with values from Linke's (*13*) compilation, 324.15 K and 11.36 mol·kg^{-1}, and from Eddy and Menzies (*70*), 323.95 K and 11.39 mol·kg^{-1}. The literature is unclear concerning the existence of lower temperature invariant equilibria. Nikolaev and Ravich (*78*) report the existence of a pentahydrate solute from their solubility measurements; supporting evidence of this stoichiometry was lacking. Due to the uncertainty of the nature of lower temperature crystal phases, we do not present the thermodynamic properties of the low temperature eutectic points. The 298.15 K solubility calculated from the fitted equations is 9.191 mol·kg^{-1} and is between the values given in Table 3 and the value selected by Linke, both of which were described above. Figure 7 is a plot of the solubilities of NaBr(cr) and NaBr·2H$_2$O(cr) compared with the present model. Agreement is excellent from about 250 to 440 K.

Measurements of the solvent freezing point for temperatures of 270−252.3 K have been reported by Nikolaev and Ravich (*78*). Their value of $\Delta_{fus}T$, 3.1 K, for a 1.065 mol·kg^{-1} solution was different from the results from

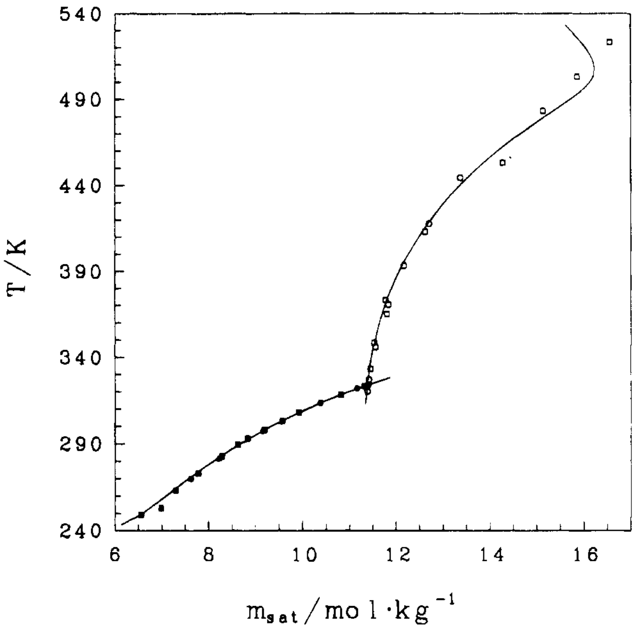

Figure 7. Solubilities of NaBr(cr) and NaBr·2H$_2$O(cr) compared to the fitted model: ■, ref 13 for NaBr·2H$_2$O(cr); □, ref 13 for NaBr(cr); ★, ref 13 for NaBr(cr) + NaBr·2H$_2$O(cr); ●, ref 70 for NaBr·2H$_2$O(cr); ○, ref 70 for NaBr(cr).

Table 7. Molar Gibbs Energy of Formation, Molar Enthalpy of Formation, and Molar Entropy of NaBr(cr) and NaBr·2H$_2$O(cr) for 298.15 K for 0.1 MPa Calculated from the Least-Squares Estimated Parameters

substance	$\Delta_f G°_m$/(kJ·mol^{-1})	$\Delta_f H°_m$/(kJ·mol^{-1})	$S°_m$/(J·K^{-1}·mol^{-1})
NaBr(cr)	−349.05	−361.147	86.82
NaBr·2H$_2$O(cr)	−828.53	−952.18	178.85

Scatchard and Prentiss (*46*) and from Damköhler and Weinzierl (*47*) by about 0.6 K. This can be taken as indicative of the magnitude of the error in Nikolaev and Ravich's values. Because of this large inaccuracy, their measurements (*78*) were not included in the fitted database. Comparison of values calculated from the fitted equations for 270−252.3 K with Nikolaev and Ravich's values gave a rms deviation of 0.4 K, which falls within the expected uncertainty of their values.

The 298.15 K, 0.1 MPa, standard-state enthalpy and Gibbs energy of formation of NaBr(cr) and NaBr·2H$_2$O(cr) can be calculated from the Gibbs energies of solution of NaBr(cr) and NaBr·2H$_2$O(cr) and the entropies of NaBr(aq), NaBr·2H$_2$O(cr), H$_2$O(l) (*4*), and NaBr(cr) (*1*) and the enthalpies of formation of NaBr(aq) (*4*) and of H$_2$O(l) (*4*). The calculated enthalpies and Gibbs energies of formation are given in Table 7. The uncertainties in the formation property values listed in Table 7 for NaBr·2H$_2$O(cr) are estimated to be 300−500 J·mol^{-1}, and for NaBr(cr) are estimated to be 300 J·mol^{-1}. The uncertainty given in Table 6 for the entropy of NaBr(aq) is not truly the uncertainty in this value. It is more properly considered as the uncertainty in the entropy of solution of NaBr(cr). This is because the entropy of NaBr(cr), taken from ref 79, appears in the calculations in combination with the entropy of NaBr(aq) to give $\Delta_{sol}S°_m$. The true uncertainty for the standard-state entropy of NaBr(aq) must contain the uncertainty in the entropy of NaBr(cr). The total uncertainty in $S°_m$ for NaBr(aq) is thus estimated to be ±0.5 J·K^{-1}·mol^{-1}. Small round-off errors may occur using the values in Table 7. This type of round-off error may be minimized by using the equations given in ref 1 and in the present work.

Values of various parameters and calculated values of ϕ and $\gamma_\pm$, against which trial calculations may be tested, are given in Tables 8−11. Values of ϕ at 298.15 K from Robinson and Stokes (*80*) and Hamer and Wu (*81*) show maximum differences from the present model of 0.6% and 1%, respectively. Because these earlier values are based on smaller databases and different choices of isopiestic reference standards, the agreement is quite reasonable.

CODATA Key Values for Thermodynamics. As stated above, in the previous representation of the experimental results for the NaBr + H$_2$O system (*1*) it was not possible to obtain consistency between all of the experimental results with thermodynamic equations. For lack of any better explanation, the blame at that time was laid upon the measurements of the enthalpy of solution of anhydrous NaBr(cr). Subsequent to that paper an attempt was made to represent the NaCl + H$_2$O system (*10*) in the same fashion as the NaBr + H$_2$O system. For the NaCl + H$_2$O system complete consistency of experiment and representation also could not be achieved; as in the NaBr + H$_2$O system, the discrepancy existed among different types of experimental measurements. Because the experimental results for NaCl + H$_2$O are more numerous and in better agreement with one another than is the case for NaBr, the cavalier dismissal of any particular type of thermodynamic measurement for that system was unacceptable. Refitting the NaCl + H$_2$O system without incorporation of the CODATA entropy of NaCl(aq) (*4*) resulted in an improved and excellent agreement of experiment and representation. With this knowledge, the NaBr + H$_2$O system was refitted without inclusion of the CODATA entropy of NaBr(aq). The resulting fit gave good agreement of experiment and representation for NaBr + H$_2$O, and this was obtained without exclusion of any particular type of thermodynamic measurement.

Thus, for both NaCl(aq) and NaBr(aq) there is an inability of the *CODATA Key Values for Thermodynamics* to agree completely with all of the different experimental results for these two aqueous systems, even though the experimental values are consistent with each other. Indeed, the differences of the key values from the measurements are several times larger than the uncertainties of the experiments. Because the thermodynamic values for most of the ions in the *CODATA Key Values for Thermodynamics* come from a representation of some of the thermodynamic results for many ions, it is reasonable to expect that the inability of the *CODATA Key Values for Thermodynamics* to accurately represent experimental

Table 8. Calculated Values of A_ϕ, $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, $C^{(0)}_{MX}$, and $C^{(1)}_{MX}$

T/K	p/MPa	A_ϕ/(kg$^{1/2}$·mol$^{-1/2}$)	$\beta^{(0)}_{MX}$/(kg·mol^{-1})	$\beta^{(1)}_{MX}$/(kg·mol^{-1})	$10^3C^{(0)}_{MX}$/(kg^2·mol^{-2})	$C^{(1)}_{MX}$/(kg^2·mol^{-2})
273.15	0.1	0.37642	0.125 915	0.210 395	−0.677 481	−0.119 507
298.15	0.1	0.39148	0.152 583	0.255 088	−2.298 80	−0.117 569
323	0.1	0.41015	0.158 797	0.288 871	−2.828 22	−0.099 304
373	0.1	0.45971	0.154 663	0.354 428	−3.122 67	−0.062 458
473	1.55	0.61683	0.126 051	0.510 300	−2.767 30	−0.006 129
573	8.6	0.95629	0.058 528	0.730 909	−0.203 18	0.126 968
598	12.	1.13291	0.028 314	0.803 928	1.433 41	0.225 700

Table 9. Calculated Values of $G^\circ_{m,2} - G^\circ_{m,2,T_r,p_r}$, $H^\circ_{m,2} - H^\circ_{m,2,T_r,p_r}$, $S^\circ_{m,2} - S^\circ_{m,2,T_r,p_r}$, $C^\circ_{p,\phi}$, and V°_ϕ

T/K	p/MPa	$(G^\circ_{m,2} - G^\circ_{m,2,T_r,p_r})$/(kJ·mol^{-1})	$(H^\circ_{m,2} - H^\circ_{m,2,T_r,p_r})$/(kJ·mol^{-1})	$(S^\circ_{m,2} - S^\circ_{m,2,T_r,p_r})$/(J·K^{-1}·mol^{-1})	$C^\circ_{p,\phi}$/(J·K^{-1}·mol^{-1})	V°_ϕ/(cm^3·mol^{-1})
273.15	0.1	3.673	3.492	12.32	−206.0	20.2
298.15	0.1	0.000	0.000	0.00	−77.1	24.0
323	0.1	−3.446	−1.804	−5.83	−51.6	25.5
373	0.1	−10.010	−5.101	−15.29	−61.3	25.2
473	1.55	−21.265	−19.074	−47.78	−200	12.7
573	8.6	−26.68	−80.73	−162.4	−1261	−68
598	12.0	−25.68	−136.18	−255.9	−3110	−157

Table 10. Calculated Values of the Osmotic Coefficient, ϕ

		ϕ				
T/K	p/MPa	m/(mol·kg^{-1}) = 0.1	m/(mol·kg^{-1}) = 0.5	m/(mol·kg^{-1}) = 1.0	m/(mol·kg^{-1}) = 4.0	m/(mol·kg^{-1}) = 8.0
273.15	0.1	0.9361	0.9262	0.9383	1.1483	1.5593
298.15	0.1	0.9377	0.9387	0.9616	1.1996	1.5587
323	0.1	0.9360	0.9413	0.9695	1.2185	1.5487
373	0.1	0.9281	0.9336	0.9646	1.2076	1.4863
473	1.55	0.8982	0.8868	0.9070	1.0836	1.2650
573	8.6	0.8269	0.7713	0.7688	0.8542	0.9797

Table 11. Calculated Values of the Stoichiometric Activity Coefficient, $\gamma_\pm$

		$\gamma_\pm$				
T/K	p/MPa	m/(mol·kg^{-1}) = 0.1	m/(mol·kg^{-1}) = 0.5	m/(mol·kg^{-1}) = 1.0	m/(mol·kg^{-1}) = 4.0	m/(mol·kg^{-1}) = 8.0
273.15	0.1	0.7866	0.6945	0.6699	0.8330	1.5755
298.15	0.1	0.7860	0.7081	0.6989	0.9431	1.7371
323	0.1	0.7791	0.7047	0.7017	0.9774	1.7603
373	0.1	0.7559	0.6747	0.6707	0.9234	1.5463
473	1.55	0.6797	0.5612	0.5324	0.6123	0.8280
573	8.6	0.5323	0.3623	0.3077	0.2535	0.2700

results, such as those for NaCl(aq) and for NaBr(aq), will exist for other aqueous ions. It is important to note that the *CODATA Key Values for Thermodynamics* text does not describe a consideration of the entropy of solution of the aqueous ions as obtained from the temperature dependences of the solubility and the activity coefficient. Lack of incorporation of these experimental results removes the largest portion of the thermodynamic consistency check from the set of possible considered experimental values. Thus, it is not surprising that the key values disagree with a more complete analysis of experimental results for NaBr(aq) and NaCl(aq) by several times the expected uncertainties of the experiments.

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Glossary

A	parameter of eqs 1 and 2
A_ϕ, A_H, A_C, A_V	Debye−Hückel coefficients for osmotic coefficient, apparent molar enthalpy, apparent molar constant-pressure heat capacity, and apparent molar volume
a_w	activity of water in a solution
b	a constant in Pitzer's ion-interaction equation, chosen to be 1.2 kg$^{1/2}$·mol$^{-1/2}$
$b_{1,j}$, $b_{2,j}$	parameters for the temperature dependence of the second virial coefficient in Pitzer's equations
$b_{3,j}$, $b_{4,j}$	parameters for the temperature dependence of the third virial coefficient in Pitzer's equations
$b_{5,j}$	parameters for the temperature and pressure dependence of the volume of a quantity of solution containing 1 kg of water in Pitzer's equations
$b_{6,j}$	parameters for the temperature dependence of the heat capacity of a volume of solution containing 1 kg of water in Pitzer's equations
C_p°	1.0 kJ·mol^{-1}·K^{-1}
$C_{p,\phi}$	apparent molar constant-pressure heat capacity
$C^\circ_{p,m,2}$	standard-state constant-pressure molar heat capacity of the solute
$C^\circ_{p,m,cr}$	standard-state constant-pressure molar heat capacity of a crystalline phase
$c_{p,s}$	specific constant-pressure heat capacity of a solution
$c_{p,w}$	specific constant-pressure heat capacity of 1 kg of water
$C_p(m_r)$	constant-pressure heat capacity of a quantity of solution of molality m_r and containing 1 kg of solvent
C_{MX}, $C^{(0)}_{MX}$, $C^{(1)}_{MX}$	ion-interaction parameters for Pitzer's equation
G	Gibbs energy (extensive)
G^E	excess Gibbs energy of a solution (extensive)
$G^\circ_{m,1}$, $G^\circ_{m,2}$	standard-state molar Gibbs energies of the solvent and the solute, respectively
$G^\circ_{m,cr}$	standard-state molar Gibbs energy of a crystalline phase
$G^\circ_{m,1,g}$	standard-state molar Gibbs energy of the solvent gas phase
$H^\circ_{m,cr}$	standard-state molar enthalpy of a crystalline phase
I	ionic strength ($I = 0.5\Sigma m_i z_i^2$)
I_r	reference ionic strength at molality m_r
L_ϕ	relative apparent molar enthalpy

M_1	molar mass of the solvent, 18.0153 × 1v0^{-3} kg·mol^{-1}
m	molality
m°	1.0 mol·kg^{-1}
m_r	reference molality
m_0	molality of NaBr stock solution from dehydration analysis
m^*	molality of the isopiestic reference standard solution (NaCl, H_2SO_4, or $CaCl_2$)
n_i	number of moles of the *i*th substance
n_r	number of moles of solute in an amount of solution of molality m_r containing 1 kg of solvent
p	pressure
p°	1.0 MPa
p_s	vapor pressure of the solution
p_w	vapor pressure of pure water
p_r	reference pressure; as a subscript to a property it denotes that the value of the property is that for the reference pressure
R	gas constant, 8.3144 × 10^{-3} kJ·mol^{-1}·K^{-1}
S^E	excess entropy of a solution (extensive)
$S^\circ_{m,cr}$	standard-state molar entropy of a crystalline phase
$S^\circ_{1,m}$, $S^\circ_{2,m}$	standard-state molar entropies of the solvent and the solute
T	temperature
T°	1.0 K
T_r	reference temperature; as a subscript to a property it denotes that the value of the property is that for the reference temperature; the value of T_r was chosen to be 298.15 K
V°	1.0 cm^3·mol^{-1}
V_ϕ	apparent molar volume
$V(m_r)$	volume of a quantity of solution of molality m_r containing 1 kg of solvent
z_M, z_X	charges of ions M and X
α	a constant in Pitzer's equation, chosen to be 2.0 kg$^{1/2}$·mol$^{-1/2}$
α_2	a constant in revised Pitzer's equation, eq 4b, chosen to be 1.7 kg$^{1/2}$·mol$^{-1/2}$
$\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$	ion-interaction parameters in Pitzer's ion-interaction equation
$\Delta_f G^\circ_m$	standard-state molar Gibbs energy change for formation from the elements
$\Delta_{dec} G^\circ_m$	standard-state molar Gibbs energy change for decomposition of a material
$\Delta_{sol} G^\circ_{anhydrous}$	standard-state molar Gibbs energy change for solution of an anhydrous solute
$\Delta_{sol} G^\circ_{dihydrate}$	standard-state molar Gibbs energy change for solution of a dihydrate solute
$\Delta_f H^\circ_m$	standard-state molar enthalpy change for formation from the elements
$\Delta_{fus} T$	difference in the freezing point temperature for a solvent from a solution and the pure solvent
$\Delta_{dil} V_\phi$	change in apparent molar volume for a change in molality
$\gamma_\pm$	stoichiometric mean activity coefficient of the solute
ϕ	molal (practical) osmotic coefficient
ϕ^*	molal (practical) osmotic coefficient of the reference electrolyte
ϱ	density
ϱ_s	density of the solution
ϱ_w	density of water
ϱ°	1.0 g·cm^{-3}
σ_{exp}	estimated root-mean-square difference (unweighted) of a set of experimental results, used in calculating the weighting factors for the least squares representation
σ_{fit}	root-mean-square difference (unweighted) of a set of experimental results from the fitted equations
ν	$\nu_M + \nu_X$
ν_M, ν_X	stoichiometric numbers of M and X ions in the electrolyte $M_{\nu_M}X_{\nu_X}$
ν^*	ionization number for complete dissociation of the isopiestic reference standard
v_w	olume of 1 kg of water

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