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Enthalpies of Dilution of $\text{NdCl}_3(\text{aq})$ at Temperatures from 297.89 K to 372.08 K and an Extended Pitzer Ion-Interaction Model for the $\text{NdCl}_3 + \text{H}_2\text{O}$ System

Charles S. Oakes[†]

OLI Systems, 108 American Road, Morris Plains, New Jersey 07950

Joseph A. Rard[‡]

Energy and Environment Directorate, Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

Donald G. Archer^{*,§}

Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8381

Enthalpy of dilution measurements were made for $\text{NdCl}_3(\text{aq})$ over the molality range 0.0080 mol·kg⁻¹ to 2.6883 mol·kg⁻¹ at temperatures from 297.89 K to 372.08 K and at a fixed pressure of 0.5 MPa. Published values of osmotic coefficients, emf's of a reversible electrochemical cell, enthalpies of dilution, apparent molar heat capacities, and apparent molar volumes of $\text{NdCl}_3(\text{aq})$ were critically assessed, and the more reliable of these results were combined with the present enthalpies of dilution to yield the parameters of an extended form of Pitzer's ion-interaction model valid to high molalities and for the temperature range 280 K to 375 K. Values of the solubility and enthalpy of solution of the hexahydrate crystal and the enthalpy of solution of the anhydrous crystal were also included in the data representation, leading to new standard properties for the solution processes of both of these crystal phases.

Introduction

Neodymium, like many of the other rare earth element metals, has important industrial uses. In particular, powerful magnets comprised of Nd, Fe, and B became available in the 1980s, and one of these, $\text{Nd}_2\text{Fe}_{14}\text{B}$, is more powerful than any discovered previously. In addition, Nd(III) compounds are used to produce a characteristic purple color in glasses and ceramic materials,¹ including glass used in welder's goggles. Neodymium-147 is a major fission product produced in high yield in nuclear reactors, although, because of its short half-life of 11 days for β^- decay,

it is not of major concern for radioactive waste management.²

Thermodynamic data for solutions of the trivalent actinide ions, especially Pu(III) and Np(III), are needed for many radioactive waste management applications. However, thermodynamic data are scarce for aqueous solutions of their salts,³ in part because of the difficulties involved with studying the properties of their highly radioactive isotopes and especially because of the difficulties in keeping plutonium and neptunium reduced to the trivalent state long enough to perform the desired thermodynamic measurements. During aqueous solubility measurements for the hydrous oxides, for example, solutions of plutonium and neptunium typically exist as a mixture of ions in several different valence states, and it is thus necessary to determine the fraction of that element present in each valence state at the end of the experiment. Because of these difficulties, thermodynamic measurements are sometimes made instead using a nonradioactive surrogate possessing similar chemical properties but whose trivalent ion is stable in aqueous solutions under the experimental conditions of interest.

Neodymium has become the surrogate of choice at Pacific Northwest National Laboratory for estimating the thermodynamic properties of aqueous Pu(III) solutions, of Np(III) solutions, and of their solid compounds.⁴ Extensive previous thermodynamic measurements are available for $\text{NdCl}_3(\text{aq})$, $\text{Nd}(\text{ClO}_4)_3(\text{aq})$, and $\text{Nd}(\text{NO}_3)_3(\text{aq})$, but nearly all of these studies are restricted to 298.15 K.

[†] E-mail: OakesCS@netscape.net.

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The system of greatest interest to us is $\text{NdCl}_3(\text{aq})$. Several sets of thermodynamic data at 298.15 K from Spedding's laboratory extend from low molalities to the saturated solutions: isopiestic vapor pressures,^{5,6} enthalpies of dilution,⁷ heat capacities,⁸ and densities/apparent molar volumes.⁹ In addition, they reported measurements at lower molalities of the emf's of concentration cells with transference for $\text{NdCl}_3(\text{aq})$,^{10,11} enthalpies of dilution,¹² densities/partial molar volumes,¹³ and also enthalpies of solution of $\text{NdCl}_3(\text{cr})$ and $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr})$ in water.^{7,12,14} Their only thermodynamic study of $\text{NdCl}_3(\text{aq})$ at other temperatures is of the densities/apparent molar volumes at temperatures from 278.206 K to 352.891 K.¹⁵ A few thermodynamic studies for $\text{NdCl}_3(\text{aq})$ have been reported at other laboratories: isopiestic measurements at 298.15 K^{16,17} and 293.15 K,¹⁸ emf measurements for concentration cells with transport at 293.15 K,¹⁸ and enthalpies of solution of $\text{NdCl}_3(\text{cr})$ in water at 298.15 K¹⁹ and for the temperature range (287.95 to 365.99) K.²⁰

Cordfunke and Konings^{21,22} have critically assessed the enthalpies of formation and of solution of various $\text{RCl}_3(\text{cr})$, where R denotes a rare earth element, and recommended $\Delta_f H_m^\circ(\text{NdCl}_3(\text{cr}), T = 298.15 \text{ K}) = -(1040.9 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H_m^\circ(\text{Nd}^{3+}(\text{aq}), T = 298.15 \text{ K}) = -(694.8 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$. Spedding et al.²³ similarly obtained $\Delta_{\text{sol}} H_m^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T = 298.15 \text{ K}) = -(38.14 \pm 0.17) \text{ kJ} \cdot \text{mol}^{-1}$ as the average from three concordant studies, $\Delta_{\text{sol}} H_m^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T = 298.15 \text{ K}) = -(34.5 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_{\text{sol}} G_m^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T = 298.15 \text{ K}) = -27.85 \text{ kJ} \cdot \text{mol}^{-1}$. The entropy of solution of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr})$ is an integral part of the information required for determining the standard entropy of the $\text{Nd}^{3+}(\text{aq})$ ion, $S_m^\circ(\text{Nd}^{3+}(\text{aq}), T = 298.15 \text{ K})$. Morss²⁴ has reviewed thermodynamic data needed for calculation of the standard thermodynamic properties of aqueous rare earth ions.

Shock and Helgeson²⁵ derived a value of the standard heat capacity, $C_{p,m,2}^\circ(\text{Nd}^{3+}(\text{aq}), T = 298.15 \text{ K}) = -181 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, from an analysis of the heat capacities of $\text{NdCl}_3(\text{aq})$ from Spedding and Jones⁸ and of $\text{Nd}(\text{ClO}_4)_3(\text{aq})$ from Spedding et al.²⁶ Puigdomenech et al.²⁷ and Xiao and Tremaine²⁸ have argued that Shock and Helgeson's value of $C_{p,m,2}^\circ(\text{Nd}^{3+}(\text{aq}), T = 298.15 \text{ K})$ is too negative by about $70 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Xiao and Tremaine obtained a more reliable and much less negative value of $C_{p,m,2}^\circ(\text{Nd}^{3+}(\text{aq}), T = 298.15 \text{ K}) = -111.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ based on flow microcalorimetric measurements using $\text{Nd}(\text{ClO}_4)_3(\text{aq})$ solutions acidified with HClO_4 .

Heat capacities of $\text{NdCl}_3(\text{aq})$ and other $\text{Nd}^{3+}(\text{aq})$ salts at temperatures other than 298.15 K are rather limited. Krestkov et al.²⁰ measured the enthalpies of solution of $\text{NdCl}_3(\text{cr})$ in $\text{H}_2\text{O}(\text{l})$ at temperatures from 287.95 K to 365.99 K, extrapolated these results to infinite dilution to obtain the standard enthalpy of solution $\Delta_{\text{sol}} H_m^\circ(\text{NdCl}_3(\text{cr}), T)$, and used the variation of this quantity with temperature to estimate the standard heat capacity change for dissolution $\Delta_{\text{sol}} C_{p,m}^\circ(\text{NdCl}_3(\text{cr}), T)$ at temperatures from 273.15 K to 373.15 K. This approach is basically the "integral heat" method described by Jekel et al.²⁹ The resulting values of $\Delta_{\text{sol}} C_{p,m}^\circ(\text{NdCl}_3(\text{cr}), T)$ may be added to the heat capacities of $\text{NdCl}_3(\text{cr})$, $C_{p,m}^\circ(\text{NdCl}_3(\text{cr}), T)$, to yield $C_{p,m,2}^\circ(\text{NdCl}_3(\text{aq}), T)$. The values of $C_{p,m}^\circ(\text{NdCl}_3(\text{cr}), T)$ necessary for this analysis are available from 5.31 K to 348.81 K.³⁰ However, the "integral heat" method of obtaining heat capacities involves taking the small differences between large enthalpies of solution, and it could be subject to large errors, depending on how the heat capacity of solution is calculated. Unfortunately, Krestkov et al.²⁰ did not report

the experimental enthalpies of solution, so it is not possible to estimate the precision or accuracy of their derived values of $\Delta_{\text{sol}} C_{p,m,2}^\circ(\text{NdCl}_3(\text{cr}), T)$.

Besides their measurements at 298.2 K, Xiao and Tremaine²⁸ reported apparent molar heat capacities and apparent molar volumes of aqueous $\text{Nd}(\text{ClO}_4)_3$ solutions containing excess HClO_4 at temperatures of 283.2 K, 313.2 K, and 328.2 K. These properties may be corrected for the presence of HClO_4 and extrapolated to infinite dilution to yield the corresponding standard partial molar heat capacities $C_{p,m,2}^\circ(\text{Nd}(\text{ClO}_4)_3(\text{aq}), T)$ and standard partial molar volumes $V_{m,2}^\circ(\text{Nd}(\text{ClO}_4)_3(\text{aq}), T)$ for unacidified $\text{Nd}(\text{ClO}_4)_3(\text{aq})$ at these four temperatures. The results may then be used to calculate the corresponding $C_{p,m,2}^\circ(\text{NdCl}_3(\text{aq}), T)$ and $V_{m,2}^\circ(\text{NdCl}_3(\text{aq}), T)$ using the additive properties of ionic partial molar heat capacities and ionic partial molar volumes at infinite dilution. In anticipation of this analysis, Oakes and Rai³¹ compiled and critically analyzed available thermodynamic data for $\text{HClO}_4(\text{aq})$. Unfortunately, the uncertainty of the available data for $\text{HClO}_4(\text{aq})$ introduces significant errors into the additivity-calculated values for $C_{p,m,2}^\circ(\text{NdCl}_3(\text{aq}))$. We estimate these errors contribute approximately $\pm 30 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ at 300 K to the additivity-calculated values. Nonetheless, values of $C_{p,m,2}^\circ(\text{NdCl}_3(\text{aq}))$ obtained from an additivity relation involving Xiao and Tremaine's $\text{Nd}(\text{ClO}_4)_3$ measurements were useful in the resolution of two conflicting data sets. However, we did not consider the additivity-calculated values to be sufficiently accurate to use as a replacement of variables in our representation of the $\text{NdCl}_3(\text{aq})$ data.

Pitzer et al.³² represented the thermodynamic data for the various $\text{RCl}_3(\text{aq})$, $\text{R}(\text{ClO}_4)_3(\text{aq})$, and $\text{R}(\text{NO}_3)_3(\text{aq})$ at 298.15 K using the usual three-parameter form of Pitzer's ion-interaction model.³³ The quality of the representations of the thermodynamic data over the whole molality range was adequate for $\text{RCl}_3(\text{aq})$ even to saturation, but for $\text{R}(\text{ClO}_4)_3(\text{aq})$ and $\text{R}(\text{NO}_3)_3(\text{aq})$ it was necessary to restrict the molality ranges being represented to obtain model fits of comparable accuracy. For these salts, the highest molality included in data representations varied with the individual salt and with the property being modeled; these molality ranges were consequently restricted to values of $\leq 1.4 \text{ mol} \cdot \text{kg}^{-1}$ to $\leq 2.2 \text{ mol} \cdot \text{kg}^{-1}$. If $\text{R}(\text{ClO}_4)_3(\text{aq})$ and $\text{R}(\text{NO}_3)_3(\text{aq})$ data at higher molalities were included in calculations for the same three-parameter equations, the result was a considerable degradation of the quality of the fits and large systematic deviations between the parametrized model and the experimental values. Archer^{34,35} subsequently introduced an ionic strength dependence for the third virial coefficient of Pitzer's model, which extends the molality range and improves the accuracy of the representations of thermodynamic data, especially for very soluble electrolytes. This approach has been further generalized to include higher order virial terms.³⁶ These extended equations have not previously been applied to rare earth salt solutions.

Because of the paucity of published thermodynamic data for $\text{NdCl}_3(\text{aq})$ at temperatures other than 298.15 K, new enthalpy of dilution measurements were made for the temperature range 297.89 K to 372.08 K, for molalities ranging up to $2.6883 \text{ mol} \cdot \text{kg}^{-1}$, and at a pressure of 0.5 MPa. Published thermodynamic data for $\text{NdCl}_3(\text{aq})$ were critically assessed and recalculated for consistency, and the more reliable of these published results were combined with our new enthalpies of dilution and used to evaluate the parameters of Archer's^{34,35} extended form of Pitzer's model.

Experimental Section

All experimental measurements were made at Pacific Northwest National Laboratory (PNNL).

Solution Preparations and Molality Determination.

A concentrated stock solution of $\text{NdCl}_3(\text{aq})$ was prepared using Alfa/AESAR reaction grade $\text{Nd}_2\text{O}_3(\text{s})$, lot P3229A, and Fisher "trace metal grade" concentrated $\text{HCl}(\text{aq})$, lot 418030, using the basic procedure described by Spedding et al.¹³ An excess of this $\text{Nd}_2\text{O}_3(\text{s})$ was reacted with $\text{HCl}(\text{aq})$, and the reaction mixture was then heated to increase the reaction rate. After most of the Nd_2O_3 had reacted, the excess oxide was removed using coarse filter paper. The remaining fine particles of unreacted oxide and larger colloids were subsequently removed by filtering the solution through a $0.2\ \mu\text{m}$ nylon membrane filter. The equivalence pH of the $\text{NdCl}_3(\text{aq})$ was obtained as follows. The pH values were obtained using a commercial digital pH meter that was calibrated with standard buffer solutions. The titration was conducted with $(0.1000 \pm 0.0005)\ \text{mol}\cdot\text{dm}^{-3}\ \text{HCl}(\text{aq})$ added in aliquots from a weight buret. After each addition, the pH was allowed to stabilize and was then recorded. This titration curve, which was S-shaped in accord with the titration of a weak base with a strong acid, yielded an equivalence point $\text{pH} = 2.85$ for the $\text{NdCl}_3(\text{aq})$ solution. The remainder of the stock solution was adjusted to $\text{pH} \approx 2.7$ using the same dilute $\text{HCl}(\text{aq})$, and the solution was then heated overnight, which caused the pH to increase slightly. This pH adjustment and heating procedure were repeated several more times until a stable $\text{pH} \approx 2.8$ was achieved. According to Spedding et al.,¹³ solutions prepared in this manner are free of colloidal material and hydrolyzed rare earth ions and have the correct stoichiometric 3:1 ratio of Cl^- to R^{3+} .

The purity of the reaction grade $\text{Nd}_2\text{O}_3(\text{s})$ used for preparation of the $\text{NdCl}_3(\text{aq})$ primary stock solution, as specified by the supplier, was 99.99% on a rare earth oxide basis. A certificate of analysis for this particular lot, based on an unspecified emission spectroscopic technique, gave the measured mass fraction impurity concentrations as being 2×10^{-6} each of Sm and Gd, 5×10^{-6} each of Pr and Yb, 7×10^{-6} each of Dy and Er, 3×10^{-6} of Mg, 1.5×10^{-5} of Ca, 2.0×10^{-5} of Al, and 2.5×10^{-5} of Si. Water used in preparing solutions and for the enthalpy of dilution experiments was purified first by reverse osmosis, followed by passage through a Millipore deionization unit.

The molality of the primary $\text{NdCl}_3(\text{aq})$ stock solution was determined to be $(2.6883 \pm 0.0020)\ \text{mol}\cdot\text{kg}^{-1}$, by quantitative conversion of duplicate mass aliquots to anhydrous $\text{Nd}_2(\text{SO}_4)_3(\text{s})$, followed by determining the masses of the residues.³⁷ Buoyancy corrections were made for the $\text{NdCl}_3(\text{aq})$ stock solution using the densities from Spedding et al.⁹ and for $\text{Nd}_2(\text{SO}_4)_3(\text{s})$ using the density from Sirotinkin et al.³⁸ The assumed molar masses are $250.60\ \text{g}\cdot\text{mol}^{-1}$ for NdCl_3 and $576.67\ \text{g}\cdot\text{mol}^{-1}$ for $\text{Nd}_2(\text{SO}_4)_3$. Two secondary $\text{NdCl}_3(\text{aq})$ stock solutions were subsequently prepared by mass dilution of the concentrated primary stock solution with purified $\text{H}_2\text{O}(\text{l})$, and duplicate analyses of each solution yielded molalities of $(0.4950 \pm 0.0003)\ \text{mol}\cdot\text{kg}^{-1}$ and $(0.079\ 83 \pm 0.000\ 06)\ \text{mol}\cdot\text{kg}^{-1}$.

As noted above, the equivalence pH of our $(2.6883 \pm 0.0020)\ \text{mol}\cdot\text{kg}^{-1}\ \text{NdCl}_3(\text{aq})$ solution at room temperature was determined to be $\text{pH} = 2.85$ by potentiometric pH titration. Examination of Figure 7 of Spedding et al.,³⁹ which is a plot of the pHs of stoichiometric $\text{RCl}_3(\text{aq})$ solutions as a function of molality, indicates that a $2.7\ \text{mol}\cdot\text{kg}^{-1}\ \text{NdCl}_3(\text{aq})$ solution should have $\text{pH} \approx 2.5$, which is slightly more acidic. The effect of these small pH

differences on the enthalpies of dilution should be insignificant.

Calorimeter and Measurement Technique. The enthalpies of dilution were measured using a SETARAM Inc. (France), C80 II, Calvet-type dilution calorimeter. The experimental procedures used for measuring the enthalpies of dilution are essentially the same as those described by Oakes et al.⁴⁰ for their $\text{Ca}(\text{NO}_3)_2(\text{aq})$ measurements, and the detailed information need not be repeated here. Solutions of $\text{NdCl}_3(\text{aq})$ are fairly viscous at high molalities, and Oakes et al.⁴⁰ found that the usual SETARAM flow-through mixing cell may give erroneous results for very viscous solutions due to incomplete mixing of the solutions with $\text{H}_2\text{O}(\text{l})$ in the mixing chamber. In addition, $\text{NdCl}_3(\text{aq})$ solutions are acidic and contain high molalities of chloride ion, a combination that is corrosive to some metals and alloys, especially at high temperatures. Consequently, all enthalpy of dilution measurements were made using a flow-through mixing cell constructed at PNNL. All of the heated tubing in this cell (i.e., the mixing chamber and the inflow and outflow lines within the body of the calorimeter) was constructed from platinum–rhodium alloy. A detailed schematic diagram of this mixing cell and a description of its features are given in the Appendix of ref 40.

Table 1 summarizes the experimental enthalpies of dilution, along with the molality of each $\text{NdCl}_3(\text{aq})$ solution before and after it was mixed with water, and the average solution temperature during that series of experiments.

Consideration of Hydrolysis, Hydration, and Complex Formation in $\text{RCl}_3(\text{aq})$ Solutions

Aqueous solutions of the trivalent rare earth ions, depending on their molality and pH, may undergo hydrolysis to form $\text{R}(\text{OH})^{2+}$, $\text{R}(\text{OH})_2^+$, $\text{R}(\text{OH})_3^0$, $\text{R}_2(\text{OH})_2^{4+}$, $\text{R}_2(\text{OH})_3^{3+}$, and other small hydroxy polymers.⁴¹ However, because of the insolubility of the rare earth trihydroxides and basic salts, the molalities of the dissolved rare earth hydroxy species are never large. The equivalent pHs of $\text{NdCl}_3(\text{aq})$ solutions are also rather acidic, which suppresses the formation of higher order hydroxy complexes. Thus, we need only consider the first hydrolysis step:



Klungness and Byrne⁴² reported that $\log_{10} \beta_1^\circ = -8.18$ at 298.15 K and $\Delta_r H_m^\circ = (41 \pm 8)\ \text{kJ}\cdot\text{mol}^{-1}$, from which we conclude that the contribution of hydrolysis to the thermodynamic properties of our $\text{NdCl}_3(\text{aq})$ solutions is negligible under the experimental conditions at lower temperatures and is probably only a minor factor at the higher temperatures.

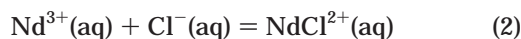
In the absence of hydrolysis and significant complex formation, the $\text{R}^{3+}(\text{aq})$ ions undergo a decrease of one water in their primary hydration number in going from $\text{La}^{3+}(\text{aq})$ to $\text{Lu}^{3+}(\text{aq})$, as a result of the lanthanide contraction.^{13,32,41,43,44} Xiao and Tremaine²⁸ pointed out that if some of the intermediate $\text{R}^{3+}(\text{aq})$ exist as equilibrium mixtures of the two primary hydration numbers, then there would be a contribution to the apparent molar heat capacities of their solutions resulting from the change in equilibrium composition with respect to temperature. However, there is no published determination of the variation of this primary hydration number equilibrium with temperature for the $\text{R}^{3+}(\text{aq})$.

Table 1. Measured Values of the Molar Enthalpies of Dilution, $\Delta_{\text{dil}}H_m^a$

$m_i/\text{mol}\cdot\text{kg}^{-1}$	$m_f/\text{mol}\cdot\text{kg}^{-1}$	$\Delta_{\text{dil}}H_m/\text{J}\cdot\text{mol}^{-1}$	$\{\Delta_{\text{dil}}H_m(\text{obs}) - \Delta_{\text{dil}}H_m(\text{calc})\}/\text{J}\cdot\text{mol}^{-1}$	$m_i/\text{mol}\cdot\text{kg}^{-1}$	$m_f/\text{mol}\cdot\text{kg}^{-1}$	$\Delta_{\text{dil}}H_m/\text{J}\cdot\text{mol}^{-1}$	$\{\Delta_{\text{dil}}H_m(\text{obs}) - \Delta_{\text{dil}}H_m(\text{calc})\}/\text{J}\cdot\text{mol}^{-1}$
Series 1, $T_{\text{ave}} = 297.89$ K, $\sigma_{\text{rms}}(\Delta_{\text{dil}}H_m) = 421$ J·mol ⁻¹							
2.6883	2.1859	-3 339 (-3 487) ^b	109	2.6883	0.7619	-10 719 (-11 306) ^b	518
2.6883	1.8358	-5 379 (-5 652) ^b	206	2.6883	0.4401	-12 285 (-12 988) ^b	658
2.6883	1.2902	-8 209 (-8 658) ^b	359				
Series 2, $T_{\text{ave}} = 322.63$ K, $\sigma_{\text{rms}}(\Delta_{\text{dil}}H_m) = 517$ J·mol ⁻¹							
2.6883	2.1859	-4 572	-32	2.6883	0.7619	-15 505	628
2.6883	1.8358	-7 473	70	2.6883	0.4401	-18 019	744
2.6883	1.2902	-11 663	331	2.6883	0.2500	-19 893	733
Series 3, $T_{\text{ave}} = 322.61$ K, $\sigma_{\text{rms}}(\Delta_{\text{dil}}H_m) = 312$ J·mol ⁻¹							
0.4950	0.3454	-1461	-120	0.4950	0.0859	-5395	-459
0.4950	0.2462	-2499	-205	0.4950	0.0490	-6256	-170
0.4950	0.1474	-3888	-177	0.4950	0.0490	-6593 ^c	-508
Series 4, $T_{\text{ave}} = 322.62$ K, $\sigma_{\text{rms}}(\Delta_{\text{dil}}H_m) = 494$ J·mol ⁻¹							
0.07983	0.0559	-899	-166	0.079 83	0.0140	-2894	251
0.07983	0.0399	-1621	-236	0.079 83	0.0080	-4886	-977
0.07983	0.0239	-1952	347				
Series 5, $T_{\text{ave}} = 347.36$ K, $\sigma_{\text{rms}}(\Delta_{\text{dil}}H_m) = 297$ J·mol ⁻¹							
2.6883	2.1859	-5 719	-294	2.6883	0.7619	-20 348	273
2.6883	1.8358	-9 422	-221	2.6883	0.4401	-23 809	409
2.6883	1.2902	-15 140	-106	2.6883	0.2500	-26 369	480
2.6883	1.2902	-15 010 ^c	24				
Series 6, $T_{\text{ave}} = 347.34$ K, $\sigma_{\text{rms}}(\Delta_{\text{dil}}H_m) = 237$ J·mol ⁻¹							
0.4950	0.3454	-2 123	-259	0.4950	0.0859	-7 056	98
0.4950	0.2462	-3 570	-224	0.4950	0.0490	-8 504	382
0.4950	0.1474	-5 392	-83				
Series 7, $T_{\text{ave}} = 347.35$ K, $\sigma_{\text{rms}}(\Delta_{\text{dil}}H_m) = 393$ J·mol ⁻¹							
0.079 83	0.0559	-1153	-47	0.079 83	0.0140	-4238	434
0.079 83	0.0399	-2043	40	0.079 83	0.0140	-5039 ^c	-367
0.079 83	0.0239	-2807	629	0.079 83	0.0080	-5323	450
Series 8, $T_{\text{ave}} = 372.08$ K, $\sigma_{\text{rms}}(\Delta_{\text{dil}}H_m) = 341$ J·mol ⁻¹							
2.6883	2.1859	-6 760	-521	2.6883	0.7620	-25 346	-95
2.6883	1.8358	-11 399	-609	2.6883	0.4401	-29 970	-20
2.6883	1.2902	-18 472	-390	2.6883	0.4189	-30 512	-216
2.6883	0.8488	-24 332	-273	2.6883	0.2500	-33 451	54
Series 9, $T_{\text{ave}} = 372.07$ K, $\sigma_{\text{rms}}(\Delta_{\text{dil}}H_m) = 391$ J·mol ⁻¹							
0.4950	0.4076	-1745	-350	0.4950	0.1474	-7315	-58
0.4950	0.3454	-2830	-349	0.4950	0.0859	-9523	369
0.4950	0.2462	-4782	-279	0.4950	0.0490	-11 693	674
Series 10, $T_{\text{ave}} = 372.06$ K, $\sigma_{\text{rms}}(\Delta_{\text{dil}}H_m) = 522$ J·mol ⁻¹							
0.079 83	0.0559	-1584	-3	0.079 83	0.0239	-4571 ^c	313
0.079 83	0.0399	-2772	201	0.079 83	0.0140	-5465	1146
0.079 83	0.0399	-2834 ^c	139	0.079 83	0.0140	-5897 ^c	714
0.079 83	0.0239	-4442	442	0.079 83	0.0080	-8154	-20

^a The initial and final molalities are m_i and m_f , respectively, T_{ave} is the mean temperature for each series of measurements; all measurements were made at the fixed pressure 0.5 MPa. The values of $\sigma_{\text{rms}}(\Delta_{\text{dil}}H_m)$ are the unweighted root mean square errors for the individual series of experiments relative to the accepted extended Pitzer model fit. These error values reflect a combination of the experimental error, the possible systematic bias of the extended Pitzer model, and the consistency of the present measurements with other thermodynamic data for $\text{NdCl}_3(\text{aq})$ included in the model. ^b These are values of $\Delta_{\text{dil}}H_m = L_\phi(m_i) - L_\phi(m_f)$ that were calculated for these initial and final molalities using eq 7 of Spedding et al.⁷ The values from this earlier study pertain to the slightly higher temperature of $T_{\text{ave}} = 298.15$ K and the lower pressure of 0.1 MPa. Adjustment for the 0.26 K temperature difference will reduce the differences by about 10%. ^c This experiment and the one given immediately above are replicate enthalpy of dilution measurements, using the same ratio of masses of $\text{NdCl}_3(\text{aq})$ and $\text{H}_2\text{O}(\text{l})$.

Solutions of $\text{NdCl}_3(\text{aq})$ also undergo some complex formation:



At high chloride-to-neodymium ratios, $\text{NdCl}_2^{+}(\text{aq})$ and possibly higher order chloride complexes may also form. Millero⁴⁵ used Pitzer's ion-interaction model³³ to extrapolate published stability constants for reaction 2 to infinite dilution at the temperature 298.15 K and obtained $\log_{10} \beta_1^{\circ} = 0.32$. Subsequently, Gammons et al.⁴⁶ studied the variation of the solubility of $\text{AgCl}(\text{cr})$ in aqueous solutions of NdCl_3 containing mixtures of NaCl and HCl ,

and of $\text{Nd}_2\text{O}_3(\text{s})$ in aqueous HCl , over a wide range of temperature and ionic strength. These results were used by them to derive the following values for the cumulative association constants: $\log_{10} \beta_1^{\circ} = 0.06 \pm 0.5$ and $\log_{10} \beta_2^{\circ} = -0.38 \pm 0.5$ at 298.15 K, $\log_{10} \beta_1^{\circ} = 0.21 \pm 0.3$ and $\log_{10} \beta_2^{\circ} = -0.33 \pm 0.5$ at 323.15 K, and $\log_{10} \beta_1^{\circ} = 0.66 \pm 0.2$ and $\log_{10} \beta_2^{\circ} = 0.13 \pm 0.5$ at 373.15 K.

Although these association constants imply that formation of the monochloroneodymium(III) and dichloroneodymium(III) complexes may become extensive at higher molalities, these complexes are believed to be of the outer sphere type.^{6,7,9,15,39} The calculations reported by Pitzer et al.³² at 298.15 K imply that the thermodynamic effects of

Table 2. Summary of the Fitted Thermodynamic Data for NdCl₃(aq)

ref	<i>m</i> /mol·kg ⁻¹	<i>T</i> /K	no. ^a	property	σ_{est}^b	σ_{rms}^c
16	0.07–2.05	298.15	33	ϕ	0.005	0.0087
6	0.11–3.93	298.15	57	ϕ	0.002	0.0043
6	0.005–0.033	298.15	7	ϕ (from emf) ^d	0.0015	0.0085
this work	0.008–2.69	298–372	62	$\Delta_{\text{dil}}H_{\text{m}}$	0.3–0.5 ^{e,f}	0.40 ^e
7	0.001–3.93	298.15	59	$\Delta_{\text{dil}}H_{\text{m}}$	0.04 ^e	0.037 ^e
12	0.006–0.19	298.15	16	$\Delta_{\text{dil}}H_{\text{m}}$	0.05 ^e	0.095 ^e
14	0.028–0.0620	298.15	2	$\Delta_{\text{sol}}H_{\text{m}}(\text{hexahydrate})$	0.2 ^e	0.38 ^e
12	0.015–0.12	298.15	12	$\Delta_{\text{sol}}H_{\text{m}}(\text{hexahydrate})$	0.2 ^e	0.11 ^e
7	0.0009–0.0028	298.15	3	$\Delta_{\text{sol}}H_{\text{m}}(\text{hexahydrate})$	0.2 ^e	0.068 ^e
60	0.037	298.15	1	$\Delta_{\text{sol}}H_{\text{m}}(\text{hexahydrate})$	2 ^e	2.2 ^e
61	0.0037 ^g	298.15	1	$\Delta_{\text{sol}}H_{\text{m}}(\text{hexahydrate})$	2 ^e	0.2 ^e
63	0.011	292.95	1	$\Delta_{\text{sol}}H_{\text{m}}(\text{anhydrous})$	1 ^e	0.71 ^e
14	0.01–0.36	298.15	6	$\Delta_{\text{sol}}H_{\text{m}}(\text{anhydrous})$	1.4 ^e	1.5 ^e
62	3.5×10^{-4}	298.15	1	$\Delta_{\text{sol}}H_{\text{m}}(\text{anhydrous})$	U	6.4
20	0	288–366	10	$\Delta_{\text{sol}}H_{\text{m}}(\text{anhydrous})$	0.54–0.64 ^e	0.79 ^e
64	0	298.15	1	$\Delta_{\text{sol}}H_{\text{m}}(\text{anhydrous})$	1 ^e	1.3 ^e
19	0.01, 0.03	298.15	2	$\Delta_{\text{sol}}H_{\text{m}}(\text{anhydrous})$	0.4 ^e	0.25 ^e
61	0.0037	298.15	1	$\Delta_{\text{sol}}H_{\text{m}}(\text{anhydrous})$	U ^e	3.5 ^e
5	<i>m</i> _{sat}	298.15	1	<i>m</i> _{sat}	0.05 ^e	0.02 ^e
6	<i>m</i> _{sat}	298.15	1	<i>m</i> _{sat}	0.05 ^e	0.01 ^e
59	<i>m</i> _{sat}	373–393	4	<i>m</i> _{sat} ^h	0.45 ^e	0.42 ^e
58	<i>m</i> _{sat}	273–333	3	<i>m</i> _{sat}	0.75 ^e	0.31 ^e
56	<i>m</i> _{sat}	299–364	12	<i>m</i> _{sat}	0.75 ^e	0.59 ^e
57	<i>m</i> _{sat}	283–323	5	<i>m</i> _{sat}	0.25 ^e	0.16 ^e
8	0.1–3.93	298.15	18	<i>C</i> _{p,φ}	0.004 ⁱ	0.006 ⁱ
9	0.026–3.93	298.15	22	ρ/ρ_{w}	0.15 ^j	0.081 ^j
13	0.002–0.35	298.15	12	ρ/ρ_{w}	0.15 ^j	0.19 ^j
15	0.10–3.41	278–353	303	ρ/ρ_{w}	0.15 ^j	0.096 ^j

^a Number of measurements included in the least-squares process. ^b Estimated square root of variance for weighting the measurements in the least-squares process. A “U” indicates that the measurement was given no weight in the least-squares process. ^c Root mean square deviation of the measurements from the representation. ^d Osmotic coefficients calculated from concentration-cell emf measurements of Spedding and Dye.¹¹ ^e Units are kJ·mol⁻¹. ^f Dilutions from the nominal 0.08 mol·kg⁻¹ solution $\sigma_{\text{est}} = 0.5$ kJ·mol⁻¹; other dilutions $\sigma_{\text{est}} = 0.3$ kJ·mol⁻¹. ^g Composition information is unclear in ref 61. From the description of the calorimeter, values of (0.004–0.009) mol·kg⁻¹ are extractable; from “dissolution rate 1:15 000” we interpreted $m = 0.0037$ mol·kg⁻¹. None of these compositions are consistent with ref 61’s statement “virtually ideal solutions are formed”. A composition of 0.0037 mol·kg⁻¹ would produce a nonideality effect of about 1.6 kJ·mol⁻¹ from Debye–Hückel considerations alone. Neglect of nonideality effects from compositions of these magnitudes may explain partially ref 61’s observation that “our values for the hexahydrates are 1–1.5 kJ·mol⁻¹ less negative than those from the literature.” ^h Taken from a figure given in ref 59. ⁱ Units are kJ·K⁻¹·mol⁻¹. ^j Units are cm³·mol⁻¹.

these outer sphere complexes may be absorbed into the parameters of Pitzer’s ion-interaction model for NdCl₃(aq), without explicitly considering the presence of these complexes. Thus, we formally treat NdCl₃(aq) as being a fully dissociated electrolyte within the framework of our thermodynamic models.

Analysis and Recalculation of Experimental Results

Gibbs Energy Properties. Table 2 summarizes available thermodynamic data for NdCl₃(aq). Isopiestic vapor pressure measurements have been reported at 298.15 K for various RCl₃(aq), including NdCl₃(aq), from three investigations. Mason¹⁶ reported isopiestic results for NdCl₃(aq) from 0.074 30 mol·kg⁻¹ to 2.0517 mol·kg⁻¹ using KCl(aq) and NaCl(aq) as reference standards; Kotlyar-Shapiro et al.¹⁷ reported results from 1.279 mol·kg⁻¹ to 3.714 mol·kg⁻¹ using NaCl(aq), CaCl₂(aq), and H₂SO₄(aq) as reference standards; and Spedding et al.⁶ reported results from 0.107 20 mol·kg⁻¹ to 3.9307 mol·kg⁻¹ using KCl(aq) and CaCl₂(aq) as reference standards. The highest molality studied by Spedding et al. was that of the saturated solution in equilibrium with the thermodynamically stable phase NdCl₃·6H₂O(cr). Isopiestic measurements at 293.15 K were also described by Kaneko et al.,¹⁸ but they did not report the measured isopiestic molalities and only gave the parameters of a least-squares estimated empirical equation that represented the dependence of the derived values of the osmotic coefficients on the molality of NdCl₃(aq).

The molality-based osmotic coefficients ϕ of NdCl₃(aq) were recalculated from the measured isopiestic equilibrium molalities using the fundamental equation for isopiestic equilibrium⁴⁷

$$\phi = \nu^* m^* \phi^* / \nu m \quad (3)$$

where m is the equilibrium molality of NdCl₃(aq) and $\nu = 4$ is the stoichiometric ionization number, m^* is the equilibrium molality of the isopiestic reference standard, ν^* is its stoichiometric ionization number, and ϕ^* is the osmotic coefficient of the reference standard. The available isopiestic studies were published over a 59 year time period, during which several different evaluations were accepted for the osmotic coefficient of each of the reference standards. The ϕ values given in the various published isopiestic studies^{6,16–18} needed to be recalculated on a consistent basis to reduce inconsistencies that are not present in the original data but which may arise from the use of different sources of ϕ^* values.

Whenever possible, ϕ values from the available isopiestic studies were recalculated consistently using ϕ^* values from one of the recent critically assessed and consistent literature sources for each reference standard. These reference properties were calculated using Archer’s extended Pitzer model for NaCl(aq),³⁵ Archer’s ion-interaction model for KCl(aq),⁴⁸ and Rard and Clegg’s AEPEWHOV model for CaCl₂(aq).⁴⁹ The osmotic coefficients from two of the isopiestic studies could not be corrected for changes in the osmotic coefficients of the reference standards. Kaneko et al.¹⁸ did not report the measured isopiestic molalities, and

although Kotlyar-Shapiro et al.¹⁷ reported the isopiestic molalities of the $\text{NdCl}_3(\text{aq})$ solutions, those of the reference standards were not given.

Three isopiestic studies are available for $\text{NdCl}_3(\text{aq})$ at 298.15 K, and all of these studies overlap in the investigated molality ranges. Values of ϕ of $\text{NdCl}_3(\text{aq})$ derived from the study of Mason¹⁶ are typically higher than those from the study of Spedding et al.⁶ by 0.3% to 0.6%, which is reasonable agreement considering that the samples of individual rare earths available at the time of Mason's study were probably much less pure than those available to Spedding et al. In contrast, osmotic coefficients from the study of Kotlyar-Shapiro et al.¹⁷ are significantly lower than those from the other two studies by $\approx 4\%$ at lower molalities but with the discrepancies increasing to $\approx 8\%$ at higher molalities. Kotlyar-Shapiro et al. referenced an earlier paper by Kirgintsev et al.⁵⁰ for a description of their isopiestic apparatus. According to that report,⁵⁰ the isopiestic apparatus was not rotated nor were the solutions otherwise mixed during the equilibrations, and it is probable that concentration gradients were still present in all of the solutions at the end of the experiments. If so, the reported "isopiestic" molalities are not the true equilibrium molalities, and consequently, the results of Kotlyar-Shapiro et al.¹⁷ were rejected. Values of ϕ at 293.15 K were calculated from the equation and parameters of Kaneko et al.¹⁸ These calculated ϕ values are between 2% and 8% higher than anticipated from the isopiestic data at 298.15 K,⁶ in combination with the critically assessed calorimetric data, which suggests that either the actual experimental results (which were not reported) or their equation parameters are in error. Neither of these latter two studies will be considered further.

Isopiestic measurements do not usually extend much below $0.1 \text{ mol}\cdot\text{kg}^{-1}$ and generally are less precise below $\approx 0.3 \text{ mol}\cdot\text{kg}^{-1}$ than those at higher molalities.⁴⁷ Some other types of activity measurements at lower molalities are thus desirable to bridge the gap between the Debye–Hückel equation region and the lowest molality isopiestic data. Some such activity measurements are available for $\text{NdCl}_3(\text{aq})$ solutions at lower molalities, from emf measurements using concentration cells with transport in combination with transference number measurements. The earliest measurements by Spedding et al.¹⁰ at 298.15 K were rejected by Spedding and Dye¹¹ because the solutions used in the earlier study were not acidified sufficiently to suppress hydrolysis. Spedding and Dye¹¹ also reported new measurements of the emf's and transference numbers of $\text{NdCl}_3(\text{aq})$ using the same type of cells. The Spedding and Dye emf's were subsequently used by Spedding et al.⁶ to derive seven values of ϕ from $0.005\ 00$ to $0.033\ 52 \text{ mol}\cdot\text{kg}^{-1}$, and their reported ϕ values were included in the database used for evaluating our $\text{NdCl}_3(\text{aq})$ ion-interaction model parameters. Kaneko et al.¹⁸ reported making similar emf and transference number measurements at 293.15 K, but unfortunately they did not report any of the measured emf's or transference numbers.

Enthalpies of Dilution. The enthalpies of dilution $\Delta_{\text{dil}}H_m$ of $\text{NdCl}_3(\text{aq})$ at 298.15 K and a pressure of $\approx 0.1 \text{ MPa}$ have been given in three reports from Spedding's laboratory.^{7,12,14} These $\Delta_{\text{dil}}H_m$ measurements were made from $0.000\ 066 \text{ mol}\cdot\text{kg}^{-1}$ to $0.1879 \text{ mol}\cdot\text{kg}^{-1}$,¹² and from $0.000\ 97 \text{ mol}\cdot\text{kg}^{-1}$ to $3.929 \text{ mol}\cdot\text{kg}^{-1}$,⁷ using adiabatic dilution calorimetry. The enthalpies of dilution from these two studies agreed well, with an average absolute difference of only $\approx 0.025 \text{ kJ}\cdot\text{mol}^{-1}$ between the two sets in the region of overlap. A third set of $\Delta_{\text{dil}}H_m$ values was calculated by

Spedding and Miller¹⁴ from the concentration dependence of their enthalpies of aqueous solution of $\text{NdCl}_3(\text{cr})$. Their calculated values¹⁴ are not in good agreement with the other values,^{7,12} differing by $\approx 1 \text{ kJ}\cdot\text{mol}^{-1}$, suggesting some systematic error of at least this magnitude in the measured enthalpies of solution. Values of the relative apparent molar heat capacities reported by Spedding and Miller¹⁴ are also significantly discrepant from those reported in other studies (vide infra). Spedding and Miller¹⁴ made their measurements by dissolving $\text{NdCl}_3(\text{cr})$ in unacidified water. Spedding and Dye¹¹ found that solutions prepared in this way exhibited a faint Tyndal cone, indicating that some colloidal hydrous rare earth oxide probably formed during Spedding and Miller's experiments, and thus, their measured enthalpies may contain a contribution of unknown magnitude from hydrolytic precipitation. We cannot however estimate the magnitude of this effect and therefore cannot correct the measurements for it.

Our new measured values of $\Delta_{\text{dil}}H_m$ are given in Table 1. Because they are the only $\Delta_{\text{dil}}H_m$ values that have been measured at the higher pressure of 0.5 MPa, and because none of these new measurements were made exactly at 298.15 K, a direct comparison with the earlier work is not strictly possible. However, the pressure dependence of $\Delta_{\text{dil}}H_m$ is directly related to the apparent molar volume V_ϕ and its first temperature derivative at the final molality after dilution m_f and at the initial molality before dilution m_i :

$$(\partial\Delta_{\text{dil}}H_m/\partial p)_{T,m} = V_\phi(m_f) - V_\phi(m_i) - T\{\partial V_\phi(m_f)/\partial T\}_{p,m} + T\{\partial V_\phi(m_i)/\partial T\}_{p,m} \quad (4)$$

On the basis of the volumetric data for $\text{NdCl}_3(\text{aq})$ reported by Gildseth et al.,¹⁵ we concluded that the effect on $\Delta_{\text{dil}}H_m$ from changing the pressure from 0.5 MPa to 0.1 MPa is completely negligible compared to the direct experimental uncertainties of the $\Delta_{\text{dil}}H_m$ values.

Instead of correcting the present $\Delta_{\text{dil}}H_m$ measurements to 298.15 K and 0.1 MPa, the comparison of the consistency of the new measurements reported here with previous results will be given below, on the basis of their deviations from the extended Pitzer model.

Apparent Molar Heat Capacities. Heat capacities of $\text{NdCl}_3(\text{aq})$ have been reported at 298.15 K and 0.1 MPa in two studies. Spedding and Miller¹⁴ reported values of relative apparent molar heat capacity J_ϕ , where $J_\phi = C_{p,\phi} - C_{p,\phi}^\circ$, $C_{p,\phi}$ is the apparent molar heat capacity of the solute, and $C_{p,\phi}^\circ$ is the standard apparent molar heat capacity ($C_{p,\phi}^\circ = C_{p,m,2}^\circ$ for $\text{NdCl}_3(\text{aq})$). Smoothed values of J_ϕ were reported at round values of $m^{1/2} = (0.01 \text{ to } 0.6) \text{ mol}^{1/2}\cdot\text{kg}^{-1/2}$. Spedding and Miller did not describe how these heat capacities were measured, but they probably were determined by adding known amounts of electrical energy to the $\text{NdCl}_3(\text{aq})$ solutions produced during their enthalpy of solution measurements and measuring the resulting temperature increases. Spedding and Jones⁸ used adiabatic ("batch") calorimetry to make 18 measurements of specific heat capacity from $0.099\ 58 \text{ mol}\cdot\text{kg}^{-1}$ to $3.9291 \text{ mol}\cdot\text{kg}^{-1}$, where the highest molality is that of the saturated solution. Figure 1 shows the values of $C_{p,\phi}$ from Spedding and Jones. Values of $C_{p,\phi}$ calculated from Spedding and Miller's J_ϕ , assuming a near coincidence at the largest value of composition for the latter, are also shown. Finally, the value calculated from additivity, discussed previously, is also shown. The measurement apparatus used by Spedding and Jones⁸ should have been capable of greater accuracy than the apparatus of Spedding and

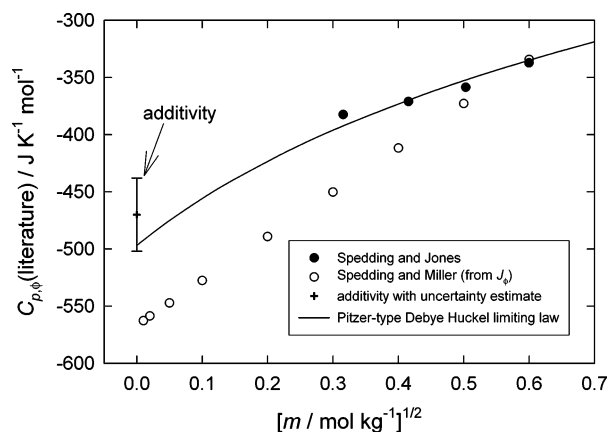


Figure 1. Values of apparent molar heat capacity against square root of molality of $\text{NdCl}_3(\text{aq})$. The symbols are as follows: solid circles, Spedding and Jones;⁸ open circles, calculated from Spedding and Miller's¹⁴ J_ϕ values. The symbol with an error bar was calculated from the ion-additivity principle, and the error bar represents estimated uncertainties from the $C_{p,\phi}$ values. The solid line was calculated from a form of a Debye-Hückel limiting law expression and an assumed $C_{p,\phi}$ value.

Miller,¹⁴ which suggests that most of this skewing comes from experimental errors in the Spedding and Miller J_ϕ values. Clearly, Spedding and Miller's values lead to a too negative $C_{p,\phi}$, and we consider them no further.

Heat capacities per gram of solution, $c_{p,s}$ ("specific heats"), from adiabatic calorimetry were reported to be uncertain by $\approx 0.05\%$.⁸ This level of inaccuracy yields fairly accurate values of $C_{p,\phi}$ at the higher molalities investigated, but the uncertainty for $C_{p,\phi}$ becomes larger at low values of molalities. This may be seen from the equation used for calculation of $C_{p,\phi}$:

$$C_{p,\phi} = Mc_{p,s} + (c_{p,s} - c_{p,w})(10^3 \text{ g}\cdot\text{kg}^{-1})/m \quad (5)$$

where M is the molar mass of the solute and $c_{p,w}$ is the heat capacity in joules per gram of water, from whence it can be shown that the propagation of error formula has a $1/m$ dependence. Puigdomenech et al.²⁷ noted that the reported values²⁵ of $C_{p,\phi}$ derived from adiabatic calorimetry appeared to be too negative by (50 to 100) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and Figure 1 shows that such a negative value is not in accord with the values from adiabatic calorimetry. The large systematic errors in Shock and Helgeson's $C_{p,\phi}$ values,²⁵ confirmed by Xiao and Tremaine²⁸ using flow microcalorimetry, apparently occurred from extrapolation errors.

The heat capacities from Xiao and Tremaine²⁸ were based on heat capacities and densities of $\text{H}_2\text{O}(\text{l})$ calculated from the comprehensive equation of state of Hill,⁵¹ which is the same equation used by us here for properties of $\text{H}_2\text{O}(\text{l})$. Earlier heat capacity measurements at 298.15 K of Spedding and Jones⁸ were based on $c_{p,w} = (0.9989)(4.184) = 4.1794 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$. At 298.15 K and 0.1 MPa, the equation of state from Hill⁵¹ yields $c_{p,w} = 4.1800 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$. Inspection of eq 5 indicates that the earlier values of $C_{p,\phi}$ may be adjusted to $c_{p,w} = 4.1800 \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$ simply by multiplying them by $(4.1800/4.1794) = 1.00014$, which was done even though this correction is essentially insignificant compared to their $\approx 0.05\%$ measurement uncertainty.

Densities and Apparent Molar Volumes. Densities of $\text{NdCl}_3(\text{aq})$ were reported in three studies from Spedding's laboratory.^{9,13,15} Very precise values of the "specific gravities" (i.e., the density ratio of solution to water) at 298.15

K were reported by Spedding et al.¹³ for molalities of from $0.001\,907 \text{ mol}\cdot\text{kg}^{-1}$ to $0.352\,21 \text{ mol}\cdot\text{kg}^{-1}$ using a magnetically controlled float apparatus and from $0.025\,985 \text{ mol}\cdot\text{kg}^{-1}$ to $3.9292 \text{ mol}\cdot\text{kg}^{-1}$ using pycnometry,⁹ where the highest molality is that of the saturated solution. Gildseth et al.¹⁵ also measured the densities of $\text{NdCl}_3(\text{aq})$ for temperatures of 278.206 K to 352.891 K using a mercury displacement dilatometer. Gildseth et al. determined their solution molalities by measuring densities in the vicinity of 298 K, interpolating the measured density values to 298.15 K, and then back-calculating the molalities from variation of the density with molality obtained from the pycnometric measurements,⁹ which guarantees consistency between the results of these two studies.

The apparent molar volume of a solute in water is related to the densities of solution and solvent by the relation

$$V_\phi = M/\rho - \{(\rho - \rho_w)/(\rho\rho_w m)\}(10^3 \text{ g}\cdot\text{kg}^{-1}) \quad (6)$$

where ρ and ρ_w are the densities of the solution and the solvent, respectively, in units of grams per cubic centimeter and $V_\phi = V_{m,2}$ for $\text{NdCl}_3(\text{aq})$. All of the density measurements of solutions from refs 9 and 13 depended on calibrations of the pycnometers or of the magnetic-float densimeter with an established density value for water. We therefore converted those reported density values to ρ/ρ_w using the values of ρ_w used therein. For the dilatometrically obtained density values in ref 15, we used the equation given therein for the density of water as a function of temperature to calculate ρ_w and from there calculated values of ρ/ρ_w . The fitting program uses the equation of state linked to it to generate density of water values at the respective conditions to calculate revised solution densities, and from there it calculates the apparent molar volume. This corrects for differences in the accepted density of water over time.

The apparent molar volume measurements at 298.15 K from the pycnometers and from the magnetic-float densimeter agree well, within $0.2 \text{ cm}^3\cdot\text{mol}^{-1}$, in the region of overlap. The dilatometric data do not supply independent confirmation of the other measurements at 298.15 K.

Application of an Extended Pitzer Ion-Interaction Model to $\text{NdCl}_3(\text{aq})$. Treatment of the Thermodynamic Data

Ion-Interaction Model. Some extension to Pitzer's ion-interaction model³³ is necessary to obtain a representation that approaches the measurement uncertainties over the full range of available compositions. Kodýtek and Dolejš⁵² represented the available osmotic coefficients and mean molal activity coefficients of $\text{RCl}_3(\text{aq})$, $\text{R}(\text{ClO}_4)_3(\text{aq})$, and $\text{R}(\text{NO}_3)_3(\text{aq})$ at the temperature 298.15 K with the standard form of Pitzer's ion-interaction model, but they also included the $\beta_{\text{MX}}^{(2)}$ parameter that is normally used only for 2:2 electrolytes and other higher charge types.³³ Although these fits represented the osmotic coefficients to near experimental accuracy, they were limited to molalities $\leq 2.0 \text{ mol}\cdot\text{kg}^{-1}$ and yielded values of $(3/2)\beta_{\text{MX}}^{(2)} = 8.0 \text{ kg}\cdot\text{mol}^{-1}$ for $\text{RCl}_3(\text{aq})$. As discussed by Pitzer,³³ the $\beta_{\text{MX}}^{(2)}$ parameter was introduced to represent complex formation at low molalities, and it should have negative, rather than positive, values. The positive values of $\beta_{\text{MX}}^{(2)}$ found by Kodýtek and Dolejš⁵² indicate that the improved representation was simply the result of including an additional adjustable parameter in the model and was not the result of using a more realistic ion-interaction model.

The model used here is the Pitzer ion-interaction equation with inclusion of Archer's ionic strength dependence of the third virial coefficient.^{34,35} The resultant equation for the excess Gibbs energy is

$$\frac{G^{\text{ex}}}{n_w RT} = -4IA_\phi \ln\{1 + b(I/m^\circ)^{1/2}\}/b + 2\nu_M \nu_X \{(m/m^\circ)^2 B_{MX} + (m/m^\circ)^3 \nu_M z_M C_{MX}\} \quad (7)$$

where

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)}[1 - \{1 + \alpha I^{1/2}\} \exp\{-\alpha I^{1/2}\}]/\{\alpha^2 I\} \quad (8)$$

and

$$C_{MX} = C_{MX}^{(0)} + 4C_{MX}^{(1)}[6 - \{6 + 6\alpha_2 I^{1/2} + 3\alpha_2^2 I + \alpha_2^3 I^{3/2}\} \exp\{-\alpha_2 I^{1/2}\}]/\{\alpha_2^4 I^2\} \quad (9)$$

where $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $C_{MX}^{(0)}$, 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 $1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ and $1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$, 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 Hill⁵¹ and the dielectric constant equation from Archer and Wang.⁵³ The value of α_2 used in the fitted equation was $1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$.

The excess Gibbs energy G^{ex} is related to the Gibbs energy of the solution G by

$$G^{\text{ex}} = G - n_1 G_{m,1}^\circ - n_2 G_{m,2}^\circ + RT \nu n_2 \{1 - \ln(m/m^\circ) - (1/\nu) \ln(\nu_M^{\nu_M} \nu_X^{\nu_X})\} \quad (10)$$

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 $1.0 \text{ mol} \cdot \text{kg}^{-1}$. The standard-state molar Gibbs energies for solvent and solute are $G_{m,1}^\circ$ and $G_{m,2}^\circ$, respectively. The standard states were chosen to be pure liquid for the solvent and the hypothetical one molal 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 7 leads to the osmotic coefficient ϕ and the stoichiometric activity coefficient γ_\pm

$$\phi - 1 = -|z_M z_X| A_\phi \frac{I^{1/2}}{1 + bI^{1/2}} + (m/m^\circ) \frac{2\nu_M \nu_X}{\nu} (\beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-\alpha I^{1/2})) + (m/m^\circ)^2 \frac{4\nu_M^2 \nu_X^2 z_M}{\nu} (C_{MX}^{(0)} + C_{MX}^{(1)} \exp(-\alpha_2 I^{1/2})) \quad (11)$$

$$\ln \gamma_\pm = -|z_M z_X| A_\phi \left(\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right) + (m/m^\circ) \frac{2\nu_M \nu_X}{\nu} (2\beta_{MX}^{(0)} + 2\beta_{MX}^{(1)} g(\alpha I^{1/2})) + (m/m^\circ)^2 \frac{2\nu_M^2 \nu_X^2 z_M}{\nu} (3C_{MX}^{(0)} + 4C_{MX}^{(1)} h(\alpha_2 I^{1/2})) \quad (12)$$

where

$$g(x) = [1 - (1 + x - x^2/2) \exp(-x)]/x^2 \quad (13)$$

and

$$h(x) = [6 - (6 + 6x + 3x^2 + x^3 - x^4/2) \exp(-x)]/x^4 \quad (14)$$

The osmotic coefficient is related to the activity of water by $\phi = -\ln a_w (M_1 \nu m)^{-1}$, where M_1 is the molar mass of the solvent, in kilograms per mole.

Appropriate temperature derivatives give equations for enthalpy and heat capacity. The relative apparent molar enthalpy L_ϕ is

$$L_\phi = \nu |z_M z_X| A_H \ln(1 + bI^{1/2})/2b - 2\nu_M \nu_X RT^2 [(m/m^\circ) B_{MX}^L + (m/m^\circ)^2 \nu_M z_M C_{MX}^L] \quad (15)$$

where

$$B_{MX}^L = \left(\frac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_p + 2 \left(\frac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_p j(\alpha I^{1/2}) \quad (16)$$

$$C_{MX}^L = \left(\frac{\partial C_{MX}^{(0)}}{\partial T} \right)_p + 4 \left(\frac{\partial C_{MX}^{(1)}}{\partial T} \right)_p k(\alpha_2 I^{1/2}) \quad (17)$$

where

$$j(x) = [1 - (1 + x) \exp(-x)]/x^2 \quad (18)$$

$$k(x) = [6 - (6 + 6x + 3x^2 + x^3) \exp(-x)]/(x^4) \quad (19)$$

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

$$C_{p,\phi} = C_{p,m,2}^\circ + \nu |z_M z_X| A_C \ln(1 + bI^{1/2})/2b - 2\nu_M \nu_X RT^2 [(m/m^\circ) B_{MX}^C + (m/m^\circ)^2 \nu_M z_M C_{MX}^C] \quad (20)$$

where

$$B_{MX}^C = \left(\frac{\partial^2 \beta_{MX}^{(0)}}{\partial T^2} \right)_p + \frac{2}{T} \left(\frac{\partial \beta_{MX}^{(0)}}{\partial T} \right)_p + 2 \left\{ \left(\frac{\partial^2 \beta_{MX}^{(1)}}{\partial T^2} \right)_p + \frac{2}{T} \left(\frac{\partial \beta_{MX}^{(1)}}{\partial T} \right)_p \right\} j(\alpha I^{1/2}) \quad (21)$$

$$C_{MX}^C = \left(\frac{\partial^2 C_{MX}^{(0)}}{\partial T^2} \right)_p + \frac{2}{T} \left(\frac{\partial C_{MX}^{(0)}}{\partial T} \right)_p + 4 \left\{ \left(\frac{\partial^2 C_{MX}^{(1)}}{\partial T^2} \right)_p + \frac{2}{T} \left(\frac{\partial C_{MX}^{(1)}}{\partial T} \right)_p \right\} k(\alpha_2 I^{1/2}) \quad (22)$$

where A_C is the Debye–Hückel coefficient for apparent molar heat capacity and $C_{p,m,2}^\circ$ is the standard-state molar heat capacity of the solute.

The apparent molar volume is

$$V_\phi = V_{m,2}^\circ + \nu |z_M z_X| A_V \ln(1 + bI^{1/2})/2b + 2\nu_M \nu_X RT \{ (m) B_{MX}^V + (m^2) \nu_M z_M C_{MX}^V \} \quad (23)$$

where

$$B_{MX}^V = \left(\frac{\partial \beta_{MX}^{(0)}}{\partial p} \right)_T + 2 \left(\frac{\partial \beta_{MX}^{(1)}}{\partial p} \right)_T j(\alpha I^{1/2}) \quad (24)$$

$$C_{MX}^V = \left(\frac{\partial C_{MX}^{(0)}}{\partial p} \right)_T + 4 \left(\frac{\partial C_{MX}^{(1)}}{\partial p} \right)_T k(\alpha_2 I^{1/2}) \quad (25)$$

where A_V is the Debye–Hückel coefficient for apparent molar volume and $V_{m,2}^\circ$ is the standard-state molar volume of the solute.

The equation relating the solubility of the hexahydrate solid phase to the Gibbs energies of the solution components is

$$\Delta_{\text{sol}} G^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr})) = G_{m,2}^\circ + 6G_{m,1}^\circ - G_m^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr})) - 4RT \ln(m_s \gamma_{\pm,s}/m^\circ) - 6RT \ln a_{w,s} - RT \ln 27 \quad (26)$$

where $G_{m,2}^\circ$, $G_{m,1}^\circ$, and $G_m^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}))$ are the standard-state molar Gibbs energies for the solute, the pure liquid water, and the hexahydrate crystal phase all at a given T and p , respectively, $\Delta_{\text{sol}} G^\circ(i\text{th phase})$ is the standard-state molar Gibbs energy for the solution process of the i th 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. The $\ln 27$ term in eq 26 arises from the multiplicative factor, which, in turn, arises from the fact that the chloride molality is three times that of neodymium ion, and that this multiplicative factor is cubed in the equilibrium expression. Of course, $G_{m,2}^\circ$, $G_{m,1}^\circ$, and $G_{m,\text{cr},i}^\circ$ cannot be evaluated, and so eq 26 was rewritten as

$$\Delta_{\text{sol}} G^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T) = \Delta_{\text{sol}} G^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T_r) + \{G_{m,2,T}^\circ - G_{m,2,T_r}^\circ\} - \{G_m^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T) - G_m^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T_r)\} + 6\{G_{m,1,T}^\circ - G_{m,1,T_r}^\circ\} = -4RT \ln(m_s \gamma_{\pm,s}/m^\circ) - 6RT \ln a_{w,s} - RT \ln 27 \quad (27)$$

The third braced term of eq 27 was obtained from the equation of state from Hill.⁵¹ The second braced term of eq 27 was expressed as

$$\{G_m^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T) - G_m^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T_r)\} = - (T - T_r) S_m^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T_r) + C_{p,m}(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T_r) \{ (T - T_r) - T \ln(T/T_r) \} \quad (28)$$

where $C_{p,m}(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T_r)$ and $S_m^\circ(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}), T_r)$ for the hexahydrate crystal at 298.15 K and 0.1 MPa were taken to be (361 and 417) J·K⁻¹·mol⁻¹, respectively. As we have no information on the temperature dependence of $C_{p,m}(\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr}))$, we took it to be constant over the temperature range considered here. These two values were obtained from the low-temperature measurements reported by Pfeffer.⁵⁴ (Pfeffer's measurements extended from 1.2 K to 223 K. We have used the extrapolated 298.15 K values reported in ref 55.) Solubility measurements for the hexahydrate phase were included in the global data fit. The standard Gibbs energy of solution and the entropy of the solute at the reference temperature T_r and the reference pressure p_r , $\Delta_{\text{sol}} G_{\text{hexahydrate}, T_r, p_r}^\circ$ and S_{2,m, T_r, p_r}° , respectively, were treated as adjustable parameters. Enthalpies of solution of the anhydrous and hexahydrate phases were

also included in the representation. This required one additional parameter, $\Delta_{\text{sol}} G_{\text{anhydrous}, T_r, p_r}^\circ$, which is the standard-state Gibbs energy of solution of NdCl₃(cr), at T_r and p_r .

The adjustable parameters describing $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $C_{MX}^{(0)}$, and $C_{MX}^{(1)}$ were assumed to be linear combinations of functions of temperature and pressure as

$$\beta_{MX}^{(0)} = f_1(T) \quad (29)$$

$$\beta_{MX}^{(1)} = f_2(T) \quad (30)$$

$$C_{MX}^{(0)} = f_3(T) \quad (31)$$

$$C_{MX}^{(1)} = f_4(T) \quad (32)$$

where

$$f_i(T) = b_{i,1} + b_{i,2} 10^{-2} (T - T_r)/T^\circ + b_{i,3} 10^{-5} \{ (T - T_r)/T^\circ \}^2 + b_{i,4} T^\circ 10^2 / (T - 225 \text{ K}) + b_{i,5} (p - p_r)/p^\circ + b_{i,6} (p - p_r)(T - T_r)/(T^\circ p^\circ) + b_{i,7} (p - p_r)(T - T_r)^2/(T^\circ{}^2 p^\circ) \quad (33)$$

where T_r and p_r were taken to be 298.15 K and 0.1 MPa, respectively, and T° and p° were 1 K and 1 MPa, respectively. Seven of the twenty-eight possible $b_{i,j}$ were not required to represent the selected measurements within experimental error.

The standard-state volume of the solute was taken to be

$$V_{m,2}^\circ/(1000 V^\circ) = b_{5,1} + b_{5,2} 10^{-1} (T/300 \text{ K}) + b_{5,3} (T/300 \text{ K})^2 \quad (34)$$

where V° is 1 cm³·mol⁻¹. The least-squares estimated parameters are given in Table 3. Some calculated values of the ion-interaction parameters, against which programs may be tested, are given in Table 4.

The uncertainty listed in Table 3 for $S_m^\circ(\text{NdCl}_3(\text{aq}), T_r, p_r)$ is not truly the uncertainty in this value. It is more properly considered as the uncertainty in the entropy of solution of the hexahydrate crystal. This is because the entropy of NdCl₃·6H₂O and of water appears in the calculations in combination with the entropy of NdCl₃(aq) to give $\Delta_{\text{sol}} S^\circ$. Because the entropy of the hexahydrate crystal is an extrapolated value, its uncertainty is non-negligible.

Differences of osmotic coefficients from values calculated from the model presented here are shown in Figure 2. There appears to be some cycling present. Inclusion of an additional m^3 term into the fitted equation did not eliminate the cycling and improved the rms errors by only about 10%. We therefore did not include the higher order molality term in the representation. Near $m \approx 1.5$ mol·kg⁻¹, the residuals for ref 6 exhibit a change in sign of their derivative with respect to molality, that is, a minimum of one of the cycles. This concentration is where the isopiestic standard was switched from KCl(aq) to CaCl₂(aq). Slight mismatch of the references is probably a contributing factor to the change in pattern of residuals at that concentration.

Figures 3 and 4 show the solute activity coefficient and the osmotic coefficient as functions of temperature and molality. The enthalpies of dilution above 300 K exist only to about 2.7 mol·kg⁻¹, and thus the plotted functions above 3 mol·kg⁻¹ might seem to be only extrapolations and of dubious reliability. There are two arguments against this. The first argument is that the heat capacity measurements

Table 3. Least-Squares Estimated Parameters for Eqs 7–34

parameter	value	parameter	value	parameter	value ^a
$b_{1,1}$	0.684 469 0	$b_{2,1}$	3.598 050	$b_{3,1}$	$-0.762\,621\,3 \times 10^{-2}$
$b_{1,2}$	$-0.028\,535\,51$	$b_{2,2}$	1.061 280	$b_{3,2}$	$-0.974\,894\,9 \times 10^{-2}$
$b_{1,3}$	$-1.495\,381$	$b_{2,3}$		$b_{3,3}$	0.102 028 2
$b_{1,4}$	$-0.030\,576\,60$	$b_{2,4}$	0.169 569 4	$b_{3,4}$	
$b_{1,5}$	$0.250\,699\,5 \times 10^{-3}$	$b_{2,5}$	$-0.162\,719\,5 \times 10^{-2}$	$b_{3,5}$	$-0.511\,139\,6 \times 10^{-5}$
$b_{1,6}$	$-0.454\,372\,7 \times 10^{-5}$	$b_{2,6}$	$-0.223\,083\,4 \times 10^{-4}$	$b_{3,6}$	$0.171\,575\,6 \times 10^{-6}$
$b_{1,7}$	$0.496\,719\,9 \times 10^{-7}$	$b_{2,7}$		$b_{3,7}$	$-0.200\,332\,3 \times 10^{-8}$
$b_{4,1}$	$-0.663\,461\,2$	$b_{5,1}$	$-0.318\,748\,2$	$\Delta_{\text{sol}} G^\circ(\text{NdCl}_3(\text{cr}), 298.15\text{ K}, 0.1\text{ MPa})$	$(-97.67 \pm 0.43)\text{ kJ}\cdot\text{mol}^{-1}$
$b_{4,2}$	$-0.125\,268\,6$	$b_{5,2}$	6.434 198	$\Delta_{\text{sol}} G^\circ(\text{NdCl}_3\cdot 6\text{H}_2\text{O}(\text{cr}), 298.15\text{ K}, 0.1\text{ MPa})$	$(-27.854 \pm 0.10)\text{ kJ}\cdot\text{mol}^{-1}$
$b_{4,3}$	6.400 741	$b_{5,3}$	$-0.314\,418\,3$	$S_{\text{m}}^\circ(\text{NdCl}_3(\text{aq}), 298.15\text{ K}, 0.1\text{ MPa})$	$(-37.50 \pm 0.53)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$b_{4,4}$				$C_{\text{p,m}}^\circ(\text{NdCl}_3(\text{aq}), 298.15\text{ K}, 0.1\text{ MPa})$	$(-464.4 \pm 12)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$b_{4,5}$					
$b_{4,6}$					
$b_{4,7}$					

^a The \pm values are 95% confidence intervals within the global data representation.

Table 4. Calculated Values of A_ϕ , $\beta_{\text{MX}}^{(0)}$, $\beta_{\text{MX}}^{(1)}$, $C_{\text{MX}}^{(0)}$, and $C_{\text{MX}}^{(1)}$

T/K	p/MPa	$A_\phi/\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$	$\beta_{\text{MX}}^{(0)}/\text{kg}\cdot\text{mol}^{-1}$	$\beta_{\text{MX}}^{(1)}/\text{kg}\cdot\text{mol}^{-1}$	$10^3 C_{\text{MX}}^{(0)}/\text{kg}^2\cdot\text{mol}^{-2}$	$C_{\text{MX}}^{(1)}/\text{kg}^2\cdot\text{mol}^{-2}$
298.15	0.1	0.391 476	0.642 669	3.829 86	-7.626 21	-0.663 461
323.15	0.1	0.410 277	0.636 836	4.036 14	-9.425 77	-0.654 774
348.15	0.1	0.433 068	0.607 988	4.266 38	-9.949 98	-0.566 077
373.15	0.1	0.459 887	0.558 313	4.508 47	-9.198 84	-0.397 371

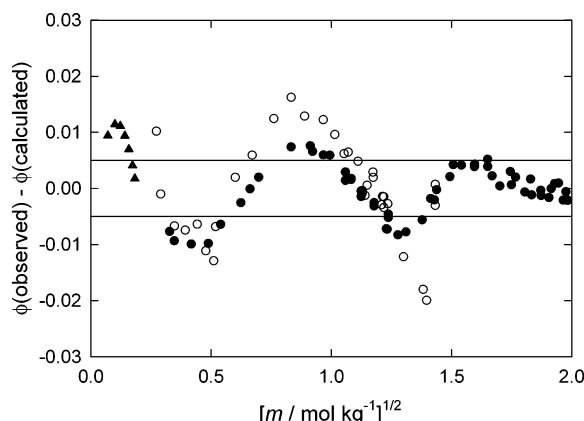


Figure 2. Comparison of calculated osmotic coefficients to those measured. The symbols are as follows: solid circles, Spedding et al.;⁶ solid triangles, Spedding et al.⁶ calculated from Spedding and Dye's¹¹ emf concentration cell with transference; open circles, Mason.¹⁶

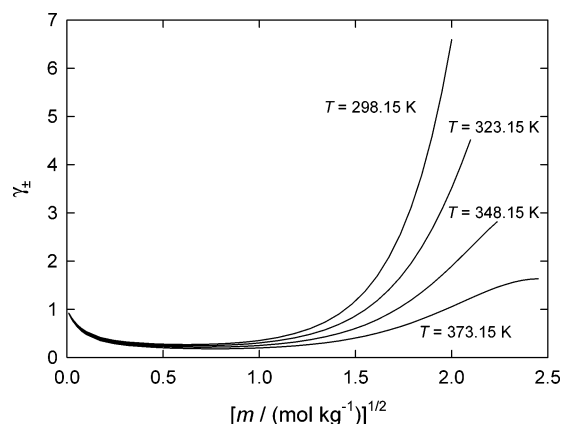


Figure 3. Calculated values of the solute mean molal activity coefficient of $\text{NdCl}_3(\text{aq})$ against square root of molality and for temperatures from 298.15 K to 373.15 K.

extend to nearly $4\text{ mol}\cdot\text{kg}^{-1}$ at 298 K and these help guide the extrapolation with respect to temperature for at least some of the temperature range. The second argument is that the solubility results exert some control on the

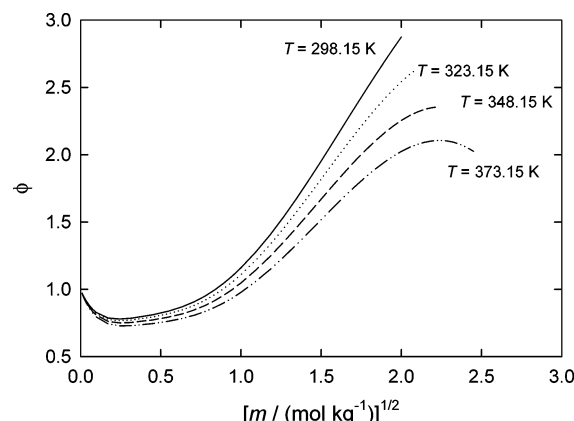


Figure 4. Calculated values of the osmotic coefficient of $\text{NdCl}_3(\text{aq})$ against square root of molality and for temperatures from 298.15 K to 373.15 K.

functions at saturation because both $a_{\text{w,sat}}$ and $\gamma_{\pm,\text{sat}}$ are involved in the calculation of saturation molality.

Measurements of solution heat capacity exist only for 298.15 K, and these lead to a value of the standard-state heat capacity at 298.15 K. Three other conceivable sources could lead to the temperature dependence of the standard-state heat capacity. These are the enthalpy of solution values from Krestkov et al.,²⁰ the temperature dependence of the solubility measurements, and additivity relations. Figure 5 shows values related to an additivity calculation, as discussed earlier. It is clear that, for the range of temperature for which solubility and enthalpy of solution data (295 K to 380 K) exist, the standard-state heat capacity varies only slowly with temperature. Within the inaccuracy of the available data, this temperature dependence is not statistically significant and the temperature variation falls within the uncertainty of the additivity calculation, $\pm 30\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The enthalpy of solution measurements from Krestkov et al. are not sufficiently accurate, and the solubility measurements do not extend over a wide enough temperature range, for either to define the temperature variation of $C_{\text{p,m},2}^\circ$.

There are no other values given in the literature of the temperature dependence of $V_{2,\text{m}}^\circ$ with which to compare. The values given by Gildseth et al.¹⁵ were calculated from

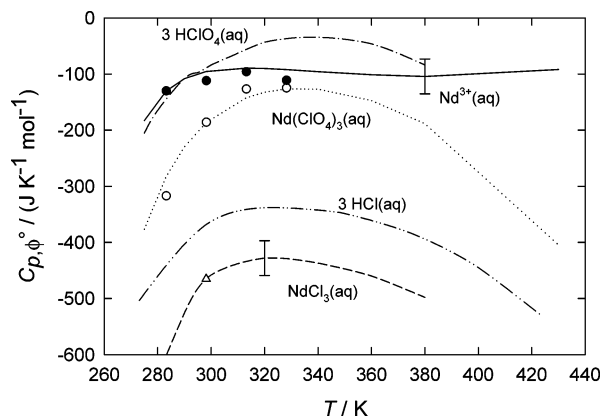


Figure 5. Standard-state apparent molar heat capacity against temperature for some substances. The dash-dot curves show $3 C_{p,\phi}$ for HCl and HClO_4 from Holmes et al.⁶⁶ and Oakes and Rai³¹ respectively. The dotted line is obtained from Xiao and Tremaine's²⁸ heat capacity measurements for $\text{Nd}(\text{ClO}_4)_3(\text{aq})$; their individual $C_{p,\phi}$ values are shown as empty circles. Xiao and Tremaine's $C_{p,\phi}$ values for the $\text{Nd}^{3+}(\text{aq})$ ion obtained from additivity are shown as solid circles. We also show the additivity-calculated values for this quantity as a solid line, which we obtained using the above-cited reference for $\text{HClO}_4(\text{aq})$. The error bar attached to that curve, $\pm 30 \text{ J K}^{-1} \text{mol}^{-1}$, is our estimate of the uncertainty in the additivity-obtained value and is determined primarily from the uncertainty estimated for the $C_{p,\phi}$ values for $\text{HClO}_4(\text{aq})$. The short dashed line shows $C_{p,\phi}$ for $\text{NdCl}_3(\text{aq})$ obtained from additivity, using the above-cited references for HCl(aq) and $\text{HClO}_4(\text{aq})$, and our estimate of the uncertainty of this quantity. Also shown in the figure, as an open triangle, is the $C_{p,\phi}$ value obtained from representation of the present measurements.

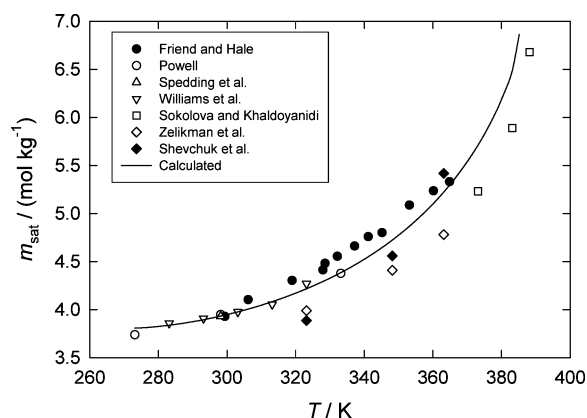


Figure 6. Values of the solubility of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ against temperature. The symbols are as follows: open circles, Powell;⁵⁸ open triangle, Saeger and Spedding⁵ and also Spedding et al.;⁶ open upside down triangles, Williams et al.;⁵⁷ filled circles, Friend and Hale;⁵⁶ squares, values extracted from a figure from Sokolova and Khaldoyanidi;⁵⁹ open diamonds, Zelikman et al.;⁶⁷ filled diamonds, Shevchuk et al.⁶⁸ The line was calculated from the fitted equations.

their use of Masson's equation. Masson's equation does not incorporate the correct limiting law behavior, and the use of it did not represent adequately the magnetic-float measurements at 298.15 K. Spedding et al.¹³ gave a value of $V_{2,m}(T = 298.15 \text{ K}) = 10.18 \text{ cm}^3 \text{mol}^{-1}$, which compares to our value of $10.15 \text{ cm}^3 \text{mol}^{-1}$. The small difference is due entirely to the difference in the density of water used in the two studies.

Solubility measurements and calculated values of solubility are shown in Figure 6. The measurements from Williams et al.,⁵⁷ Powell,⁵⁸ Spedding et al.,⁶ and Saeger and Spedding⁵ are in reasonably good agreement with each other and with the calculated solubility curve. The measurements from Friend and Hale⁵⁶ show some differences

from the others and from the fitted equation. The values from Zelikman et al.⁶⁷ and Shevchuk et al.⁶⁸ are inconsistent with the other values and with the enthalpy of solution of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{cr})$. We note that the temperature dependence of the fitted equation, particularly in the vicinity of 298.15 K, is determined primarily from the osmotic coefficients; the enthalpies of dilution and the solution heat capacities, which extend to saturation at 298 K; the enthalpy of solution measurements of the hexahydrate crystal; the properties of water; and the entropy of the crystal phase determined from low-temperature heat capacity measurements. No parameter is determined exclusively by the solubility measurements. Sokolova and Khaldoyanidi⁵⁹ have made DTA measurements that they interpreted as showing that a peritectic equilibrium point exists between the hexahydrate crystal and a heptahydrate of NdCl_3 , in contact with the solution, at 290 K. If this is so, then the two lowest temperature solubility points (one from Williams et al.,⁵⁷ the other from Powell⁵⁸) might not correspond to an equilibrium measurement of the hexahydrate solubility. None of the references described a quantification of the structure of the precipitated phases at the lowest temperatures. At the higher temperatures, the solubility of the hexahydrate phase increases rapidly with temperature, approaching the melting temperature of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$. Some reported values of the melting temperature are 396 K,⁵⁹ 397 K,⁵⁷ and 400 K.⁶⁵ The melting temperature and the solubilities above 373 K have very high ionic strengths ($I = 55.5 \text{ mol kg}^{-1}$ at the melting temperature), which we consider to be outside the region of applicability of molality-based equations. Additionally, there are no excess property data for $I > 24 \text{ mol kg}^{-1}$, other than that extractable from the solubilities themselves, with which to determine an empirical model.

We have no determinations of the solubility of the anhydrous phase, and the Gibbs energy of solution parameter, which is tabulated in Table 3, was least-squares estimated from the enthalpies of solution of the anhydrous phases combined with the entropy of the ions (another parameter) and the entropy of the crystalline anhydrous phase determined from low-temperature heat capacity measurements from Sommers and Westrum.³⁰

Summary

We have presented here new enthalpy of dilution measurements from near ambient conditions to near 373 K. These measurements were combined with other reliable measurements of excess thermodynamic properties and phase equilibria in an equation of state for the $\text{NdCl}_3 + \text{H}_2\text{O}$ system.

Acknowledgment

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