

# Thermodynamic Properties of Aqueous Polyatomic Ions at Extreme Temperatures and Pressures

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Recently a theoretical treatment (*J. Phys. Chem. B* **2009**, *113*, 2398–2404) was developed for predicting the standard state thermodynamic properties of electrolytes up to and beyond the critical temperature of water (1273 K and at pressures up to 1000 MPa). In general, the model requires sufficient data at 298.15 K including the Gibbs free energy of hydration and at two higher temperatures to fix two constants for each electrolyte. This communication describes an extension of this “two constant” theory to thermodynamic properties of polyatomic ions for which no accurate data for the Gibbs free energy of hydration exists at 298.15 K.

## 1. Introduction

Recently we reported a functional form for the Gibbs free energy of hydration of electrolytes in aqueous solutions, a unified theory of electrolytes, for prediction of the standard state thermodynamic properties of electrolytes to extreme temperatures and pressures.<sup>1</sup> This functional form not only fits direct measurements of Gibbs free energies of solutions over a wide range of temperature and pressure up to critical point of water and even to the supercritical region but also acts as an equation of state in the sense that its derivatives account for all known accurate measurements of standard state partial molal entropies and volumes of +1, +2, and +3 electrolytes.<sup>1,2a</sup> It is a simple model to implement and corrects empirically for deficiencies of the classical Born model.

The equation requires knowing the Gibbs free energy of hydration at some temperature, usually 298.15 K, and only two parameters for each electrolyte at temperatures above 298.15 K. Once these parameters are fixed, the model is used to predict the standard state partial molal Gibbs free energies of electrolytes up to supercritical temperatures, 1273 K.<sup>1,2</sup> The temperature and pressure behavior of electrolytes can now be accurately predicted from existing low temperature data alone.<sup>1</sup> The model has also been used successfully to predict the standard state partial molal entropies, heat capacities, and volumes of 15 important electrolytes to the highest temperatures of known reliable experimental data, 623 K.<sup>1,2a</sup>

The objective of this manuscript is to describe an extension of this “two constants” theory to thermodynamic properties of polyatomic ions for which no reliable data for the Gibbs free energy of hydration at 298.15 K are available.

## 2. Calculations and Results

The unified theory<sup>1</sup> for the calculation of the standard state Gibbs free energies of hydration of ions,  $\Delta_{\text{h}}\bar{G}^{\circ}$ , at  $T$  and  $p$  is given by

$$\Delta_{\text{h}}\bar{G}^*(T,p) = [\Delta_{\text{h}}\bar{G}^*(T_{\text{r}},p) + C_{\text{S}}T_{\text{r}} - C_{\text{H}}]F_1(D) - C_{\text{S}}T + C_{\text{H}} \quad (1a)$$

where

$$F_1(D) = \left[ \frac{D(T,p) - 1}{D(T_{\text{r}},p) - 1} \right] \left[ \frac{D(T_{\text{r}},p)}{D(T,p)} \right] \quad (1b)$$

and

$$\Delta_{\text{h}}\bar{G}^* = \Delta_{\text{h}}\bar{G}^{\circ} - \Delta_{\text{ss}}\bar{G}^{\circ} = \Delta_{\text{h}}\bar{G}^{\circ} - \nu RT \ln \left( \frac{m^{\circ} d^{\circ} RT}{1000 p^{\circ}} \right) \quad (1c)$$

where  $T_{\text{r}}$  equal to 298.15 K is the reference temperature,  $\Delta_{\text{ss}}\bar{G}^{\circ}$  is the standard state conversion term for the hypothetically ideal 0.1 MPa gaseous ions being hydrated to the hypothetically ideal 1  $m$  aqueous solution,  $m^{\circ}$  is equal to 1 mol/kg,  $d^{\circ}$  is the density of the pure solvent in g/cm<sup>3</sup>,  $p^{\circ}$  is equal to 0.1 MPa,  $R$  is the ideal gas constant, and  $D$  is the bulk dielectric constant of the solvent.<sup>3</sup> The model parameters  $C_{\text{H}}$  and  $C_{\text{S}}$  are obtained using eq 1 and experimental standard state Gibbs free energies of hydration,  $\Delta_{\text{h}}\bar{G}^{\circ}$ , for at least two temperatures besides 298.15 K. The required values of  $\Delta_{\text{h}}\bar{G}^{\circ}(298.15 \text{ K})$  for simple ions are commonly obtained from the Gibbs free energies of formations,  $\Delta_{\text{f}}\bar{G}^{\circ}$ , tabulated in standard tables.<sup>4,5</sup>

$$\Delta_{\text{h}}\bar{G}^{\circ}(298.15 \text{ K}) = \Delta_{\text{f}}\bar{G}^{\circ}(\text{aq}, 298.15 \text{ K}) - \Delta_{\text{f}}\bar{G}^{\circ}(\text{g}, 298.15 \text{ K}) \quad (2)$$

Since the values of  $\Delta_{\text{f}}\bar{G}^{\circ}(\text{g}, 298.15 \text{ K})$  for polyatomic ions are usually not available, another approach must be taken. It is a property of eq 1 that the standard state corrected Gibbs free energies of hydration relative to reference temperature are given by

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$$\Delta_h[\bar{G}^*(T,p) - \bar{G}^*(T_r,p)] = [\Delta_h\bar{G}^*(T_r,p) + C_S T_r](F_1(D) - 1) - C_S \Delta T \quad (3a)$$

and by redefining the constants  $\Delta_h\bar{G}^*(T_r,p)$  and  $C_H$  as one new constant, eq 3b is obtained:

$$\Delta_h\bar{G}^*(T_r,p) = \Delta_h\bar{G}^*(T_r,p) - C_H \quad (3b)$$

These new parameters  $\Delta_h\bar{G}^*(T_r,p)$  and  $C_S$  are now fixed from eq 3a and experimental standard state Gibbs free energies as follows. The difference between the hydration energies at two temperatures is related to the experimental free energies of transfer of an electrolyte from one temperature to the other,  $\bar{G}_2^o(T, \text{aq}) - \bar{G}_2^o(T_r, \text{aq})$ :

$$\Delta_h(\bar{G}^o(T,p) - \bar{G}^o(T_r,p)) = (\bar{G}_2^o(T,p,\text{aq}) - \bar{G}_2^o(T_r,p,\text{aq})) - (G^o(T,g) - G^o(T_r,g)) \quad (4)$$

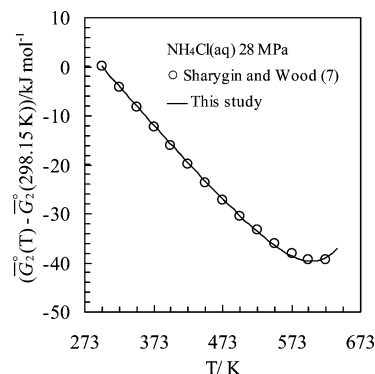
where values of  $G^o(T,g) - G^o(T_r,g)$  for heating of the gaseous ions are calculated from eq 5:

$$G^o(T,g) - G^o(T_r,g) = -S^o(T_r,g)\Delta T + \int_{T_r}^T C_p^o(T,g) dT - T \int_{T_r}^T C_p^o(T,g) d \ln T \quad (5)$$

The required values for entropies and heat capacities of important gaseous polyatomic ions can be calculated from known molecular constants and are available in literature<sup>6</sup> and those of simple ions are from JANAF tables.<sup>5</sup>

**2.1. Aqueous Ammonium Chloride.** Values of  $\Delta_h\bar{G}^*(T_r,p)$  and  $C_S$  for aqueous ammonium chloride,  $\text{NH}_4\text{Cl}(\text{aq})$ , obtained from eq 3, using the experimental  $\bar{G}_2^o(T, \text{aq}) - \bar{G}_2^o(298.15 \text{ K}, \text{aq})$  at 28 MPa, are summarized in Table 1. The Gibbs free energies of transfer of  $\text{NH}_4\text{Cl}(\text{aq})$  were calculated from the standard state partial molar heat capacities at 28 MPa<sup>7</sup> and entropy at 298.15 K<sup>4</sup> with an equation similar to eq 5. The standard state partial molar volume and heat capacities,  $\bar{C}_{p,2}^o$ , of  $\text{NH}_4\text{Cl}(\text{aq})$  at pressures of 10 and 28 MPa, and temperatures up to 623.15 K are estimated from experimental apparent molar volume and heat capacities of concentrated solutions ( $m \geq 0.1$ ) of  $\text{NH}_4\text{Cl}(\text{aq})$  reported by Sharygin and Wood.<sup>7</sup> In Figure 1, the experimental values of  $\bar{G}_2^o(T, \text{aq}) - \bar{G}_2^o(298.15 \text{ K}, \text{aq})$  are compared with those predicted from the unified theory, eq 3, using the parameter values from Table 1. From the same parameters,  $\Delta_h\bar{G}^*(T_r,p)$  and  $C_S$ , the standard state partial molar volume,  $\bar{V}_2^o$ , of  $\text{NH}_4\text{Cl}(\text{aq})$  at 10 MPa and 28 MPa are calculated and compared with the experimental values in Table 2. The comparison indicates good agreement up to 573.15 K at 10 and 28 MPa. At 28 MPa and 623.15 K, the value for  $\bar{V}_2^o(\text{NH}_4\text{Cl}, \text{aq})$  reported by Sharygin and Wood<sup>7</sup> is less negative than the corresponding value predicted from the unified theory.<sup>1</sup> This could in part be the result of extrapolation of their measured apparent molar volumes from concentrated solutions ( $m > 0.1$ ) to infinite dilution and with no consideration for ion association (or incomplete dissociation) in their model.

**2.2. Aqueous Sodium Nitrate.** The unified theory (eq 3) parameter values for aqueous sodium nitrate,  $\text{NaNO}_3(\text{aq})$ , calculated from low temperature ( $T \leq 373.15 \text{ K}$  and at  $p_{\text{sat}}$ )  $\bar{G}_2^o(T, \text{aq}) - \bar{G}_2^o(298.15 \text{ K}, \text{aq})$ , are summarized in Table 1. These Gibbs free energies of transfer are from Archer<sup>8</sup> up to 373.15



**Figure 1.** Comparison of the experimental and calculated (eq 3) standard state Gibbs free energies of transfer relative to 298.15 K for  $\text{NH}_4\text{Cl}(\text{aq})$  at 28 MPa.

**TABLE 1: Parameters for Some Representative Polyatomic Electrolytes Calculated from Eq 3**

electrolyte	$\Delta_h\bar{G}^*/\text{kJ mol}^{-1} \text{ }^a$	$-C_S / \text{J mol}^{-1} \text{ K}^{-1}$
$\text{H}^+ - \text{Na}^+ \text{ } ^b$	-200.239	10.976
$\text{NaNO}_3$	-754.941	74.546
$\text{NH}_4\text{Cl}$	-675.708	70.401
$\text{NaOH} \text{ } ^b$	-651.579	169.498
$\text{NaReO}_4 \text{ } ^b$	-691.978	65.278
$\text{NaB}(\text{OH})_4$	-190.452	169.100
$\text{NaHCO}_3$	-545.703	154.672
$\text{NaHSO}_4$	-1267.777	76.054
$\text{NaH}_2\text{PO}_4$	-670.763	159.249
$\text{Na}_2\text{SO}_4$	-2475.551	167.906
$\text{Na}_2\text{CO}_3$	-1525.647	301.353
$\text{Na}_2\text{HPO}_4$	-1445.552	309.168
$\text{Na}_3\text{PO}_4$	-2197.395	494.694

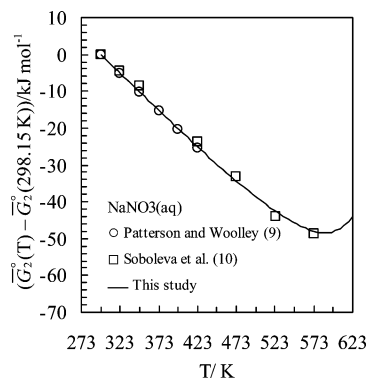
<sup>a</sup>  $\Delta_h\bar{G}^* = \Delta_h\bar{G}^* - C_H$ . <sup>b</sup> Djamali and Cobble,<sup>1</sup>  $\text{HCl}(\text{aq}) - \text{NaCl}(\text{aq})$ .

**TABLE 2: Comparison of Calculated and Experimental Values of Standard State Partial Molal Volume ( $\text{cm}^3 \text{ mol}^{-1}$ ) of Aqueous Ammonium Chloride**

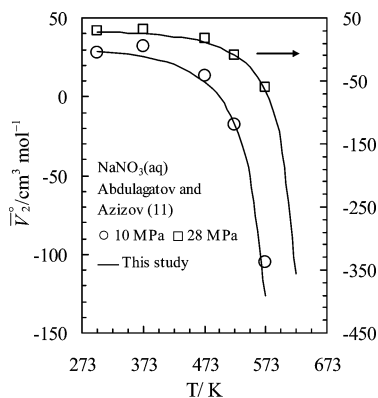
<i>T</i> , K	10 MPa			28 MPa		
	$\bar{V}_2^o \text{ } ^a$	$\sigma^a$	$\bar{V}_2^o \text{ } ^b$	$\bar{V}_2^o \text{ } ^a$	$\sigma^a$	$\bar{V}_2^o \text{ } ^b$
298.15	36.2	0.5	36.2	36.7	0.5	36.7
323.15			35.4			36.0
348.15			34.4			35.1
373.15	34.0	0.8	33.0	35.0	0.8	33.8
398.15			31.1			32.2
423.15			28.5			29.9
448.15	22.6	1.5	24.7	25.0	2.0	26.7
473.15			19.1			22.2
498.15			10.1			15.4
523.15	-5.7	3.0	-5.1	3.5	3.0	4.7
548.15			-33.9			-13.1
573.15	-83.3	8.0	-100.4	-42.5	6.0	-45.6
598.15						-114.2
623.15				-211.0	20.0	-302.2

<sup>a</sup> Sharygin and Wood,<sup>7</sup> estimated error by authors. <sup>b</sup> This study, calculated from the unified theory of electrolytes<sup>1</sup> using parameters from table 1.

K. In Figure 2, the predicted values of  $\bar{G}_2^o(T, \text{aq}) - \bar{G}_2^o(298.15 \text{ K}, \text{aq})$ , using the unified theory and the parameter values from Table 1, are compared with those calculated from experimental values of  $\bar{C}_{p,2}^o$ <sup>9</sup> to 423.15 K and the experimental values of  $\bar{G}_2^o(T, \text{aq}) - \bar{G}_2^o(298.15 \text{ K}, \text{aq})$  reported by Soboleva et al.<sup>10</sup> up to 573.15 K. From the same parameters,  $\Delta_h\bar{G}^*(T_r,p)$  and  $C_S$ , the standard state partial molar volume,  $\bar{V}_2^o$ , for  $\text{NaNO}_3(\text{aq})$  at 10 and 28 MPa are predicted and the results are compared with



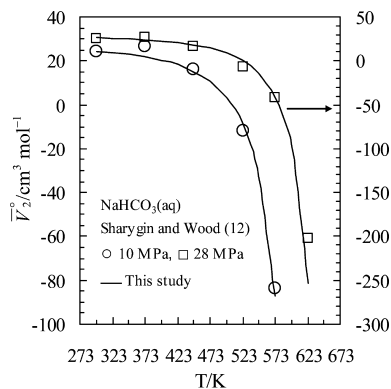
**Figure 2.** Comparison of the experimental and calculated (eq 3) standard state Gibbs free energies of transfer relative to 298.15 K for  $\text{NaNO}_3(\text{aq})$  at  $p_{\text{sat}}$ .



**Figure 3.** Standard state partial molar volume of  $\text{NaNO}_3(\text{aq})$  at 10 and 28 MPa.

the literature<sup>11</sup> up to 573.15 K (Figure 3). The experimental values of  $\bar{V}_2^o$  for  $\text{NaNO}_3(\text{aq})$  have large uncertainties since they were estimated from the density of concentrated solution ( $m \geq 0.1$ ) of  $\text{NaNO}_3(\text{aq})$ .<sup>11</sup>

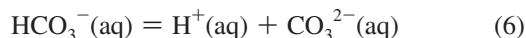
**2.3. Aqueous Sodium Carbonate and Sodium Bicarbonate.** Sharygin and Wood<sup>12</sup> reported the experimental values for apparent molar heat capacities and volumes of concentrated solutions ( $m \geq 0.1$ ) of sodium carbonate,  $\text{Na}_2\text{CO}_3(\text{aq})$ , and sodium bicarbonate,  $\text{NaHCO}_3(\text{aq})$ , at pressures of 10 and 28 MPa up to 623.15 K. The analysis of these experimental values becomes quite complex, in particular at higher temperatures, due to the presence of significant hydrolysis of the carbonate ion, disproportionation of the bicarbonate ion, and the association of carbonate and bicarbonate ions with the sodium ion. However, once the parameters of the unified theory are fixed using the lower temperature experimental values, it will be possible to predict the thermodynamic properties of these important electrolytes as a function of temperature and pressure. The parameter values for  $\text{NaHCO}_3(\text{aq})$ , calculated from eq 3 using the experimental values for the Gibbs free energies of  $\text{NaHCO}_3(\text{aq})$ , are given in Table 1. The values of  $\bar{G}_2^o(T, \text{aq}) - \bar{G}_2^o(298.15 \text{ K}, \text{aq})$  for  $\text{NaHCO}_3(\text{aq})$  were calculated from the lower temperature ( $T \leq 473.15 \text{ K}$ )  $\bar{C}_{p,2}^o$  values at 28 MPa of Sharygin and Wood<sup>12</sup> using eq 5. These parameters were then used to predict thermodynamic properties of  $\text{NaHCO}_3(\text{aq})$  to higher temperatures and at different pressures. At temperatures  $T \leq 573.15 \text{ K}$  the experimental values of  $\bar{V}_2^o$  for  $\text{NaHCO}_3(\text{aq})$  at 28 and 10 MPa<sup>12</sup> are in reasonable agreement with the corresponding values calculated from eq 3 (Figure 4). Above 573.15 K at 28 MPa the values of  $\bar{V}_2^o$  for  $\text{NaHCO}_3(\text{aq})$  from the unified theory is more negative than those reported by Sharygin



**Figure 4.** Standard state partial molar volume of  $\text{NaHCO}_3(\text{aq})$  at 10 and 28 MPa.

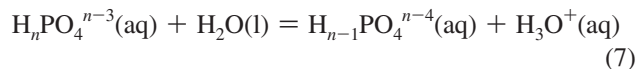
and Wood,<sup>12</sup> possibly due to their lack of correction of experimental values for side reactions mentioned above.

The second dissociation of carbonic acid, reaction 6, has been reported up to 593.15 K by many investigators.<sup>13–16</sup>

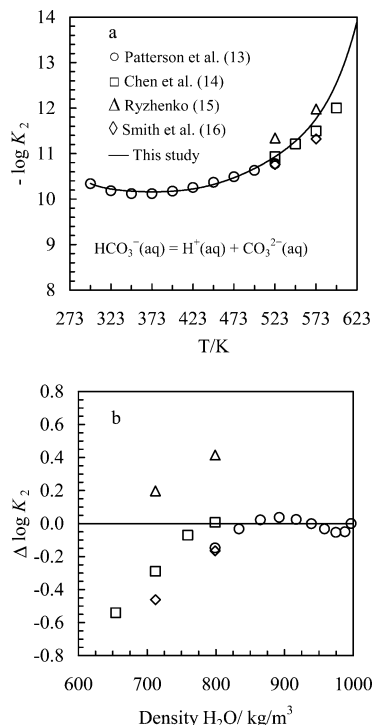


However, large discrepancies exist between the reported  $\log K_2$  values for the second dissociation of carbonic acid at high temperatures.<sup>13–16</sup> Although a detailed analysis of these discrepancies is outside the scope of this research, it is interesting to compare the values of  $\log K_2$  for the second dissociation of carbonic acid predicted from the unified theory with the corresponding experimental values in the literature. The required parameters for the model were fixed from the experimental values for the second dissociation of carbonic acid reported by Patterson et al.<sup>13</sup> at  $T \leq 473.15 \text{ K}$  and  $p_{\text{sat}}$ . These comparisons are summarized in Figure 5. The values of  $\bar{V}_2^o$  for  $\text{Na}_2\text{CO}_3(\text{aq})$  at 10 MPa, calculated from the same parameter values, is compared with experimental values<sup>12,17</sup> in Figure 6. The comparison indicates a reasonable agreement, considering the difficulties of extrapolating the experimental values of apparent molar volume to standard state condition from a region outside the validity of the limiting law.

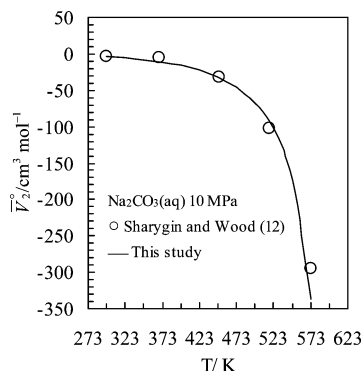
**2.4. Dissociation Equilibria of Phosphoric Acid.** The present unified theory (eq 3) can now be tested for prediction and extension of thermodynamic properties of some typical and important chemical reactions to high temperatures and pressures. In this section thermodynamic properties of completely dissociated  $\text{NaH}_2\text{PO}_4(\text{aq})$ ,  $\text{Na}_2\text{HPO}_4(\text{aq})$ , and  $\text{Na}_3\text{PO}_4(\text{aq})$  are calculated from the unified theory. The parameter values listed in Table 1 are calculated as follows. Mesmer and Baes<sup>18</sup> and Bates,<sup>19</sup> using potentiometric acidity measurements, have studied the dissociation equilibria of phosphoric acid ( $K_{a,n}$ ,  $n = 1, 2, 3$ ) up to 573 K and at ionic strength from 0.05–1.0  $m$  and Read<sup>20</sup> measured first dissociation constant ( $K_{a,1}$ ) of phosphoric acid at low concentrations ( $10^{-3} m$ ) up to 473.15 K by conductance measurements. It is useful to write the acid dissociation reactions,  $K_{a,n}$ :



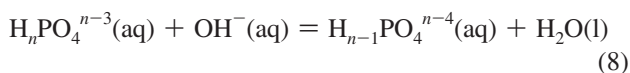
into the neutralization reactions,  $K_{N,n}$  ( $=K_{a,n}/K_w$ ):



**Figure 5.** (a) Comparison of the experimental and predicted values of  $\log K_2$  for the second ionization of carbonic acid at  $p_{\text{sat}}$ . (b) Deviations of experimental from calculated values as a function of water density. The symbols for data points are the same as in the case of Figure 5a.

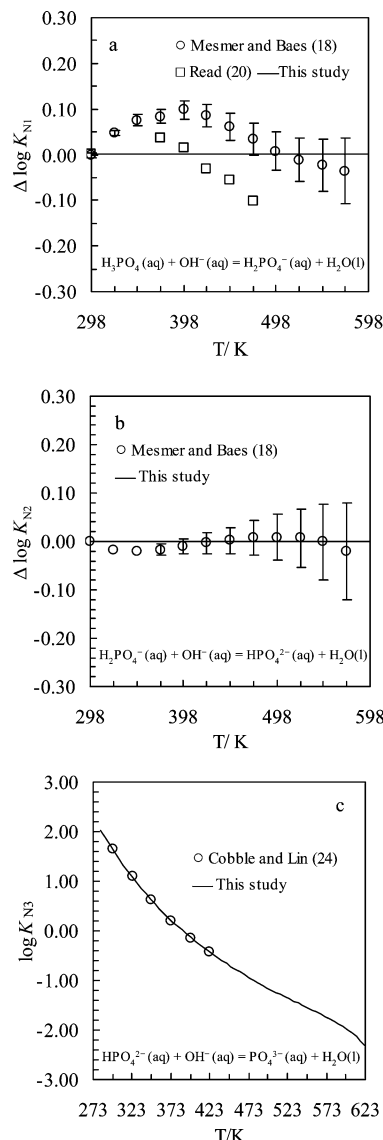


**Figure 6.** Standard state partial molar volume of  $\text{Na}_2\text{CO}_3(\text{aq})$  at 10 MPa.



A better comparison is made with the neutralization reactions because it is more accurately determined since the free hydrogen and hydroxide ion concentrations were low in the experimental measurements and there is partial cancellation of the free energies of dilution due to the same number of charge on both sides of eq 8.

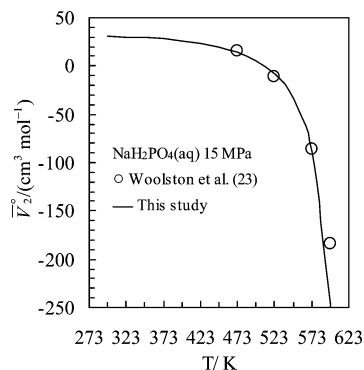
The parameters of the unified model were fixed from the experimental values of Read<sup>20</sup> and Mesmer and Baes.<sup>18</sup> The predicted values of  $\log K_{N,n}$  for the neutralization reaction from the unified model are in good agreement with those reported by Read<sup>20</sup> and Mesmer and Baes<sup>18</sup> over the entire temperature range (Figure 7a). The parameter values for the unified model for  $\text{NaH}_2\text{PO}_4(\text{aq})$  were calculated as follows. From the first neutralization reaction eq 8 the Gibbs free energies of transfer of  $\text{NaH}_2\text{PO}_4(\text{aq})$  relative to reference temperature of 298.15 K is given by



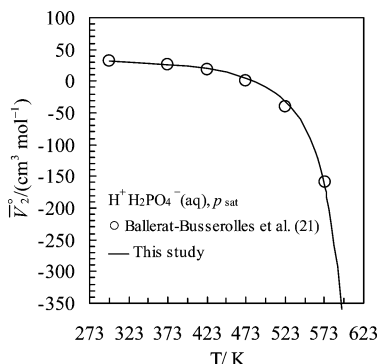
**Figure 7.** Deviations of experimental from calculated values for neutralization reactions of phosphoric acid at  $p_{\text{sat}}$ : (a) first neutralization reaction; (b) second neutralization reaction; (c) third neutralization reaction.

$$(\bar{G}_2^\circ(T) - \bar{G}_2^\circ(T_r))(\text{NaH}_2\text{PO}_4, \text{aq}) = (\bar{G}_2^\circ(T) - \bar{G}_2^\circ(T_r))(\text{NaOH}, \text{aq}) - (G_1^\circ(T) - G_1^\circ(T_r))(\text{H}_2\text{O}, \text{l}) + (\bar{G}^\circ(T) - \bar{G}^\circ(T_r))(\text{H}_3\text{PO}_4^\circ, \text{aq}) + \Delta_{\text{rxn}}(\bar{G}^\circ(T) - \bar{G}^\circ(T_r)) \quad (9)$$

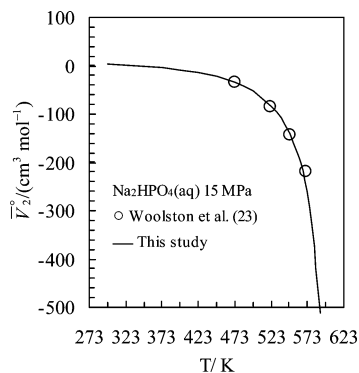
where the standard state Gibbs free energies of  $\text{NaOH}(\text{aq})$  are from Djamali and Cobble,<sup>2b</sup> molecular  $\text{H}_3\text{PO}_4^\circ(\text{aq})$  are from Ballerat-Busserolles et al.,<sup>21</sup>  $\text{H}_2\text{O}(\text{l})$ , are from the steam tables,<sup>22</sup> and  $\Delta_{\text{rxn}}(\bar{G}^\circ(T) - \bar{G}^\circ(T_r))$  are from experimental data of Read<sup>20</sup> at  $T \leq 473.15$  K and Mesmer and Baes<sup>18</sup> at temperatures above 473.15 K. Reasonable agreement at temperatures  $T \leq 573.15$  K is also observed when the experimental standard state partial molar volumes of  $\text{NaH}_2\text{PO}_4(\text{aq})$  at 10 and 28 MPa<sup>23</sup> are compared with the corresponding values calculated from the same parameter values obtained from eq 3 (Figure 8). Above 573.15 K and at 28 MPa, the predicted values of  $\bar{V}_2^\circ$  for  $\text{NaH}_2\text{PO}_4(\text{aq})$  are more negative than those reported by Woolston et al.<sup>23</sup> The values of  $\bar{V}_2^\circ$  from these authors<sup>23</sup> are estimated from apparent molar volumes of concentrated solution ( $m \geq 0.1$ ) and with no corrections made for ion association. Experimental values for  $\bar{V}_2^\circ(\text{H}^+\text{H}_2\text{PO}_4^-, \text{aq})$  at  $p_{\text{sat}}$  were also calculated



**Figure 8.** Standard state partial molar volume of  $\text{NaH}_2\text{PO}_4(\text{aq})$  at 15 MPa.



**Figure 9.** Standard state partial molar volume of  $\text{H}^+\text{H}_2\text{PO}_4^-(\text{aq})$  at  $p_{\text{sat}}$ .

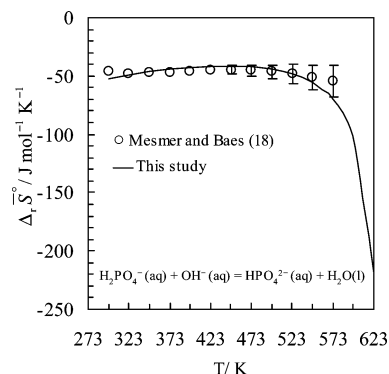


**Figure 10.** Standard state partial molar volume of  $\text{Na}_2\text{HPO}_4(\text{aq})$  at 15 MPa.

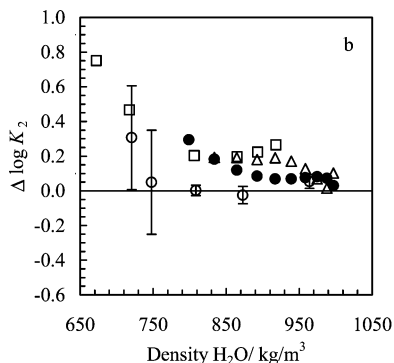
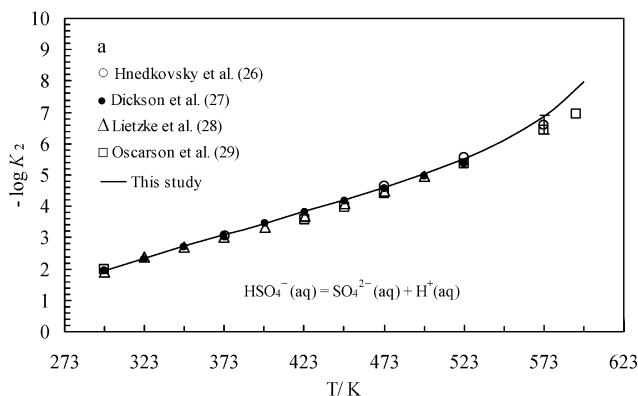
from unified theory parameters for  $\text{NaH}_2\text{PO}_4(\text{aq})$  and the corresponding values for  $(\text{HCl}-\text{NaCl}, \text{aq})$  from Djamali and Cobble,<sup>1</sup> using ionic additivity. Figure 9 shows that the predicted values from the unified theory for  $\bar{V}_2^\circ(\text{H}^+\text{H}_2\text{PO}_4^-, \text{aq})$  at  $p_{\text{sat}}$  are also in reasonable agreement with the corresponding values reported by Ballerat-Busserolles et al.<sup>21</sup>

The unified model parameter values for  $\text{Na}_2\text{HPO}_4(\text{aq})$  were fixed from the lower temperature ( $T \leq 423$  K) experimental values of Mesmer and Baes<sup>18</sup> for  $\log K_{\text{N},2}$ . The predicted values of  $\log K_{\text{N},2}$  for the second neutralization reaction from the unified model are also in excellent agreement with those reported by Mesmer and Baes<sup>18</sup> over the entire temperature range from 298.15 to 573.15 K (Figure 7b). In Figure 10, the values of  $\bar{V}_2^\circ(\text{Na}_2\text{HPO}_4, \text{aq})$  from this study, calculated from the same parameter values obtained from eq 3, are compared with the experimental standard state partial molar volume of  $\text{Na}_2\text{HPO}_4(\text{aq})$  at 10 MPa.<sup>23</sup>

A comparison of the change in standard state entropies for the second neutralization reaction 8,  $\Delta_r \bar{S}^\circ$ , with temperatures



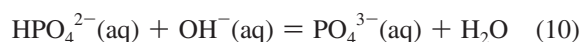
**Figure 11.** Comparison of experimental and calculated values of  $\Delta_r \bar{S}^\circ$  for neutralization reaction of phosphoric acid at  $p_{\text{sat}}$ .



**Figure 12.** (a) Comparison of the experimental and predicted values of  $\log K_2$  for the second ionization of sulfuric acid at 12.5 MPa. (b) Deviations of experimental from calculated values as a function of water density. The symbols for data points are the same as in the case of Figure 12a.

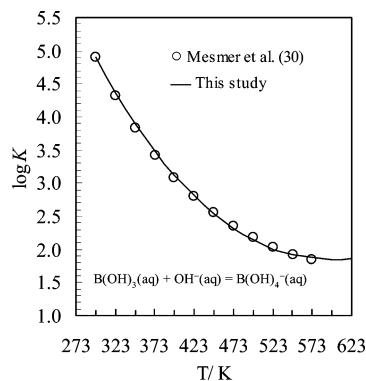
from the unified model with the values reported by Mesmer and Baes<sup>18</sup> is given in Figure 11. The two sets of data for  $\Delta_r \bar{S}^\circ$  agree within the uncertainties of experimental data at all temperatures to 573 K. Obtaining  $\Delta_r \bar{S}^\circ$  values from the temperature coefficients of the free energies alone over small temperature ranges is known to be subject to large errors. The  $\Delta_r \bar{S}^\circ$  values from the unified model were calculated using the same parameters fixed from the low temperature free energy data.

Mesmer and Baes<sup>18</sup> have also measured the third neutralization of phosphoric acid in 0.5 and 1.0 *m* KCl solutions up to 423 K.



Above 423 K,  $\text{PO}_4^{3-}(\text{aq})$  is such a strong base that direct measurements of reaction 10 are not practical. However, it is

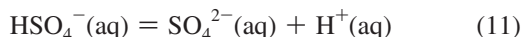




**Figure 13.** Comparison of the experimental and calculated (eq 3) standard state Gibbs free energies of transfer relative to 298.15 K for  $\text{NaB(OH)}_4(\text{aq})$  at  $p_{\text{sat}}$ .

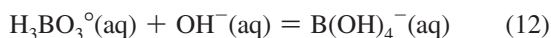
possible to extend the values of  $\log K_{N,3}$  for this reaction up to much higher temperatures and pressures. The values of  $\log K_{N,3}$  for the third neutralization of phosphoric acid calculated from the present unified model are compared with those estimated by Cobble and Lin<sup>24</sup> from experimental data reported by Mesmer and Baes<sup>18</sup> in Figure 7c.

**2.5. Aqueous Sodium Sulfate and Sodium Bisulfate.** The unified model parameter values in Table 1 for aqueous sodium sulfate are calculated from the experimental values of Gibbs free energies of transfer for sodium sulfate reported by Djamali et al.<sup>25</sup> The parameter values in Table 1 for sodium bisulfate are calculated from the differences between the parameter values for the second dissociation of sulfuric acid, reaction 11, the corresponding values for sodium sulfate from above, and differences in the corresponding values of  $(\text{Na}^+ - \text{H}^+, \text{aq})$ .<sup>1</sup> The unified theory parameter values for the second dissociation of sulfuric acid



calculated using the reported values up to 523.15 K at 12.5 MPa.<sup>26</sup> The values of  $\log K_2$  for the second dissociation of sulfuric acid from this study are compared with the corresponding experimental values from literature<sup>26–29</sup> in Figure 12.

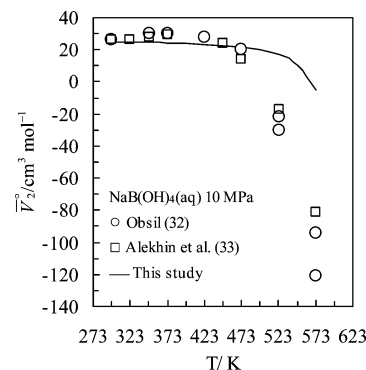
**2.6. Boric Acid Solution.** Boric acid–borate equilibria have been studied by means of a hydrogen electrode concentration cell from 323.15 to 568.15 K<sup>30</sup>



from where

$$(\bar{G}_2(T) - \bar{G}_2(T_r))(\text{NaB(OH)}_4, \text{aq}) = (\bar{G}_2(T) - \bar{G}_2(T_r))(\text{NaOH}, \text{aq}) + (\bar{G}^\circ(T) - \bar{G}^\circ(T_r))(\text{H}_3\text{BO}_3^\circ, \text{aq}) + \Delta_{\text{rxn}}(\bar{G}^\circ(T) - \bar{G}^\circ(T_r)) \quad (13)$$

The standard state Gibbs free energies of transfer for  $\text{NaOH}(\text{aq})$  are from Djamali and Cobble,<sup>2c</sup> the values for neutral  $\text{H}_3\text{BO}_3(\text{aq})$  are from Hnedkovsky et al.,<sup>31</sup> and the corresponding values for the reaction 11 are from Mesmer et al.<sup>30</sup> The unified theory eq 3 parameter values are fixed using  $(\bar{G}_2(T) - \bar{G}_2(T_r))(\text{NaB(OH)}_4, \text{aq})$  from this study (Figure 13) and are listed in Table 1. The standard state partial molar volume for  $\text{NaB(OH)}_4(\text{aq})$  calculated from the parameters



**Figure 14.** Standard state partial molar volume of  $\text{NaB(OH)}_4(\text{aq})$  at 10 MPa.

values in Table 1 are compared with experimental  $\bar{V}_2^\circ$  of  $\text{NaB(OH)}_4(\text{aq})$  in Figure 14. At temperatures above 473.15 K, large differences between the values of  $\bar{V}_2^\circ$  from this study and literature values<sup>32,33</sup> are observed. It should also be noted that in the same temperature range, there is a large disagreement between the values of  $\bar{V}_2^\circ$  reported by different investigators.<sup>32,33</sup>

### 3. Conclusion

The experimental thermodynamic properties for polyatomic ions have usually larger uncertainties at higher temperatures ( $T \geq 523.15$  K), mainly because the required auxiliary data for side reactions (for example, ion association) are generally not available. The above examples illustrate that when good standard state Gibbs free energies are available at lower temperatures, then the unified model<sup>1</sup> can be used to accurately extend the thermodynamic properties for polyatomic ions up to much higher temperatures and pressures, even without knowing the Gibbs free energy of hydration at 298.15 K. The standard state partial molar volumes for the polyatomic electrolytes calculated from the unified theory<sup>1</sup> are in good agreement with the experimental values from literature. This is a very important indication of the internal consistency of the predicted thermodynamic properties.

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