

Standard State Thermodynamic Properties of Completely Dissociated Hydrochloric Acid and Aqueous Sodium Hydroxide at Extreme Temperatures and Pressures

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Standard state thermodynamic properties for completely dissociated hydrochloric acid were fixed by ionic additivity, using the data from other strong electrolytes perrenic acid, sodium perrenate, and sodium chloride from 298.15 to 598.15 K and at p_{sat} . The standard electrode potential for the important silver–silver chloride electrode system and the equilibrium constants for the volatility of HCl from aqueous solutions were then calculated and compared with literature data. Using the experimental data from this study and auxiliary data from literature, the logarithm of the molal association constant of HCl at the critical temperature of water and at 673.15 K up to 1000 MPa was predicted from the unified theory of electrolytes (UTE). The standard state thermodynamic properties for completely dissociated aqueous sodium hydroxide were also calculated by ionic additivity over the same temperature range from aqueous sodium chloride, hydrochloric acid, and the dissociation constant of water. The results were compared with literature data.

1. Introduction

Hydrochloric acid, HCl(aq), is probably the prime example of an acid of the 1–1 charge type and is the most common of this class of compounds.¹ Thermodynamic properties of HCl(aq) are of interest in practical applications and as a fundamental investigation of the properties of representative strong acids. In addition, detailed analysis of measurements of pH at high temperature will require knowledge of the thermodynamic behavior of H⁺(aq). Thermodynamic properties of HCl(aq) are also important in connection with material and acid transport in geothermal reservoirs and in steam generators since many chlorides are volatile, particularly un-ionized HCl.²

The hydrogen ion is a unique +1 cation, and above 523 K, the rapid decrease of the solvent dielectric constant with temperature is known to favor formation of ion pairs (or undissociated species)^{3,4} even for some solutes which are strong electrolytes at room temperature (e.g., aqueous HCl).⁵ Under these conditions, extrapolation of results from other laboratories at finite concentrations ($m > 0.05$) to infinite dilution for determination of standard state values is not accurate for many species and cannot be guided by strong electrolyte models. In recent studies of thermodynamic properties of HCl(aq),⁵ the model dependence of the high temperature thermodynamic properties and the importance of precise experimental measurements extending to very low molalities at temperatures where ion pairing is important were emphasized.

At high temperatures hydrochloric acid is completely dissociated only in very dilute solutions.^{1,5} While those dilutions can now be reached by calorimeters in this laboratory, it is very difficult to use pure small amounts of HCl(g) for carrying out such heats of solution to the required accuracy.

However, reliable standard state partial molal thermodynamic functions can now be derived for completely dissociated

hydrochloric acid by ionic additivity relationships from other strong electrolytes from 298 to 598 K. These properties were generated by combining the data on HReO₄(aq),^{6,7a} NaReO₄(aq),^{6,7b} and NaCl(aq)^{6,7c} according to ionic additivity:

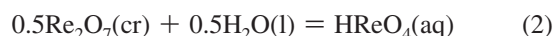
$$\bar{X}^{\circ}(\text{HCl}, \text{aq}) = \bar{X}^{\circ}(\text{HReO}_4, \text{aq}) + \bar{X}^{\circ}(\text{NaCl}, \text{aq}) - \bar{X}^{\circ}(\text{NaReO}_4, \text{aq}) \quad (1)$$

where \bar{X}° represents the standard state partial molal thermodynamic properties of interest.

The accurate values of standard state Gibbs free energies of HCl(aq) provide an opportunity to examine the very important Ag/AgCl electrode system. This and the hydrogen electrode are the best examples of high temperature thermodynamically reversible systems and have been used empirically as reference electrodes in both fundamental and practical high temperature applications (e.g., geothermal and power plant measurements of pH). Further, the measured differences between the thermodynamic properties of H⁺(aq) and those of Na⁺(aq) over the available temperature range, when combined with known standard state data for the dissociation constant of water from hydrogen electrode measurements,⁸ make it possible to calculate many of the thermodynamic properties of NaOH(aq) by ionic additivity over the same temperature range. The thermodynamic properties of NaOH(aq) are of interest as a representative 1:1 strong base.

2. Calculations and Results

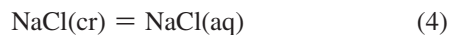
2.1. Hydrochloric Acid. The properties of completely ionized HCl(aq) were obtained by addition of the original calorimetric data for the following substances:



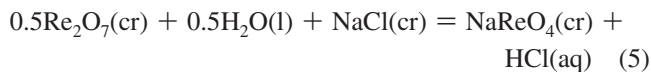
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which gives:



from which the standard state molal enthalpy change for the reaction 5, $\Delta_r \bar{H}^\circ(5)$, is determined as follows:

$$\Delta_r \rho^\circ(5) = \rho^\circ(2) + \rho^\circ(3) + \rho^\circ(4) \quad (6)$$

where numbers in the parentheses refer to specific reactions. The values of ρ , were obtained by subtracting the theoretical Debye–Hückel heat of dilution from each measured enthalpy of solution at a given temperature and concentration:

$$\rho = \Delta_{\text{sol}} \bar{H}^\circ - 2.303RT^2 v_+ v_- (I/m^\circ) \text{d}B/\text{d}T \quad (7)$$

where

$$\rho \equiv \Delta_{\text{sol}} \bar{H} - (v/2)|Z_+ Z_-|A'_H(I/m^\circ)^{1/2} \alpha((I/m^\circ)^{1/2}) \quad (8)$$

with

$$\alpha(x) = [1/(1 + x^{1/2}) - \sigma(x)/3] \quad (9)$$

and

$$\sigma(x) = 3/x^3[(1 + x) - 1/(1 + x) - 2 \ln(1 + x)] \quad (10)$$

where $A'_H = 3/2 A_H$, and $\text{d}B/\text{d}T$ is an adjustable but constant parameter at low concentrations at each temperature, and $m^\circ = 1 \text{ mol kg}^{-1}$. The values of the limiting law slopes, A_H , are from Bradley and Pitzer.⁹ The values of ρ , calculated from each heat of solution measurement, are plotted against the final ionic strength, and the extrapolated value at infinite dilution, ρ° , at each temperature is obtained by a weighted linear least-squares method. These $\Delta_r \rho^\circ$ are then related to $\Delta_r \bar{H}^\circ$ using eq 11:^{6,7}

$$\Delta_r \bar{H}^\circ = \Delta_r \rho^\circ + \Delta_r \bar{V}^\circ \Delta_{\text{vap}} \bar{E} / \Delta_{\text{vap}} \bar{v} \quad (11)$$

and

$$\Delta_r \bar{V}^\circ(5) = \bar{V}_2^\circ(\text{HCl}, \text{aq}) + V_2^\circ(\text{NaReO}_4, \text{cr}) - V_2^\circ(\text{NaCl}, \text{cr}) - 0.5(V_2^\circ(\text{Re}_2\text{O}_7, \text{cr}) + V_1^\circ(\text{H}_2\text{O}, \text{l})) \quad (12)$$

where $\Delta_r \bar{V}^\circ$ is the standard state change of molal volume for reaction 5, \bar{V}_2° is the standard state partial molal volume of $\text{HCl}(\text{aq})$,¹⁰ V_2° are the molar volumes of specified solids calculated from their room temperature densities,¹¹ and $V_1^\circ(\text{H}_2\text{O}, \text{l})$ values are from steam tables.¹²

The enthalpies for reaction 5 at p_{sat} are fitted, using a weighted least-squares method, with eq 13:

$$\Delta_r \bar{H}^\circ = a_1 + a_2 T + a_3 T^2 + a_4 T^2 / (a_5 - T)^2 + a_6 T^2 / (T - a_7)^2 \quad (13)$$

Each data point was weighted with the inverse of the squares of the respective standard deviations, $\sigma_{\rho, v}^2$. As a check of the self-consistency of the enthalpy and heat capacity data the enthalpy for reaction 5 at 298.15 K can be calculated from the enthalpy of reaction at each experimental temperature:

$$\Delta_r \bar{H}^\circ(298.15 \text{ K}) = \Delta_r \bar{H}^\circ(T) - \int_{298.15}^T \Delta_r \bar{C}_p^\circ \text{d}T - \int_{298.15}^T [\Delta_r \bar{V}^\circ - T(\partial \Delta_r \bar{V}^\circ / \partial T)_p] (\partial p / \partial T)_{\text{sat}} \text{d}T \quad (14)$$

Values of $\Delta_r \bar{H}^\circ(298.15 \text{ K})$ for reaction 5 calculated from experimental $\Delta_r \bar{H}^\circ(T)$ at each experimental temperature at p_{sat} are plotted in Figure 1. While such an analysis gives a better value for $\Delta_r \bar{H}^\circ(298.15 \text{ K})$ than can be determined from measurements at that one temperature, it is used here to check the internal consistency of the adopted standard state heat capacities, the molal volumes, and their temperature derivatives at each temperature. The average of all the calculated $\Delta_r \bar{H}^\circ(298.15 \text{ K})$ values for reaction 5 of $-56.621 \pm 0.038 \text{ kJ mol}^{-1}$ is consistent except at one temperature, 542.75 K.

From $\Delta_r \bar{H}^\circ(298.15 \text{ K})$ for reaction 5, the standard state enthalpy of formation of $\text{HCl}(\text{aq})$ at 298.15 K and 0.1 MPa can be obtained from the following eq:

$$\Delta_r \bar{H}^\circ(\text{HCl}, \text{aq}) = \Delta_r \bar{H}^\circ(5) + \Delta_r \bar{H}^\circ(\text{NaCl}, \text{cr}) + 0.5(\Delta_r \bar{H}^\circ(\text{Re}_2\text{O}_7, \text{cr})) + \Delta_r \bar{H}^\circ(\text{H}_2\text{O}, \text{l}) - \Delta_r \bar{H}^\circ(\text{NaReO}_4, \text{cr}) \quad (15)$$

where $\Delta_r \bar{H}^\circ(\text{Re}_2\text{O}_7, \text{cr})$, $\Delta_r \bar{H}^\circ(\text{NaCl}, \text{cr})$, $\Delta_r \bar{H}^\circ(\text{H}_2\text{O}, \text{l})$ at 298.15 K and 0.1 MPa are from the Wagman et al.¹³ and $\Delta_r \bar{H}^\circ(\text{NaReO}_4, \text{cr})$ is from Djmal.⁶ The value for $\Delta_r \bar{H}^\circ(\text{HCl}, \text{aq})$ of $-167.071 \pm 0.038 \text{ kJ mol}^{-1}$ is in excellent agreement with that calculated from the NBS tables,¹³ $-167.159 \text{ kJ mol}^{-1}$, and that of CoData¹⁴ of $-167.08 \pm 0.10 \text{ kJ mol}^{-1}$.

The standard state partial molal enthalpies of transfer $\text{HCl}(\text{aq})$ at p_{sat} , $\bar{H}_2^\circ(T, p_{\text{sat}}) - \bar{H}_2^\circ(298.15 \text{ K}, 0.1 \text{ MPa})$, are calculated from eq 13 and listed in Table 1. The molar enthalpies of transfer for the pure substances are calculated by the extension of 298.15 K values from their known molar heat capacities^{6,15,16} and molar volumes.^{11,12}

These enthalpies of transfer of $\text{HCl}(\text{aq})$ were fitted with eq 13 and the fitting parameters listed in Table 2. The resulting standard state partial molal heat capacities for $\text{HCl}(\text{aq})$ calculated from eq 16 are given in Table 3:

$$\bar{C}_{p,2}^\circ = (\partial(\bar{H}_2^\circ(T, p_{\text{sat}}) - \bar{H}_2^\circ(T_r, p_r)) / \partial T)_{\text{sat}} - (\bar{V}_2^\circ - T(\partial \bar{V}_2^\circ / \partial T)_p)(\partial p / \partial T)_{\text{sat}} \quad (16)$$

The molal volume contribution to $\bar{C}_{p,2}^\circ$ is listed in the third column of Table 3, in order to demonstrate that a 10% uncertainty in this term will introduce errors of less than 2% in $\bar{C}_{p,2}^\circ$ at 598.15 K. The values for \bar{V}_2° and its temperature derivative calculated from UTE¹⁰ are also listed in Table 1. The uncertainties in these properties are directly proportional to the uncertainties in dielectric constant and its temperature and pressure derivatives. The probable error in the values of $\bar{C}_{p,2}^\circ$ for $\text{HCl}(\text{aq})$

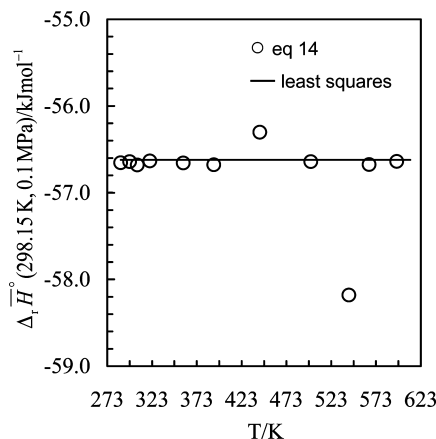


Figure 1. Analysis of standard state molal enthalpies for reaction 5 at 298.15 K and 0.1 MPa from data at higher temperatures. The least-squares fit has a slope of exactly zero (as required).

are estimated to be 7, 15, 30, 120 J mol⁻¹ K⁻¹ at temperatures of 473.15, 523.15, 573.15, 598.15 K, respectively.

The previous experimental values of $\bar{C}_{p,2}^\circ$ for ionized HCl(aq) are limited with respect to temperature and pressure and at higher temperatures are all determined from high concentration data. Tremaine et al.¹⁷ used a flow microcalorimeter for the measurement of the apparent molal heat capacity of HCl(aq), $C_{p,\phi}$, to 413 K in concentrated (≥ 0.1 m) solutions and extrapolated the results to infinite dilution to obtain $\bar{C}_{p,2}^\circ$. Holmes et al.¹ derived an expression for $\bar{C}_{p,2}^\circ$ from measurements of the heats of dilution of HCl(aq) (298–623 K) at $m \geq 0.1$ and fit of various types of thermodynamic results for HCl(aq), and reported $\bar{C}_{p,2}^\circ$ for HCl(aq) to 423 K. Previously reported values of $\bar{C}_{p,2}^\circ$ for HCl(aq) are summarized in Table 3; at $T \leq 423$ K; the results for $\bar{C}_{p,2}^\circ$ from this study are in good agreement with Holmes et al.¹ The $\bar{C}_{p,2}^\circ$ values by Tremaine et al.¹⁷ are also in reasonable agreement with the lower temperature results from this study, considering the errors associated with extrapolation from higher concentrations ($m \geq 0.1$) to infinite dilution.

The $\bar{C}_{p,2}^\circ$ values for HCl(aq) reported by Shock et al.,¹⁸ which were fitted to experimental results below 413 K, are the same as those of Tremaine et al.¹⁷ up to 423 K. At $T > 423$ K their values of $\bar{C}_{p,2}^\circ$ are much less negative than the $\bar{C}_{p,2}^\circ$ value obtained from this study, undoubtedly because above that temperature hydrochloric acid is no longer a strong electrolyte even at low concentrations. The $\bar{C}_{p,2}^\circ$ at p_{sat} for HCl(aq) from this study are recommended since they are based on experimental results down

TABLE 2: Empirical Parameters for Calculating the Standard State Partial Molal Enthalpies Relative to Reference Temperature of 298.15 K from eq 13

	$\bar{H}_2^\circ(T) - \bar{H}_2^\circ(T_r)$	
	HCl(aq)	NaOH(aq)
a_1	2.863919×10^{01}	1.551963×10^{01}
a_2	$-1.056587 \times 10^{-01}$	$-1.803433 \times 10^{-01}$
a_3	4.812718×10^{-05}	4.958091×10^{-04}
a_4	-2.683986×10^{00}	-4.813752×10^{01}
a_5	6.601691×10^{02}	9.011009×10^{02}
a_6	3.251935×10^{-03}	4.783640×10^{-01}
a_7	2.714463×10^{02}	2.135805×10^{02}

to very dilute solutions (10^{-4} m), are over a much wider temperature range, and do not actually involve direct measurements on HCl(aq).

Sharygin and Wood¹⁹ also estimated $\bar{C}_{p,2}^\circ$ for HCl(aq) at 28 MPa from the apparent molal heat capacities ($m \geq 0.1$) by extrapolation to infinite dilution using the Pitzer ion-interaction model.²⁰ For comparison with the $\bar{C}_{p,2}^\circ$ at p_{sat} from this study, Sharygin and Wood¹⁹ results at 28 MPa can, in principle, be adjusted to p_{sat} using

$$\bar{C}_{p,2}^\circ(p_{\text{sat}}) = \bar{C}_{p,2}^\circ(28 \text{ MPa}) - T \int_{28}^{p_{\text{sat}}} (\partial^2 \bar{V}_2 / \partial T^2)_p dp \quad (17)$$

This pressure adjustment requires accurate information on the first and second temperature derivatives of \bar{V}_2 . Sharygin and Wood¹⁹ measured densities of HCl(aq) ($m \geq 0.1$) at temperatures from 298.15 to 623 K and pressures of 10 and 28 MPa with a vibrating-tube flow densimeter from which \bar{V}_2° for HCl(aq) at 10 and 28 MPa are estimated. The standard state partial molal volumes, \bar{V}_2° , for HCl(aq) are then fitted to eq 13, from which $(\partial^2 \bar{V}_2 / \partial T^2)_p$ was calculated. The standard state partial molal heat capacities of Sharygin and Wood¹⁹ thus corrected to p_{sat} are compared in Table 4 with the results from this study. At lower temperatures, $T < 473$ K, the agreement is quite satisfactory (± 5 J mol⁻¹ K⁻¹) considering the relatively high concentrations involved ($m \geq 0.1$). At $T \geq 473$ K the differences between the two sets of $\bar{C}_{p,2}^\circ$ at p_{sat} are much larger and increase with increasing temperature. The magnitude of the discrepancies between the two sets of $\bar{C}_{p,2}^\circ$ from 473 to 523 K are undoubtedly due to extrapolation errors in $\bar{C}_{p,2}^\circ$, estimated from Sharygin and Wood¹⁹ $C_{p,\phi}$, due to the long extrapolation from ($m \geq 0.1$) to infinite dilution and some uncertainties associated with extrapolation to p_{sat} . At $T > 523$ K the discrepancies between $\bar{C}_{p,2}^\circ$ from this study and those of Sharygin and Wood¹⁹ adjusted to

TABLE 1: Standard State Thermodynamic Properties of HCl(aq) at p_{sat}

T (K)	$\bar{H}_2^\circ(T) - \bar{H}_2^\circ(T_r)^a$ (kJ mol ⁻¹)	$\bar{G}_2^\circ(T) - \bar{G}_2^\circ(T_r)^b$ (kJ mol ⁻¹)	$\bar{S}_2^\circ^c$ (J mol ⁻¹ K ⁻¹)	$\bar{C}_{p,2}^\circ^d$ (J mol ⁻¹ K ⁻¹)	$\bar{V}_2^\circ^e$ (cm ³ mol ⁻¹)	$(d\bar{V}_2/dT)_p^e$ (cm ³ mol ⁻¹ K ⁻¹)	$(d\bar{V}_2/dp)_T^e$ (cm ³ mol ⁻¹ MPa ⁻¹)
298.15	0.000	0.000	56.50 ^f	-126.9	18.0	-5.689×10^{-02}	3.801×10^{-02}
323.15	-2.819	-1.295	47.41	-108.6	17.0	-6.149×10^{-02}	4.400×10^{-02}
348.15	-5.589	-2.377	39.16	-114.2	15.6	-8.356×10^{-02}	5.216×10^{-02}
373.15	-8.578	-3.253	30.87	-126.5	13.6	-1.146×10^{-01}	6.452×10^{-02}
398.15	-11.963	-3.914	22.09	-146.6	10.8	-1.601×10^{-01}	8.516×10^{-02}
423.15	-15.982	-4.345	12.31	-179.0	6.7	-2.293×10^{-01}	1.235×10^{-01}
448.15	-21.018	-4.511	0.75	-232.4	0.6	-3.392×10^{-01}	1.898×10^{-01}
473.15	-27.741	-4.358	-13.82	-324.0	-8.6	-5.219×10^{-01}	3.133×10^{-01}
498.15	-37.405	-3.795	-33.65	-491.2	-23.3	-8.448×10^{-01}	5.577×10^{-01}
523.15	-52.566	-2.665	-63.18	-822.7	-48.6	-1.463×10^{00}	$1.081 \times 10^{+00}$
548.15	-79.063	-0.676	-112.27	-1562.0	-96.2	-2.787×10^{00}	$2.334 \times 10^{+00}$
573.15	-132.554	2.793	-206.75	-3524.1	-198.7	-6.131×10^{00}	$5.867 \times 10^{+00}$
598.15	-266.979	9.334	-433.78	-10430.1	-471.3	-1.719×10^{01}	$1.884 \times 10^{+01}$

^a Equation 15. ^b Equation 18. ^c $\bar{S}_2^\circ(T) = [(\bar{H}_2^\circ(T) - \bar{H}_2^\circ(T_r)) - (\bar{G}_2^\circ(T) - \bar{G}_2^\circ(T_r))]/T + T_r \bar{S}_2^\circ(T_r)/T$. ^d Equation 16. ^e From the UTE.¹⁰ ^f NBS tables.¹³

TABLE 3: Comparison of the Standard State Partial Molal Heat Capacities of HCl(aq) (J mol⁻¹ K⁻¹)

T/K	$\bar{C}_{p,2}^{\circ a}$	$f(V)^{b,c}$	$\bar{C}_{p,2}^{\circ d}$	$\bar{C}_{p,2}^{\circ e}$	$C_{p,2}^{\circ f}$	$\bar{C}_{p,2}^{\circ g}$	$\bar{C}_{p,2}^{\circ h}$
298.15	-126.9	0.0	-123.2	-122.7	-126.6	-109.9	-126.5
323.15	-108.6	0.0	-109.0	-112.6	-112.0	-102.8	-114.5
348.15	-114.2	0.1	-111.0	-115.6	-114.1		
373.15	-126.5	0.2	-121.3	-126.9	-125.6	-114.5	-128.2
398.15	-146.6	0.5	-139.0	-146.4	-142.8		
423.15	-179.0	1.3	-166.6	-176.2	(-165.4)	-160.7	-189.5
448.15	-232.4	3.1	-203.6				
473.15	-324.0	7.5	-257.1			-241.3	-307.2
498.15	-491.2	18.3	-343.4				
523.15	-822.7	46.6	-494.8			-356.4	-557.4
548.15	-1562.0	127.2	-795.1				
573.15	-3524.1	391.2	-1514.8			-506.0	-1411.9
598.15	-10430.1	1496.1	-3871.6				

^a Calculated from eq 16 and parameter values of Table 2. ^b Molal volume contribution to $\bar{C}_{p,2}^{\circ}$, from unified theory of electrolytes.¹⁰ ^c $f(V) = (\bar{V}_2 - T(\partial\bar{V}_2/\partial T)_p) \cdot (\partial p/\partial T)_{\text{sat}}$. ^d Shock et al.,¹⁸ estimated from data at $T \leq 423.15$ K. ^e Holmes et al.¹ ^f Tremaine et al.¹⁷ using Pitzer model,²⁰ value at 423.15 K is extrapolated from 413.15 K. ^g Sharygin and Wood,¹⁹ 28 MPa. ^h Sharygin and Wood,¹⁹ corrected to p_{sat} .

TABLE 4: Standard State Gibbs Free Energies of Formation of HCl(aq) and NaOH(aq) at p_{sat} (kJ mol⁻¹)^a

T (K)	$\Delta_f \bar{G}_2^{\circ}(\text{HCl, aq})$	$\Delta_f \bar{G}_2^{\circ}(\text{NaOH, aq})$
298.15	-131.228 ^b	-419.150 ^b
323.15	-128.069	-414.764
348.15	-124.635	-410.057
373.15	-120.939	-405.189
398.15	-116.974	-399.919
423.15	-112.727	-394.498
448.15	-108.169	-388.819
473.15	-103.246	-382.832
498.15	-97.870	-376.459
523.15	-91.885	-369.596
548.15	-85.002	-362.135
573.15	-76.603	-353.957
598.15	-65.095	-345.206
623.15	(-47.465) ^c	(-331.150) ^c

^a Based on $\Delta_f \bar{G}_2^{\circ}$ of elements equal to zero at 298.15 K. ^b NBS tables.¹³ ^c Predicted from unified theory of electrolytes.¹⁰

p_{sat} are so large that they probably cannot be explained by the above considerations alone.

Simonson et al.⁵ have found that at temperatures above 523 K, the experimental results of enthalpies of dilution are not consistent with the assumption of complete dissociation of HCl(aq), that is, HCl(aq) is no longer acting as a strong electrolyte. Sharygin and Wood¹⁹ have also reported that the qualitative trends of $C_{p,\phi}$ at $T > 573$ K clearly indicated extensive association. Therefore, the larger discrepancies at $T > 523$ K may, besides the above considerations, be due to the lack of ion association (or complete dissociation) in the Sharygin and Wood¹⁹ model. It should be noted that their HCl(aq) standard state partial molal heat capacities are much smaller in an absolute sense than their own data for NaCl(aq).

The important standard state partial molal Gibbs free energies of transfer of HCl(aq) at p_{sat} were obtained from $\bar{H}_2^{\circ}(T, p_{\text{sat}}) - \bar{H}_2^{\circ}(298.15 \text{ K}, 0.1 \text{ MPa})$ of HCl(aq) according to

$$\bar{G}_2^{\circ}(T, p_{\text{sat}}) - \bar{G}_2^{\circ}(T_r, p_r) = -\bar{S}_2^{\circ}(T_r, p_r)\Delta T - T \int_{T_r}^T (\bar{H}_2^{\circ}(T, p_{\text{sat}}) - \bar{H}_2^{\circ}(T_r, p_r))/T^2 dT + T \int_{T_r}^T \bar{V}_2^{\circ}(T, p_{\text{sat}})/T(\partial p/\partial T)_{\text{sat}} dT \quad (18)$$

where $\bar{S}_2^{\circ}(298.15 \text{ K}, 0.1 \text{ MPa})$ is from NBS tables.¹³ The uncertainty associated with the calculation of $\bar{G}_2^{\circ}(T, p_{\text{sat}}) -$

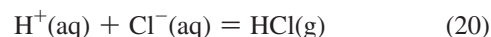
$\bar{G}_2^{\circ}(298.15 \text{ K}, 0.1 \text{ MPa})$ from eq 18 is mainly due to the uncertainty in estimation of the standard state partial molal volume, \bar{V}_2° , at p_{sat} . A 10% uncertainty in \bar{V}_2° will result in less than 0.1% error in the standard state partial molal Gibbs free energies of transfer of HCl(aq) at the highest temperature reported here, because the contributions of \bar{V}_2° to the second and third terms in eq 13 are of opposite signs and of comparable magnitude. These standard state partial molal Gibbs free energies of transfer of HCl(aq) at p_{sat} are also summarized in Table 1. Using auxiliary data on H₂(g) and Cl₂(g) from the JANAF tables¹⁶ the standard state partial molal Gibbs free energies of formation of HCl(aq) at p_{sat} were calculated and believed to be the first to represent accurately the properties of completely dissociated HCl(aq) at these high temperatures (Table 4).

2.2. Silver–Silver Chloride Electrode. The standard state potential for the silver–silver chloride, Ag/AgCl, electrode, E° , can now be reliably calculated as a function of T and at p_{sat} from the change in the standard state Gibbs free energy, $\Delta_r G^{\circ}$, for reaction 19:



The E° values calculated for eq 19 are compared with the observed E° values^{21,22} in Table 5. The agreement is very good (± 0.2 mV) up to 423.15 K, and (± 4 mV) up to 523 K. The E° values of Greeley et al.²¹ are usually considered in error at the higher temperatures¹ because of difficulty in interpretation of the effect of the increased solubility of AgCl(cr).²³ In the development of a comprehensive model for the thermodynamic properties of HCl(aq), Holmes et al.¹ did not include Greeley's result at 548.15 K and the results above 423.15 K were given reduced weight. A similar conclusion can be reached from Table 5. The standard potentials given in Table 5 are very accurate and can be used to calibrate the reproducible and stable Ag/AgCl electrode to high temperatures.

2.3. Volatility Constants for Hydrochloric Acid. Hydrochloric acid solutions show an increase in volatility with temperature and there is considerable interest in an accurate knowledge of the equilibrium constants for the volatility of HCl(aq):



The equilibrium constants, K_p° , reaction 20, at T and at p_{sat} from this study were calculated from the Gibbs free energies given in Table 4 and the JANAF tables¹⁶

$$\log K_p^\circ = (\Delta_f G^\circ(\text{HCl, g}) - \Delta_f \bar{G}_2^\circ(\text{HCl, aq})) / (\ln(10)RT) \quad (21)$$

where R is the gas constant.

Simonson and Palmer² used the experimental total stoichiometric liquid and vapor phase molalities of HCl together with the literature values of the liquid phase stoichiometric mean ionic activity coefficients, γ_{\pm} , to calculate an equilibrium constant, K_m , for volatilization reaction 20 from

$$K_m = (m_{\text{HCl(g)}} \gamma_{\text{HCl(g)}}) / (m_{\text{HCl(aq)}}^2 \gamma_{\pm}^2) \quad (22)$$

In this calculation of K_m , it was assumed that the activity coefficient for the undissociated HCl in the vapor phase, $\gamma_{\text{HCl(g)}}$, is unity. At $T \leq 523.15$ K the values for γ_{\pm} were from model I of Holmes et al.¹ and at $T > 523.15$ K the values for γ_{\pm} were from the chemical interaction (CI) model of Simonson et al.⁵ For the purposes of comparison of K_m , reported by Simonson and Palmer² with the results from this study, K_m can be related to K_p° :

$$\log K_m = \log K_p^\circ + \log(\bar{v}/RT) \quad (23)$$

where \bar{v} is the specific volume of the steam, $\text{H}_2\text{O(g)}$, obtained from steam tables.¹² The $\log K_m$ values from Simonson and Palmer² for the volatility of HCl(aq) are compared in Figure 2 with the $\log K_m$ calculated from eq 19. From 423.15 to 523.15 K, $\log K_m$ values from this study are lower than those reported by Simonson and Palmer² by an almost constant value (0.1 log unit). At 573.15 K, both sets of data agree to 0.004 log unit (<0.3%) and at 623.15 K the difference between the $\log K_m$ values increases to 0.47 log unit. Simonson and Palmer² reported some experimental difficulties in obtaining their data at 623.15 K. Therefore, the $\log K_m$ at 623.15 K from these authors may contain additional errors not known to us.

The stoichiometric mean ionic activity coefficient, γ_{\pm} , used by Simonson and Palmer² were calculated from experimental apparent relative molal enthalpies, L_q , at higher concentrations (>0.1 m). However the experimental L_q must be extrapolated

TABLE 5: Comparison of the Experimental and Calculated Electrode Potentials (Volts) for Ag/AgCl Electrode at p_{sat}^a

T (K)	E° ^b	σ^c	E° ^d	Δ^e
298.15	0.2222	0.0001	0.2222	0.0000
323.15	0.2043	0.0002	0.2043	0.0000
348.15	0.1831	0.0002	0.1833	0.0002
373.15			0.1596	
398.15	0.1328	0.0002	0.1328	0.0000
423.15	0.1030	0.0002	0.1029	-0.0001
448.15	0.0705	0.0004	0.0696	-0.0009
473.15	0.0345	0.0006	0.0324	-0.0021
498.15	-0.0054	0.0006	-0.0095	-0.0041
523.15	-0.0543	0.0040	-0.0578	-0.0035
548.15	-0.0903	0.0100	-0.1155	-0.0252
573.15			-0.1889	
598.15			-0.2944	
623.15			-0.4671	

^a For the reaction $\text{AgCl(cr)} + 0.5 \text{H}_2(\text{g}) = \text{HCl(aq)} + \text{Ag(cr)}$.

^b Experimental data below 373 K from Bates and Bower²² and above 373 K from Greeley et al.²¹ ^c E° , corrected to pressure of $\text{H}_2(\text{g})$, equal to 0.1 MPa. ^d Estimated uncertainties as stated by Greeley et al.²¹ ^e $\Delta = E^\circ(\text{calcd}) - E^\circ(\text{exptl})$.

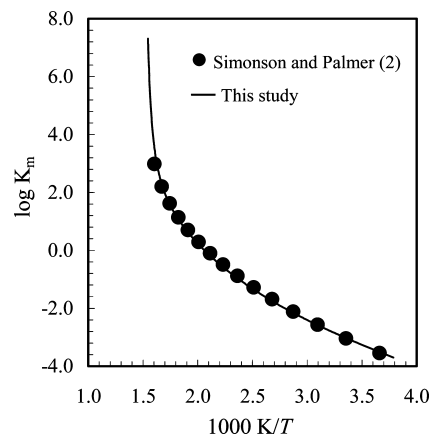


Figure 2. Logarithm of the molal equilibrium constant for volatility of completely dissociated HCl(aq), reaction 20, at p_{sat} .

to infinite dilution in order to calculate γ_{\pm} and if this extrapolation is in error, even precise enthalpy of dilution measurements will produce large errors in the resultant activity coefficients.⁵ Moreover, the extrapolation of L_q to infinite dilution even at the low concentrations (≥ 0.1 m) has been shown⁵ to be model dependent and, therefore, the derived activity coefficients as well. Simonson and Palmer² used eq 19 for calculation of K_m and since γ_{\pm} enters the equation directly, any errors in γ_{\pm} will be reflected in K_m . The $\log K_p^\circ$ (or $\log K_m$) values from this research for the standard states are to be preferred.

Fritz and Fuget²⁴ and Zeisberg²⁵ also reported equilibrium constants for volatilities of HCl(aq) to 323.15 K and to 383.15 K, respectively. The agreement with the experimental $\log K_m$ reported by Fritz and Fuget²⁴ from 273.15 to 323.15 K is (± 0.008) or better. At the time of the Zeisberg²⁵ calculations, there was but one reliable set of measurements for partial vapor pressures of hydrogen chloride at 298.15 and 303.15 K. From 273.15 to 323.15 K the agreement with the $\log K_m$ values of Zeisberg²⁵ is satisfactory (± 0.05).

Recently we reported a new functional form for the Gibbs free energy of hydration of electrolytes in aqueous solutions, a unified theory of electrolytes (UTE) for prediction of the standard state thermodynamic properties of electrolytes to extreme temperatures and pressures.¹⁰ 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 measurements of standard state partial molal entropies and volumes of +1, +2, and +3 electrolytes. It is a simple model to implement and it corrects empirically for deficiencies of the classical Born model.

The UTE model requires only two parameters, C_H and C_S , for each electrolyte at temperatures above 298.15 K. Once these parameters were fixed, the model has been used to predict the standard state partial molal Gibbs free energies of electrolytes up to supercritical temperatures.¹⁰

The temperature and pressure behavior of electrolytes can now be accurately predicted from existing low temperature data alone. The model has also been used successfully to predict and tabulate the standard state partial molal entropies, heat capacities, and volumes of 15 important electrolytes to the highest temperatures of the experimental data, 623 K.^{6,10}

At $T \geq 647.09$ K, the critical temperature of water, $\log K_m$ for reaction 20 is equal to $\log K_a$, the logarithm of the molal association constant of HCl. Using the experimental data from

TABLE 6: Unified Theory Equations for the Thermodynamic Properties of Electrolytes^a

$$\Delta_h \bar{G}^*(T, p) = [\Delta_h \bar{G}^*(T_r, p_r) + C_S T_r - C_H] F_1(D) - \frac{C_S T + C_H}{\nu S^\circ(g) + \Delta_{ss} \bar{S}^\circ} \quad (24a)$$

$$\Delta_h \bar{G}^* = \Delta_h \bar{G}^\circ - \Delta_{ss} \bar{G}^\circ = \Delta_h \bar{G}^\circ - \nu RT \ln \left(\frac{m^\circ d^\circ RT}{1000 p^\circ} \right) \quad (24b)$$

$$F_1(D) = \left[\frac{D(T, p) - 1}{D(T_r, p_r) - 1} \right] \left[\frac{D(T_r, p_r)}{D(T, p)} \right] \quad (24c)$$

$$\bar{S}_2^\circ(T, p) = -(\Delta_h \bar{G}^*(T_r, p_r) + C_S T_r - C_H) F_2(D) - C_S + \nu S^\circ(g) + \Delta_{ss} \bar{S}^\circ \quad (25a)$$

$$F_2(D) = \left[\frac{D(T_r, p_r)}{D(T_r, p_r) - 1} \right] \left[\frac{1}{D(T, p)^2} \right] \left(\frac{\partial D}{\partial T} \right)_p \quad (25b)$$

$$\Delta_{ss} \bar{S}^\circ = -\nu R \left[\ln(RT d^\circ) + T \left(\frac{\partial \ln d^\circ}{\partial T} \right)_T + 1 \right] \quad (25c)$$

$$\bar{V}_2^\circ(T, p) = \{ \bar{V}_2^\circ(T_r, p_r) - (\Delta_h \bar{G}^*(T_r, p_r) + C_S T_r - C_H) F_3(T_r, p_r) \} F_1(T, p) + (\Delta_h \bar{G}^*(T_r, p_r) + C_S T_r - C_H) F_3(T, p) + [\Delta_{ss} \bar{V}^\circ(T, p) - \Delta_{ss} \bar{V}^\circ(T_r, p_r) F_1(T, p)] \quad (26a)$$

$$F_3(D) = \left[\frac{D(T_r, p_r)}{D(T_r, p_r) - 1} \right] \left[\frac{1}{D(T, p)^2} \right] \left(\frac{\partial D}{\partial p} \right)_T \quad (26b)$$

$$\Delta_{ss} \bar{V}^\circ = \nu RT \left(\frac{\partial \ln(d^\circ)}{\partial p} \right)_T \quad (26c)$$

$$\bar{C}_{p,2}^\circ(T, p) = -T(\Delta_h \bar{G}^*(T_r, p_r) + C_S T_r - C_H) F_4(D) + \nu \bar{C}_p^\circ(g) + \Delta_{ss} \bar{C}_p^\circ \quad (27a)$$

$$F_4(D) = \left(\frac{D(T_r, p_r)}{D(T_r, p_r) - 1} \right) \left(\frac{1}{D(T, p)^2} \right) \left[\left(\frac{\partial^2 D}{\partial T^2} \right)_p - \frac{2}{D(T, p)} \left(\frac{\partial D}{\partial T} \right)^2 \right] \quad (27b)$$

$$\Delta_{ss} \bar{C}_p^\circ = -\nu R \left[1 - 2T\alpha^\circ - T^2 \left(\frac{\partial \alpha^\circ}{\partial T} \right)_p \right] \quad (27c)$$

$$\alpha^\circ = -\frac{1}{d^\circ} \left(\frac{\partial d^\circ}{\partial T} \right)_p \quad (27d)$$

^a Definition of symbols: D = bulk dielectric constant of the solvent; C_S and C_H = constant parameters specific to each solute; ν = stoichiometric number of ions in the solute; $m^\circ = 1$ mol/kg; d° = density of the pure solvent in g/cm³; $p^\circ = 0.1$ MPa; α° = coefficient of thermal expansion of water; $S_p^\circ(g)$ and $C_p^\circ(g)$ = the molar entropies and molar heat capacities of the gaseous ions; $\Delta_{ss} \bar{X}^\circ$ ($X = V, C, S, G$) = the standard state correction terms.

this study, dielectric constants of water from Archer and Wang²⁶ and auxiliary data from literature,^{13,16} $\log K_a$ of HCl at 647.09 and 673.15 K up to 1000 MPa were predicted from unified theory of electrolytes,¹⁰ Table 6. The predicted values of $\log K_a$ for HCl are in satisfactory agreement with the experimental values from literature^{27–29} (Figure 3). The values of $\log K_a$ for HCl from this study at 673.15 K are also in good agreement with those reported by Tagirov et al.³⁰ at pressures $p > 60$ MPa. But at pressure of 60 MPa the difference between the $\log K_a$ value increases to 0.57 log unit (see Figure 3). However, at 60 MPa and 673.15 K the $\log K_a$ for HCl from this study is in

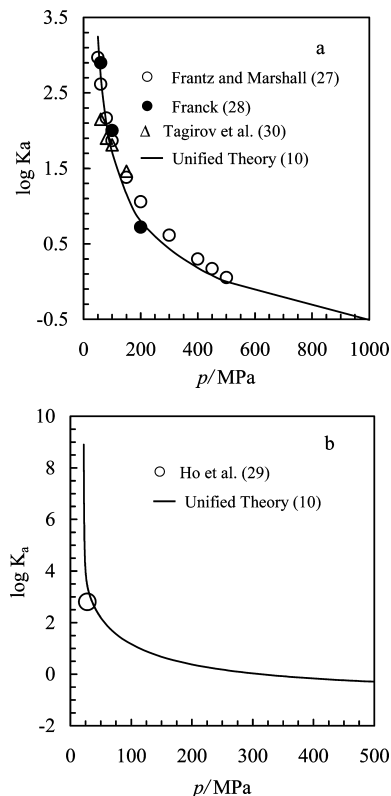


Figure 3. Comparison of the experimental values of the logarithm of the molal association constant of HCl(aq), as a function of T and p , with prediction from unified theory of electrolytes (UTE): (a) 673.15 K, (b) 647.09 K.

good agreement with those reported by Frantz and Marshall²⁷ and Franck.²⁸

2.4. Thermodynamic Properties for Aqueous Sodium Hydroxide.

From the neutralization reaction 28:



It is now possible to derive thermodynamic functions for aqueous sodium hydroxide:

$$\bar{\chi}^\circ(\text{NaOH, aq}) = \Delta_{\text{ion}} \bar{\chi}^\circ - \bar{\chi}^\circ(\text{HCl, aq}) + \bar{\chi}^\circ(\text{NaCl, aq}) + \bar{\chi}^\circ(\text{H}_2\text{O, l}) \quad (29)$$

where $\bar{\chi}^\circ$ is any standard state partial molal quantity of interest.

For example, if the enthalpies for the neutralization of water as a function of T and at p_{sat} are calculated from the formulation of Marshall and Franck⁸ and are combined with enthalpy of formation of HCl(aq) from present study, NaCl(aq) from Djamali and Cobble^{6,7} and H₂O from Keenan et al.¹² then $\Delta_f \bar{H}_2^\circ(\text{NaOH, aq})$ can be calculated from eq 29. The enthalpies for reaction 28 are calculated from the temperature dependence of equilibrium constants. It is known that such a calculation is subject to error since different and arbitrary mathematical forms for equilibrium constants may result in different values of the temperature dependence. However, the extensive data for K_w over a very wide range of temperature and pressure, using low concentration experimental conductivity data³¹ gives more confidence that these values are reasonably accurate (estimated 5–10% error).

TABLE 7: Standard State Thermodynamic Properties of NaOH(aq) at p_{sat} Derived from Calorimetric Measurements at Extreme Dilutions

T (K)	$\bar{H}_2^{\circ}(T) - \bar{H}_2^{\circ}(T_r)^a$ (kJ mol ⁻¹)	$\bar{G}_2^{\circ}(T) - \bar{G}_2^{\circ}(T_r)^b$ (kJ mol ⁻¹)	$\bar{S}_2^{\circ}{}^c$ (J mol ⁻¹ K ⁻¹)	$\bar{C}_{p,2}^{\circ}{}^d$ (J mol ⁻¹ K ⁻¹)	$\bar{V}_2^{\circ}{}^e$ (cm ³ mol ⁻¹)	$(d\bar{V}_2^{\circ}/dT)_p^e$ (cm ³ mol ⁻¹ K ⁻¹)	$(d\bar{V}_2^{\circ}/dp)_T^e$ (cm ³ mol ⁻¹ MPa ⁻¹)
298.15	0.000	0.000	48.10 ^f	-103.4	-3.4	-4.173×10^{-02}	3.801×10^{-02}
323.15	-1.909	-1.088	41.84	-55.3	-4.0	-3.946×10^{-02}	4.209×10^{-02}
348.15	-3.064	-2.059	38.30	-43.0	-4.8	-5.276×10^{-02}	4.717×10^{-02}
373.15	-4.153	-3.041	35.45	-49.1	-6.0	-7.173×10^{-02}	5.455×10^{-02}
398.15	-5.617	-3.768	31.38	-70.1	-7.7	-9.979×10^{-02}	6.702×10^{-02}
423.15	-7.817	-4.468	25.98	-106.9	-10.2	-1.429×10^{-01}	9.156×10^{-02}
448.15	-11.135	-5.017	18.35	-162.9	-13.9	-2.118×10^{-01}	1.336×10^{-01}
473.15	-16.067	-5.351	7.66	-244.5	-19.7	-3.271×10^{-01}	2.125×10^{-01}
498.15	-23.321	-5.383	-7.22	-361.9	-28.9	-5.316×10^{-01}	3.696×10^{-01}
523.15	-33.948	-4.999	-27.92	-533.7	-44.8	-9.239×10^{-01}	7.084×10^{-01}
548.15	-49.396	-4.086	-56.50	-799.4	-75.1	-1.764×10^0	$1.523 \times 10^{+00}$
573.15	-70.536	-2.521	-93.65	-1266.9	-140.8	-3.884×10^0	$3.830 \times 10^{+00}$
598.15	-87.660	-0.446	-121.83	-2378.4	-316.5	-1.086×10^1	$1.232 \times 10^{+01}$

^a Equation 29. ^b Equation 18. ^c $\bar{S}_2^{\circ}(T) = [\bar{H}_2^{\circ}(T) - \bar{H}_2^{\circ}(T_r)] - (\bar{G}_2^{\circ}(T) - \bar{G}_2^{\circ}(T_r))/T + T_r \bar{S}_2^{\circ}(T_r)/T$. ^d Equation 16. ^e From the UTE.¹⁰ ^f NBS tables.¹³

Values of $(\bar{H}_2^{\circ}(T) - \bar{H}_2^{\circ}(298.15 \text{ K}))(\text{NaOH, aq})$ are summarized in Table 7 and are then fitted to eq 13; the fitting parameters are given in Table 2. The standard state partial molal Gibbs free energies of transfer of NaOH(aq) at p_{sat} calculated from eq 18 are also summarized in Table 7. The Gibbs free energies of formation of NaOH(aq) from 298.15 to 623.15 K are calculated as follows:

$$\Delta_f \bar{G}^{\circ}(\text{NaOH, aq}) = \bar{G}_2^{\circ}(\text{NaOH, aq}) - G^{\circ}(\text{Na, cr}) - \frac{1}{2}(G^{\circ}(\text{H}_2, \text{g}) + G^{\circ}(\text{O}_2, \text{g})) \quad (30)$$

where $\bar{G}_2^{\circ}(\text{NaOH, aq})$ are the standard state partial molal Gibbs free energies from Table 7 and G° are the molar Gibbs free energies from literature.¹⁶ These Gibbs free energies of formation are listed in Table 4.

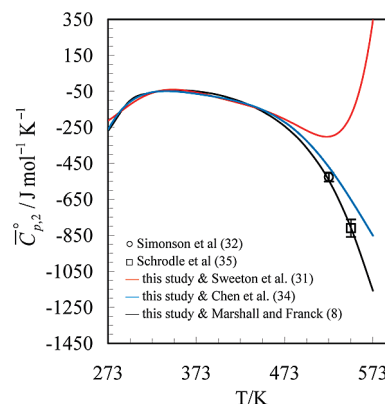
Standard state partial molal heat capacities of NaOH(aq) were then calculated from eq 16 and are listed in Table 7. Simonson et al.³² measured the molal enthalpy of dilution, $\Delta_{\text{dil}} \bar{H}$, of NaOH(aq) from 6.3 to 0.008 m at temperatures from 298.15 to 523.15 K and pressures from 7 to 40 MPa with a differential flow mixing enthalpy calorimeter. Apparent molal heat capacities, $C_{p,\varphi}$, were also measured with a flow heat capacity calorimeter from 0.1 m to 4.0 m and from 323.15 to 523.15 K at 7 MPa. An extended form of the ion-interaction model,²⁰ including an approximation for the effect of ion association, was needed to represent the results quantitatively above 473.15 K. The values of $\bar{C}_{p,2}^{\circ}$ for NaOH(aq) reported by Simonson et al.³² are listed in Table 8 for comparison with the $\bar{C}_{p,2}^{\circ}$ calculated from this study. The agreement between the two sets is satisfactory.

Conti et al.³³ have also reported $\bar{C}_{p,2}^{\circ}$ for NaOH(aq), estimated from $C_{p,\varphi}$ measured ($m \geq 0.05$) with a flow calorimeter from 323.15 to 523.15 K at unspecified pressures near p_{sat} . The agreement between $\bar{C}_{p,2}^{\circ}$ reported by Conti et al.³³ and those calculated from this study are good from 273.15 to 373.15 K. At $T \geq 398.15$ K the agreement is less satisfactory. The disagreement between $\bar{C}_{p,2}^{\circ}$ calculated from this study and model dependent values estimated from extrapolation of Conti et al.³³ $C_{p,\varphi}$ to infinite dilution at $T \geq 398.15$ K probably results from ion association (or incomplete dissociation) in the concentration range in the Conti et al.³³ model. The situation is summarized in Table 8.

TABLE 8: Comparison of Standard State Partial Molal Heat Capacities of NaOH(aq) at p_{sat} (J mol⁻¹ K⁻¹)

T (K)	$\bar{C}_{p,2}^{\circ}{}^a$	$\bar{C}_{p,2}^{\circ}{}^b$	$\bar{C}_{p,2}^{\circ}{}^c$	$\bar{C}_{p,2}^{\circ}{}^d$
273.15	-269.2	-261.6	-253.8	
298.15	-103.4	-100.9	-97.8	
323.15	-55.3	-54.7	-53.0	-54.6
348.15	-43.0	-44.1	-46.4	
373.15	-49.1	-52.4	-52.9	-51.3
398.15	-70.1		-66.4	
423.15	-106.9	-105.7	-89.7	-93.7
448.15	-162.9		-130.3	
473.15	-244.5	-225.1	-197.9	-192.4
498.15	-361.9		-304.2	
523.15	-533.7	-526.0	-461.4	-440.2
548.15	-799.4			-745.7
573.15	-1266.9			(-1532) ^e
598.15	-2378.4			

^a Calculated from eqs 16 and Table 2, at p_{sat} . ^b Simonson et al.³² at p_{sat} . ^c Conti et al.³³ at unspecified pressures near p_{sat} . ^d Schrodle et al.³⁵ at 10 MPa. ^e Extrapolated from 564 K.

**Figure 4.** Comparison of the standard state partial molal heat capacities for NaOH(aq) at p_{sat} calculated from enthalpies of ionization of water reported by different investigators.

Similarly, calculations of $\bar{C}_{p,2}^{\circ}(\text{NaOH, aq})$ at p_{sat} from enthalpies of ionization reported by Sweeton et al.³¹ and Chen et al.³⁴ are compared to this research in Figure 4. At temperatures $T \geq 473.15$ K, the values of $\bar{C}_{p,2}^{\circ}(\text{NaOH, aq})$ calculated from enthalpies of ionization of Sweeton et al.³¹ are not in good agreement with others.^{32,35} For expressing the temperature dependence of the equilibrium constants for ionization of water, Sweeton et al.³¹ assumed that the change in heat capacity at p_{sat}

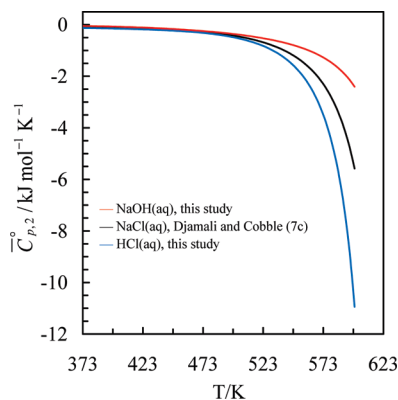


Figure 5. Comparison of standard state partial molal heat capacities of some simple 1–1 electrolytes at p_{sat} .

can be represented by the form $a + bT + c/T$.² This mathematical form for the change in heat capacity of ionization of water at p_{sat} is not sufficiently accurate. The Marshall and Franck⁸ correlation used seven constants over a wide range of temperature and incorporates the data of Sweeton et al.³¹

Chen et al.³⁴ also reported enthalpy changes for the ionization of water determined by flow calorimetry from the heats of mixing of concentrated ($m \geq 0.2$) solution of aqueous NaOH and HCl from temperature range of 523.15–623.15 K. The values of $\bar{C}_{p,2}^0(\text{NaOH}, \text{aq})$ obtained from Chen et al.³⁴ enthalpy data seem to be in modest disagreement with others from data at lower concentrations,³² probably because of the high concentrations involved (Figure 4).

The correlation of Marshall and Franck⁸ are in closer agreement with the result from this study from 273.15 to 573.15 K, the range where the standard state thermodynamic properties for NaOH(aq)^{32,35} are available.

It should also be noted that above 523.15 K the values of $\bar{C}_{p,2}^0(\text{NaOH}, \text{aq})$ reported by Schrodle et al.³⁵ may have large error since $\bar{C}_{p,2}^0(\text{NaOH}, \text{aq})$ were obtained from concentrated solution ($m \geq 0.5$) and with no correction for ion association (or incomplete dissociation).

3. Conclusion

Completely ionized hydrochloric acid is believed to be the first representative strong acid to be thermodynamically well characterized under standard state conditions to date up to 598.15 K, from calorimetric measurements down to 10^{-4} m . At these low concentrations, the extrapolated values are largely independent of the method used to extrapolate the heat of solution to infinite dilution.

The values for $\bar{C}_{p,2}^0(\text{NaOH}, \text{aq})$ obtained from this study are in good agreement with literature from temperatures 273.15 to 573.15 K.

In Figure 5, the standard state partial molal heat capacities of some simple 1:1 electrolytes from this study, HCl(aq), NaCl(aq), and NaOH(aq), indicate that the empirical rules of similarity of electrolytes³ at high temperatures are not always useful. If NaCl(aq) at infinite dilution is considered as a representative 1:1 electrolyte then HCl(aq) and NaOH(aq) at infinite dilutions are not behaving as expected. On purely electrostatic grounds one would have expected that the absolute value for $\bar{C}_{p,2}^0(\text{NaOH}, \text{aq})$ would be larger than that of NaCl(aq). Apparently HCl(aq) and NaOH(aq) are special 1:1 electrolytes at high temperatures probably because of the molecular nature of H^+ and OH^- in water as H_3O^+ , etc., or H_3O_2^- , etc., even though these ions behave well in the general but formal unified theory of electrolytes given elsewhere.¹⁰

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