

Apparent Molar Heat Capacities of Aqueous Solutions of Phosphoric Acid and Sulfur Dioxide from 303 to 623 K and a Pressure of 28 MPa

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Heat capacities of aqueous solutions of phosphoric acid from 0.1 to 0.8 mol·kg⁻¹ and sulfur dioxide from 0.2 to 0.9 mol·kg⁻¹ have been measured with a flow heat-capacity calorimeter from 303 to 623 K and a pressure of 28 MPa. At the lowest molality single-solute solutions as well as mixtures of either H₃PO₄ or SO₂ with HCl were measured to repress dissociation. Calculated apparent molar heat capacities were corrected for dissociation reactions and the chemical relaxation effect. Experimental results for mixtures were analyzed using Young's rule. Standard state partial molar heat capacities of H₃PO₄(aq) and SO₂(aq) were obtained by extrapolation to infinite dilution. A few measurements of the densities of aqueous H₃PO₄ and SO₂ were made at 25°C and a pressure of 28 MPa.

KEY WORDS: Aqueous solutions; apparent molar heat capacity; phosphoric acid; sulfur dioxide; high temperature; apparent molar volume.

1. INTRODUCTION

The high-temperature thermodynamic properties of aqueous phosphoric acid and sulfur dioxide are of great importance in a variety of geochemical and industrial processes such as hydrothermal ore depositions, water-mineral interactions, material transport in steam generators, extraction of bitumen

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and many others. While volumes, heat capacities, and other properties of aqueous solutions of H_3PO_4 and SO_2 at room temperature are fairly well known, there is a definite lack of experimental results at high temperatures.

Heat capacities and volumes for $\text{H}_3\text{PO}_4(\text{aq})$ and $\text{SO}_2(\text{aq})$ at 25°C and atmospheric pressure have been reported by Larson *et al.*⁽¹⁾ and Barbero *et al.*,⁽²⁾ respectively. Included in their analysis were appropriate corrections for dissociation reactions and changes in the equilibrium state and enthalpy due to change in temperature (chemical relaxation effect). There have been a few earlier calorimetric studies of aqueous H_3PO_4 over a wide range of temperatures.^(3,4) However, these measurements were only conducted on concentrated solutions, so they could not be used for obtaining of the standard state heat capacities. The purpose of the present work has been to measure heat capacities of aqueous solutions of H_3PO_4 and SO_2 over a wide temperature range, make corrections for dissociation reactions and chemical relaxation, and use the results to obtain the standard state values.

2. EXPERIMENTAL

The flow Picker-type, high-temperature and pressure calorimeter was used for heat capacity measurements. The design of the instrument, as well as experimental and calibration techniques, have been previously described in detail by Carter and Wood.⁽⁵⁾ The external and internal components of the calorimeter underwent modifications which have been reported by Sharygin and Wood.⁽⁶⁾ The calorimeter measured the electric power necessary to give the same temperature rise when the sample solution and pure water were flowing alternately in the instrument. The results were obtained in three sets of observations. In sets 1 and 2 measurements were made at one low molality of solute. In set 2 HCl was added to the solutions in order to repress dissociation. The molalities of HCl were equal to 0.049 and 0.051 in mixtures with H_3PO_4 and SO_2 , respectively. In set 3 single-solute solutions of $\text{H}_3\text{PO}_4(\text{aq})$ and $\text{SO}_2(\text{aq})$ at two different molalities were measured. In the measurements of set 3, values were taken near 303, 374, 448, and 523 K. In sets 1 and 2, values were obtained near the same temperatures and also at 574 and 623 K.

The specific heat capacity ratio of the sample solution $c_{p,s}$ and that of pure water $c_{p,w}$ was calculated by the equation

$$c_{p,s}/c_{p,w} = \{1 - f(P_s - P_w)/P_w\} \cdot (\rho_w/\rho_s), \quad (1)$$

where f is the correction factor for heat losses, P_s is the electric power when the sample solution was in the cell, P_w is the power when water was in the cell, and ρ_w and ρ_s are the densities of water and of solution at the experimental pressure and the temperature of the sample loop. The temperature reported

for heat capacity measurements represents the average value of the temperature before and after the cell heater

$$T = T_{\text{block}} + 0.5 \cdot \Delta T_{\text{expt}} \quad (2)$$

where the temperature before the cell heater is assumed to be equal to the temperature of the calorimeter block, T_{block} . The experimental temperature rise ΔT_{expt} was measured as the change in ratio of resistance temperature detectors before and after turning on the cell heater. The correction factor f was determined by calibration at each temperature using pure water at different flow rates. Values of ΔT_{expt} and f have been reported previously (for sets 1 and 2 in Ref. 6, for set 3 in Ref. 7).

The solution density ρ_s was calculated from

$$\rho_s^L = \rho_w^L + \Delta\rho(25^\circ\text{C}, p = 28 \text{ MPa}) \quad (3)$$

where ρ_w^L is the density of water at the sample loop temperature and pressure which was calculated from the Hill equation of state for H₂O⁽⁸⁾ and $\Delta\rho$ is the difference in densities of solution and water at 25°C and 28 MPa. The error in ρ_s^L was minimized by keeping the sample loop temperature at 25°C. For sets 1 and 2, $\Delta\rho$ was measured with our vibrating-tube, flow densimeter which has been described in detail by Majer *et al.*⁽⁹⁾ The results of these measurements as well as comparison with literature values are listed in Table I. The experimental densities and calculated apparent molar volumes for H₃PO₄(aq) and SO₂(aq) are in satisfactory agreement with results reported by Larson *et al.*⁽¹⁾ and Barbero *et al.*⁽²⁾ which were interpolated to the experimental molalities of the present study. For set 3, values of $\Delta\rho$ at the experimental molalities were calculated from the literature results for H₃PO₄(aq)^(1,10,11) and SO₂(aq)⁽²⁾ at 0.1 MPa assuming $\Delta\rho$ was not pressure dependent. Table I shows that this assumption is accurate for both solutes.

At each experimental temperature and pressure the calorimeter was tested by measuring the heat capacity for 3.0007 mol·kg⁻¹ NaCl(aq). The experimental heat capacities obtained for this solution were reported for sets 1 and 2 by Sharygin and Wood⁽⁶⁾ and for set 3 by Inglese and Wood.⁽⁷⁾ These results were in good agreement with each other and with the Archer's equation of state for NaCl.⁽¹²⁾

For sets 1 and 2, stock solutions of H₃PO₄(aq) were prepared from A.C.S. reagent concentrated phosphoric acid (Aldrich Chemical Co.; mass fraction 0.85 of H₃PO₄, largest impurity was mass fraction 2.5×10⁻⁴ of Na⁺ as reported by the supplier) and distilled and deionized water. For set 3, two stock solutions were prepared by mass from crystallized H₃PO₄ (Fluka Chemical Co.; mass fraction 0.99, largest impurity was mass fraction 5×10⁻⁵ of Na⁺ as reported by the supplier) used without further purification. The initial solution molalities for all sets were determined by titration with a

Table I. Density Differences and Apparent Molar Volumes for H₃PO₄(aq) and SO₂(aq)

<i>T</i> K	<i>p</i> MPa	<i>m</i> ^a	$\Delta\rho$ kg·m ⁻³	$V_{\phi}^{\text{exp } b}$ cm ³ ·mol ⁻¹	α^c	V_{ϕ}^d cm ³ ·mol ⁻¹
H ₃ PO ₄ (aq)						
Set 1						
298.16	28.00	0.1272	6.94	43.3	0.26	47.5
298.16	28.00	0.1272	6.90	43.5	0.26	47.7
298.15 ^e	0.10	0.1272	6.83	44.0	0.23	47.3
Set 2, m(HCl) = 0.049 mol·kg ⁻¹						
298.16	28.00	0.1213	7.18	45.8	0.16	48.4
298.16	28.00	0.1213	7.21	45.5	0.16	48.1
SO ₂ (aq)						
Set 1						
298.18	28.25	0.1935	6.04	32.6	0.32	39.8
298.18	28.15	0.1935	6.09	32.4	0.32	39.6
298.15 ^f	0.10	0.1935	6.09	32.4	0.27	38.5
Set 2, m(HCl) = 0.051 mol·kg ⁻¹						
298.16	28.00	0.1843	6.15	35.3	0.25	40.9
298.16	28.05	0.1843	6.09	35.6	0.25	41.2

^a Stoichiometric molality of H₃PO₄(aq) or SO₂(aq).

^b Calculated from Eq. (4).

^c Calculated from Eq. (9).

^d Corrected for dissociation (see discussion in the text).

^e Values of V_{ϕ}^{exp} and α were estimated using experimental results and equations from Larson *et al.*, Ref. 1.

^f Values of V_{ϕ}^{exp} and α were interpolated from the results of Barbero *et al.*, Ref. 2.

volumetric standard NaOH solution using thymolphthalein as the indicator. The titration uncertainties were estimated as less than $\pm 0.2\%$.

Stock solutions of SO₂(aq) were prepared from A.C.S. reagent concentrated sulfurous acid (Aldrich Chemical Co.; mass fraction 6×10^{-2} of SO₂) and distilled and deionized water to the desired solution molalities. The initial solution molalities of SO₂(aq) were determined by titration with a volumetric standard NaOH solution (Aldrich Chemical Co.). The solutions were stored in aluminized polyethylene bags with no gas phase present and with a special closure which enables the solution to be transferred directly from the bag into a polyethylene syringe and then into the sample loop. During storage and transfer, the solution does not come in contact with a gas phase where appreciable SO₂ could be lost. For sets 1 and 2, the concentration of each solution was determined before and immediately after all experiments. No significant differences within the estimated titration error ($\pm 0.4\%$) was detected. For set 3, the concentration of each stock solution was determined at the same day of the heat capacity measurement. Each solution was titrated

several times, so that a set of at least three results was obtained. The estimated error in molalities was $\pm 0.001 \text{ mol}\cdot\text{kg}^{-1}$.

3. RESULTS

The experimental apparent molar volumes for single-solute solutions V_{ϕ}^{exp} , which are listed in Table I (set 1), were calculated from the equation

$$V_{\phi}^{\text{exp}} = (\rho_0 - \rho)/\rho\rho_0 m + M_2/\rho, \quad (4)$$

where m denotes the stoichiometric molality, M_2 is the molar mass of solute, ρ and ρ_0 (units: $\text{kg}\cdot\text{cm}^{-3}$) are densities of a solution and pure water, respectively. The results for mixtures with HCl (set 2) were calculated as will be described below for the heat capacities. The apparent molar volumes V_{ϕ} of H₃PO₄(aq) and SO₂(aq) were calculated from the corrected V_{ϕ}^{exp} results. The corrections for the effects of dissociation were the same as in the case of heat capacity (see below), except there is no relaxation effect in density measurements. The values of V_{ϕ} are given in Table I together with the results of Larson *et al.*⁽¹⁾ and Barbero *et al.*⁽²⁾ at comparable molalities. The agreement for both H₃PO₄(aq) and SO₂(aq) is quite good, with somewhat increased uncertainty for the mixtures with HCl(aq).

The results of heat capacity measurements for H₃PO₄(aq) and SO₂(aq) are given in Tables II and III, respectively. When no HCl was added, the experimental apparent molar heat capacities $C_{p,\phi}^{\text{exp}}$ were calculated from the specific heat capacity ratio $c_{p,s}/c_{p,w}$ by using the equation:

$$C_{p,\phi}^{\text{exp}} = c_{p,w} \{ (M_2 + 1/m) \cdot (c_{p,s}/c_{p,w}) - 1/m \} \quad (5)$$

where m is the stoichiometric molality and $c_{p,w}$ was calculated at each experimental temperature and pressure using the Hill equation of state for H₂O.⁽⁸⁾ For the single-solute experiments the error estimates were calculated from the sensitivity limit in determining the ratio of powers (on average: $\pm 2.5 \times 10^{-4}$ for set 1 and $\pm 3.7 \times 10^{-4}$ for set 3) and the accuracy of the calibration factor ($\pm 0.3\%$ for set 1 and $\pm 0.5\%$ for set 3). Estimated uncertainties in $C_{p,\phi}^{\text{exp}}$ for H₃PO₄(aq) and SO₂(aq) are listed in Tables II and III, respectively.

One of the purposes of measuring $C_{p,\phi}^{\text{exp}}$ at several molalities is to obtain results for the apparent molar heat capacity at infinite dilution $C_{p,\phi}^0$, which is equivalent to the standard state partial molar heat capacity $C_{p,2}^0$. Corrections due to dissociation reactions and the chemical relaxation effect had to be applied to the values of $C_{p,\phi}^{\text{exp}}$ prior to extrapolation. Possible chemical reactions considered were: first, second, and third dissociation of H₃PO₄(aq); first and

Table II. Apparent Molar Heat Capacity of H₃PO₄(aq)

T^a K	p MPa	m^b mol·kg ⁻¹	$c_{p,s}/c_{p,w}^c$	$C_{p,\phi}^{\text{exp } d}$ J·K ⁻¹ ·mol ⁻¹	α^e	$C_{p,\phi}^f$ J·K ⁻¹ ·mol ⁻¹
set 1						
303.00	27.94	0.1272	0.9904	88 (2)	0.26	105
303.13	27.89	0.1272	0.9904	89 (2)	0.26	106
373.83	28.08	0.1272	0.9914	123 (2)	0.17	126
373.83	28.06	0.1272	0.9915	125 (2)	0.17	128
448.62	27.95	0.1272	0.9915	131 (2)	0.10	125
448.62	27.95	0.1272	0.9914	128 (2)	0.10	122
523.98	28.15	0.1272	0.9907	109 (2)	0.05	101
523.98	28.20	0.1272	0.9907	110 (2)	0.05	102
574.15	28.20	0.1272	0.9980	12 (8)	0.03	4
574.12	28.20	0.1272	0.9980	11 (8)	0.03	3
623.10	28.18	0.1272	0.9769	-565 (16)	0.01	-564
623.10	28.18	0.1272	0.9771	-555 (16)	0.01	-554
set 2, $m(\text{HCl}) = 0.049$ mol·kg ⁻¹						
303.13	27.90	0.1213	0.9886	113 (5)	0.16	120
303.13	27.90	0.1213	0.9887	116 (5)	0.16	123
376.26	28.10	0.1213	0.9892	137 (5)	0.08	132
376.26	28.10	0.1213	0.9893	140 (5)	0.08	135
448.66	27.95	0.1213	0.9886	146 (10)	0.03	139
448.68	27.95	0.1213	0.9887	149 (10)	0.03	142
523.94	28.15	0.1213	0.9867	126 (17)	0.01	121
523.93	28.25	0.1213	0.9868	130 (17)	0.01	125
574.14	28.20	0.1213	0.9829	-34 (28)	0.00	-37
574.14	28.20	0.1213	0.9835	-9 (28)	0.00	-12
623.03	28.04	0.1213	0.9854	-655 (116)	0.00	-655
623.03	28.04	0.1213	0.9849	-683 (116)	0.00	-683
set 3						
303.13	27.99	0.3865	0.9725	99 (2)	0.17	109
303.13	27.98	0.3865	0.9724	98 (2)	0.17	108
303.13	27.99	0.8223	0.9448	105 (2)	0.12	112
303.13	28.00	0.8223	0.9451	106 (2)	0.12	113
374.24	27.90	0.8223	0.9515	142 (2)	0.08	142
374.24	27.88	0.8223	0.9509	139 (2)	0.08	139
448.26	28.02	0.3865	0.9769	154 (2)	0.06	150
448.26	28.02	0.3865	0.9771	156 (2)	0.06	152
448.26	28.01	0.8223	0.9558	171 (2)	0.05	168
448.26	28.01	0.8223	0.9559	172 (2)	0.05	169
523.64	28.06	0.3865	0.9738	128 (2)	0.03	123
523.64	28.05	0.3865	0.9737	126 (2)	0.03	121
523.64	28.05	0.8223	0.9468	130 (2)	0.02	126
523.64	28.05	0.8223	0.9468	130 (2)	0.02	126

^a T is reported as the average value of the temperature from Eq. (2). The temperature rise and calibration factors are given elsewhere: for sets 1 and 2 in Ref. 6, for set 3 in Ref. 7.

^bStoichiometric molality of H₃PO₄(aq).

^c $c_{p,s}$ and $c_{p,w}$ denote the specific heat capacities of the sample solution and pure water, respectively.

^dCalculated from Eq. (5) for sets 1 and 3 and from Eq. (11) for set 2. Values in parentheses are estimated experimental uncertainties.

^eCalculated from Eq. (9).

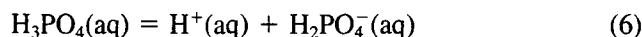
^fCorrected for dissociation and chemical relaxation.

Table III. Apparent Molar Heat Capacity $C_{p,\phi}$ of SO₂(aq)^a

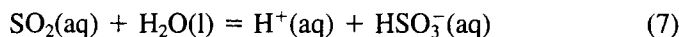
T K	p MPa	m^b mol·kg ⁻¹	$c_{p,s}/c_{p,w}$	$C_{p,\phi}^{\text{exp}}$ J·K ⁻¹ ·mol ⁻¹	α	$C_{p,\phi}$ J·K ⁻¹ ·mol ⁻¹
set 1						
303.12	27.90	0.1935	0.9948	150 (2)	0.30	150
303.11	27.91	0.1935	0.9948	151 (2)	0.30	151
373.67	28.05	0.1935	0.9960	179 (2)	0.12	146
376.29	28.18	0.1935	0.9958	176 (2)	0.12	143
448.73	27.95	0.1935	0.9945	150 (2)	0.04	129
448.73	27.95	0.1935	0.9943	147 (2)	0.04	126
523.94	28.15	0.1935	0.9943	158 (2)	0.01	148
523.94	28.15	0.1935	0.9945	162 (2)	0.01	152
574.12 ^c	28.20	0.1935	0.9942	174 (16)	0.00	168
623.09	28.12	0.1935	0.9969	314 (16)	0.00	313
623.08	28.17	0.1935	0.9971	322 (16)	0.00	321
set 2, $m(\text{HCl}) = 0.051 \text{ mol}\cdot\text{kg}^{-1}$						
303.13	28.01	0.1843	0.9920	151 (5)	0.23	135
303.13	28.00	0.1843	0.9921	153 (5)	0.23	137
376.26	28.10	0.1843	0.9928	172 (5)	0.06	139
376.26	28.10	0.1843	0.9927	170 (5)	0.06	137
448.72	27.95	0.1843	0.9908	148 (10)	0.01	138
448.72	27.95	0.1843	0.9908	148 (10)	0.01	138
523.94	28.15	0.1843	0.9901	170 (17)	0.00	168
523.94	28.15	0.1843	0.9899	164 (17)	0.00	162
574.14	28.30	0.1843	0.9897	169 (28)	0.00	168
574.14	28.30	0.1843	0.9897	169 (28)	0.00	168
623.06	28.05	0.1843	1.0074	355 (116)	0.00	355
623.06	28.05	0.1843	1.0081	381 (116)	0.00	381
set 3						
374.29	27.98	0.3442	0.9924	172 (2)	0.09	145
374.29	28.06	0.8741	0.9803	167 (2)	0.06	148
374.29	28.20	0.8741	0.9808	170 (2)	0.06	151
448.25	28.02	0.3403	0.9905	152 (2)	0.03	135
448.25	28.01	0.3403	0.9902	148 (2)	0.03	131
448.25	28.01	0.7912	0.9779	149 (2)	0.02	137
448.25	28.01	0.7912	0.9774	146 (2)	0.02	134
523.64	28.10	0.3169	0.9905	154 (2)	0.01	146
523.64	28.08	0.3169	0.9905	154 (2)	0.01	146
523.64	28.06	0.6556	0.9806	153 (2)	0.01	147
523.64	28.08	0.6556	0.9800	149 (2)	0.01	143

^aSee footnotes for Table II.^bStoichiometric molality of SO₂(aq).^cThe value of $C_{p,\phi}$ at this temperature has high uncertainty because pressure fluctuations were observed after the injection of SO₂(aq) into the calorimeter.

second dissociation of $\text{SO}_2(\text{aq})$, and dimerization of the HSO_3^- ion. Among these, only the first dissociation reactions represented by



and



were found to be of any importance for our calculations. The thermodynamic information that is necessary for the evaluation of the corrections included dissociation constants K_d , changes in enthalpies $\Delta_r H_m$, and heat capacities $\Delta_r C_{p,m}$ for reactions (6) and (7). The values of $C_{p,\phi}^{\text{exp}}$ for reaction (6), for instance, were expressed by

$$C_{p,\phi}^{\text{exp}} = C_{p,\phi}^{\text{sp}} + C_{p,\phi}^{\text{rel}} = (1 - \alpha) \cdot C_{p,\phi}(\text{H}_3\text{PO}_4) + \alpha \{ C_{p,\phi}(\text{H}^+) + C_{p,\phi}(\text{H}_2\text{PO}_4^-) \} + \Delta_r H_m \cdot (\partial\alpha/\partial T)_{p,m} \quad (8)$$

where $C_{p,\phi}^{\text{sp}}$ is the sum of the heat capacities of all species, and $C_{p,\phi}^{\text{rel}}$ is the relaxation contribution which is caused by changes in equilibrium state and enthalpy due to change in temperature in the course of heat capacity measurement. The degree of dissociation α was obtained by solving the equation for the equilibrium constant

$$K_d = \alpha^2 m \gamma_{\pm}^2 / \gamma_u (1 - \alpha) \quad (9)$$

where γ_{\pm} is the mean activity coefficient of the ions in solution and γ_u is the activity coefficient of the undissociated electrically neutral species. It was assumed that $\gamma_u = 1$ at all experimental conditions. Values of γ_{\pm} and $C_{p,\phi}$ of ionic species at the appropriate ionic strength were calculated using the Pitzer's extended Debye-Hückel limiting law.⁽¹³⁾ Dissociation constants and reaction enthalpies at reference conditions (25°C, 28 MPa) and temperature dependence of $C_{p,\phi}$ for ionic species were calculated from the Helgeson-Kirkham-Flowers (HKF) revised equation of state⁽¹⁴⁾ using the SUPCRT92 software package.⁽¹⁵⁾ The HKF model, which is based on the Born equation for a charged sphere in a dielectric continuum, predicts the standard thermodynamic properties of aqueous electrolytes to 623 K. $C_{p,\phi}(\text{H}_3\text{PO}_4)$ and $C_{p,\phi}(\text{SO}_2)$ at different temperatures were taken from our experimental results. Calculations of the corrections were repeated several times until consistent values of either $C_{p,\phi}(\text{H}_3\text{PO}_4)$ with $C_{p,\phi}^{\text{exp}}(\text{H}_3\text{PO}_4)$ or $C_{p,\phi}(\text{SO}_2)$ with $C_{p,\phi}^{\text{exp}}(\text{SO}_2)$ were achieved. The complete description of the procedure used to calculate the corrections was reported earlier by Inglese *et al.*⁽¹⁶⁾ and will not be repeated here. Indication of reliability of our corrections is provided by comparison to corrections calculated using only data from the HKF model,^(14,15) which was extended by Shock *et al.*⁽¹⁷⁾ for prediction of the standard partial molar

properties of inorganic gases, acids and other neutral aqueous species including H₃PO₄(aq) and SO₂(aq). The difference between these two sets of corrections were comparable to or smaller than the estimated uncertainties in $C_{p,\phi}^{\text{exp}}$ values, except at 303 and 374 K for SO₂(aq). The reason for this discrepancy is the difference about 50 J·K⁻¹·mol⁻¹ between $C_{p,\phi}^{\circ}$ reported by Barbero *et al.*⁽²⁾ at 25°C and $p = 0.1$ MPa and our value of $C_{p,\phi}^{\circ}$ at 303 K and $p = 28$ MPa (for $C_{p,\phi}^{\circ}$ results see discussion below). It should be noted that the value of $C_{p,\phi}^{\circ}$ from Barbero *et al.*⁽²⁾ is the only one which is used in the SUPCRT92 database.⁽¹⁵⁾ However, the value of $C_{p,\phi}^{\text{exp}}$ at the comparable molality reported by Barbero *et al.*⁽²⁾ is close to our experimental result (the difference is only 10 J·K⁻¹·mol⁻¹). This means that the large difference in $C_{p,\phi}^{\circ}$ comes mainly from using different sources of data for reaction properties in calculating corrections for our and Barbero *et al.* results⁽²⁾ and uncertainty in extrapolating our results for SO₂(aq) at 303 K to infinite dilution.

For the measurements in set 2 which were mixtures of two solutes {H₃PO₄(aq) + HCl(aq) and SO₂(aq) + HCl(aq)} the mean values of the apparent molar heat capacity were calculated from the equation

$$C_{p,\phi}^{\text{mean}} = \{c_{p,s}(1 + m_2M_2 + m_3M_3) - c_{p,w}\}/(m_2 + m_3) \quad (10)$$

where m_2 and m_3 refer to the molalities of aqueous H₃PO₄ or SO₂ and HCl, respectively. Young's rule⁽¹⁸⁾ for the apparent molar properties of mixtures was further applied to get the values of $C_{p,\phi}^{\text{exp}}$ for the pure compounds

$$C_{p,\phi}^{\text{mean}} = C_{p,\phi}^{\text{exp}}m_2/(m_2 + m_3) + C_{p,\phi,3}m_3/(m_2 + m_3) + \delta_{23}, \quad (11)$$

where δ_{23} is a correction term that is unknown but usually small at low molalities, so it was neglected. Values of $C_{p,\phi,3}$ for HCl(aq) at the molality of HCl in the mixture ($m_3 \approx 0.05$ for both mixtures) were calculated from the parametric equation derived by Sharygin and Wood.⁽¹⁹⁾ Although the degree of dissociation was suppressed by added HCl, it was still not negligible, especially at lower temperatures. Therefore, the same corrections were applied for set 2 as in the case of sets 1 and 3 and the corrected values along with the degrees of ionization are also reported in Tables II and III. In the calculation of the ionic strength of the solution, the association of HCl(aq) was also considered. The degree of ion association was estimated from the equation for the association constant taken from Mesmer *et al.*⁽²⁰⁾ The only experimental temperatures at which association of HCl(aq) plays important role are 574 K (about 8% association of the ions) and 623 K (about 45% association). Estimated uncertainties in $C_{p,\phi}^{\text{exp}}$ for set 2 were larger compared to sets 1 and 3, due to neglecting the correction term in the Young's rule equation and the errors in calculated $C_{p,\phi,3}$ for HCl(aq) with 0.05 mol·kg⁻¹. The errors in $C_{p,\phi,3}$ were the largest source of uncertainties, particularly at high temperatures: $C_{p,\phi,3} = -(102 \pm 3)$ J·K⁻¹·mol⁻¹ at 303 K, $C_{p,\phi,3} = -(105 \pm 3)$ at 374 K,

$C_{p,\phi,3} = -(174 \pm 8)$ at 449 K, $C_{p,\phi,3} = -(292 \pm 15)$ at 524 K, $C_{p,\phi,3} = -(297 \pm 20)$ at 574 K, and $C_{p,\phi,3} = (1470 \pm 100)$ at 623 K.

4. DISCUSSION

The corrected values of the apparent molar heat capacities at finite molalities were extrapolated to infinite dilution using the equation

$$C_{p,\phi} = C_{p,\phi}^{\circ} + bm(1 - \alpha) \quad (12)$$

where $C_{p,\phi}^{\circ}$ and b are adjustable parameters. A weighted fit of Eq. (12) was used to reflect the higher estimated uncertainty of the results from set 2. Parameters of Eq. (12) for both solutes are listed in Table IV. For $\text{H}_3\text{PO}_4(\text{aq})$ the differences between the results at molalities near 0.12 for mixtures and for single solutes are larger than the reproducibility of the measurements for unknown reasons. The results from the mixtures are higher at the lowest four temperatures and lower at the highest two temperatures. The uncertainties of $C_{p,\phi}^{\circ}$ in Table IV reflect these differences between sets 1 and 2. Below 525 K the uncertainty was estimated from a least-squares fit to all of the data. At the highest two temperatures only two measurements were made, both of which were near 0.12 mol·kg⁻¹. In this case the uncertainties were increased to reflect the differences between the two results and the absence of an extrapolation to infinite dilution. For $\text{SO}_2(\text{aq})$, similar differences between the mixture results at $m = 0.1843$ and the single-solute results at

Table IV. Apparent Molar Heat Capacity at Infinite Dilution $C_{p,\phi}^{\circ}$ for $\text{H}_3\text{PO}_4(\text{aq})$ and $\text{SO}_2(\text{aq})^a$

T/K	$C_{p,\phi}^{\circ}\{\text{H}_3\text{PO}_4(\text{aq})\}$	$b\{\text{H}_3\text{PO}_4(\text{aq})\}$	$C_{p,\phi}^{\circ}\{\text{SO}_2(\text{aq})\}$	$b\{\text{SO}_2(\text{aq})\}$
303	107 ± 6^b	8	$146^c \pm 12$	
374	126 ± 5	19	142 ± 5	9
448	121 ± 10	64	127 ± 5	11
523	102 ± 10	33	151 ± 6	-10
574	$-3^c \pm 16$		$168^c \pm 18$	
623	$-572^c \pm 50$		$323^c \pm 27$	

^aValues of $C_{p,\phi}^{\circ}$ and b were calculated from Eq. (12).

^bThe uncertainties correspond to the 95% confidence limit of the fit to Eq. (12).

^cThis value of $C_{p,\phi}^{\circ}$ was assumed equal to the weighted average of $C_{p,\phi}$ results from sets 1 and 2. The estimated uncertainty for this point consists of the weighted standard deviation of a single measurement and additional 5% error, based on the differences between $C_{p,\phi}$ and $C_{p,\phi}^{\circ}$ at the similar molalities from results reported by Barbero *et al.*, Ref. 2 for $\text{SO}_2(\text{aq})$, Hnědkovský *et al.*, Ref. 22 for $\text{H}_3\text{BO}_3(\text{aq})$, and Hnědkovský and Wood, Ref. 23 for $\text{NH}_3(\text{aq})$. At 574 K, the estimated uncertainties were doubled for both solutes due to the low absolute value of $C_{p,\phi}^{\circ}$ for $\text{H}_3\text{PO}_4(\text{aq})$ and lower accuracy of experimental results for $\text{SO}_2(\text{aq})$ at this temperature.

$m = 0.1935$ were noted. In this case the mixture results 303, 374, and 623 K were low. The results at 448 and 523 K were high and these results agreed at 574 K. Uncertainties were estimated in the same manner as for H₃PO₄(aq) except that at 303 K no extrapolation vs. molality was possible, so the uncertainty was increased to reflect this.

The revised version of the HKF model⁽¹⁴⁾ that has been adopted to the neutral aqueous species by Shock *et al.*⁽¹⁷⁾ was fitted to the temperature dependent $C_{p,\phi}^{\circ}$ results for H₃PO₄(aq) and SO₂(aq). The temperature dependence of $C_{p,\phi}^{\circ}$ at constant pressure is

$$C_{p,\phi} = c_1 + c_2/(T - \Theta)^2 + \omega TX \quad (13)$$

The adjustable parameters c_1 , c_2 , and ω are independent of temperature and pressure. The constant Θ is the solvent characteristic parameter equal to 228 K. The parameter X is related to the static dielectric constant of water ϵ and is given by

$$X = \{(\partial^2 \ln \epsilon / \partial T^2)_p - (\partial \ln \epsilon / \partial T)_p^2\} / \epsilon \quad (14)$$

Values of ϵ and temperature derivatives were calculated from Archer and Wang's equation.⁽²¹⁾ Parameters c_1 , c_2 , and ω for H₃PO₄(aq) and SO₂(aq), which are listed in Table V, were determined from a weighted least-squares fit of Eq. (13) to the isobaric $C_{p,\phi}^{\circ}$ results from Table IV. The fits obtained with the heat capacity results for H₃PO₄(aq) and SO₂(aq) were quite good (see Fig. 1). The standard deviation of the fit was about 6 J·K⁻¹·mol⁻¹ for both solutes which allows reasonably accurate calculation of $C_{p,\phi}^{\circ}$ values using Eq. (13).

It is interesting to compare the present $C_{p,\phi}^{\circ}$ results for H₃PO₄(aq) and SO₂(aq) with literature data for some other solutes. This comparison is shown in Fig. 1 which includes the heat capacity results for aqueous solutions of H₃BO₃, CO₂, H₂S, and NaCl. In the earlier work from this laboratory, Hnědkovský *et al.*⁽²²⁾ reported values of $C_{p,\phi}^{\circ}$ for H₃BO₃(aq) which were obtained from 303 to 703 K with the same flow calorimeter. One should expect similar behavior for H₃PO₄(aq) and H₃BO₃(aq) since both solutes are

Table V. Parameters c_1 , c_2 , and ω for Eq. (13)

Parameter	H ₃ PO ₄ (aq)	SO ₂ (aq)
c_1	1.487×10^2	1.279×10^2
c_2	-2.002×10^5	1.143×10^5
ω	8.523×10^4	-2.368×10^4
σ^a	6.3	6.2

^aStandard deviation of the fit; units: J·K⁻¹·mol⁻¹.

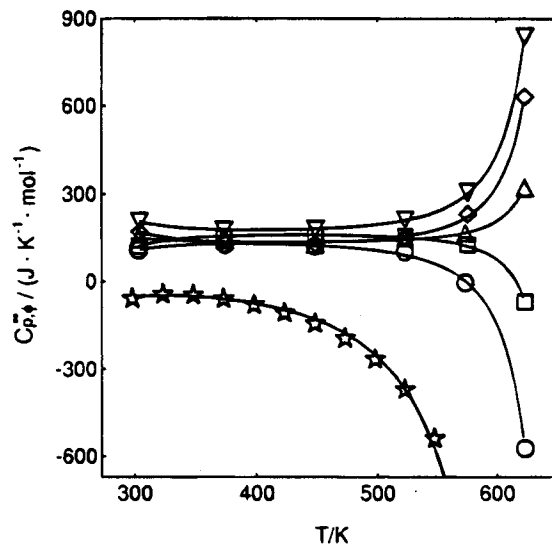


Fig. 1. Apparent molar heat capacities of $\text{H}_3\text{PO}_4(\text{aq})$ and $\text{SO}_2(\text{aq})$ at infinite dilution $C_{p,\phi}^o$ as functions of temperature at $p = 28$ MPa. Comparison with literature results for $\text{H}_3\text{BO}_3(\text{aq})$, $\text{CO}_2(\text{aq})$, $\text{H}_2\text{S}(\text{aq})$, and $\text{NaCl}(\text{aq})$. \circ , present results for $\text{H}_3\text{PO}_4(\text{aq})$; Δ , present results for $\text{SO}_2(\text{aq})$; \square , Hnědkovský *et al.*, for $\text{H}_3\text{BO}_3(\text{aq})$, Ref. 22; ∇ , Hnědkovský and Wood for $\text{CO}_2(\text{aq})$, Ref. 23; \diamond , Hnědkovský and Wood's results for $\text{H}_2\text{S}(\text{aq})$, Ref. 23; \star , Archer's equation of state for $\text{NaCl}(\text{aq})$, Ref. 12. The lines represent calculations using Eq. (13) for corresponding solutes.

very polar molecules with strong hydrogen-bonding. Figure 1 illustrates the temperature dependence of $C_{p,\phi}^o$ for $\text{H}_3\text{PO}_4(\text{aq})$ and $\text{H}_3\text{BO}_3(\text{aq})$ at 28 MPa. The heat capacity slowly increases for both solutes from 303 to 373 K, has a maximum somewhere between 373 and 450 K, then decreases with increasing of temperature. At higher temperatures, the heat capacity becomes negative for both solutes although the magnitude of this reduction is much less for $\text{H}_3\text{BO}_3(\text{aq})$. The heat capacities of several gases in water: $\text{CO}_2(\text{aq})$, $\text{H}_2\text{S}(\text{aq})$, $\text{CH}_4(\text{aq})$, and $\text{NH}_3(\text{aq})$ were reported recently by Hnědkovský and Wood⁽²³⁾ at a wide range of the experimental conditions. Assuming that the heat capacity behavior for $\text{SO}_2(\text{aq})$ should be similar to some of those gases, we chose $\text{CO}_2(\text{aq})$ and $\text{H}_2\text{S}(\text{aq})$ for comparison, since their molecular size and polarity are not too different. Our results for $C_{p,\phi}^o$ of $\text{SO}_2(\text{aq})$ are shown in Fig. 1 along with those of Hnědkovský and Wood⁽²³⁾ for $\text{CO}_2(\text{aq})$ and $\text{H}_2\text{S}(\text{aq})$ (It should be noted that the $C_{p,\phi}$ for $\text{H}_2\text{S}(\text{aq})$ and $\text{CO}_2(\text{aq})$ were not extrapolated to infinite dilution, since these results are available only for one concentration but the correction to infinite dilution is expected to be small at these temperatures.) From 303 to 523 K, the heat capacity for all gases went through a minimum near 448 K. Above 523 K, the heat capacity rapidly increases with increasing temperature for all gases. The growth of $C_{p,\phi}^o$ is the fastest for

CO₂(aq). The theory of solute behavior near the solvent critical point (Wheeler,⁽²⁴⁾ Sengers *et al.*⁽²⁵⁾) shows that in this region V_{ϕ}° and $C_{p,\phi}^{\circ}$ are indicators of the strength of solute–solvent interactions. Solutes with weaker attractive interactions with water have higher $C_{p,\phi}^{\circ}$ values below the critical temperature. The present results show that at high temperatures, $C_{p,\phi}^{\circ}$ for H₃PO₄(aq) is negative and even lower than H₃BO₃(aq), indicating stronger attractive interactions with water. However, as expected, the attractive interactions of H₃PO₄ for water are much less than the attractive interactions of NaCl for water. Results for $C_{p,\phi}^{\circ}$ of NaCl(aq) are shown in Fig. 1 along with those for other solutes. The values of $C_{p,\phi}^{\circ}$ for NaCl(aq) are negative even at low temperatures and decrease rapidly with increasing temperature. At high temperatures the values of $C_{p,\phi}^{\circ}$ for SO₂(aq) are positive, but less than those for CO₂(aq) or H₂S(aq) indicating stronger attractive interactions with water for SO₂, although not as strong as H₃BO₃-water interactions.

There are only a few heat capacity data available in the literature for H₃PO₄(aq) and SO₂(aq) to compare our results with. Egan *et al.*⁽³⁾ reported heat capacities for H₃PO₄(aq) from 0.5 to 57.0 mol·kg⁻¹, from 288 to 353 K and 0.1 MPa. We recalculated their specific heat capacities $c_{p,s}$ from 0.5 to 1.8 mol·kg⁻¹, applied all corrections and extrapolated to infinite dilution in the same way as described above. Larson *et al.*⁽¹⁾ measured heat capacities of H₃PO₄(aq) at 25°C and 0.1 MPa, and corrected the experimental results for dissociation and chemical relaxation. The $C_{p,\phi}^{\circ}$ data from Egan *et al.*⁽³⁾ and Larson *et al.*⁽¹⁾ are displayed in Fig. 2, together with our results. At 25°C our $C_{p,\phi}^{\circ} = (102 \pm 6)$ extrapolated to this temperature at 28 MPa using Eq. (13) and parameters in Table V is higher than literature values at 0.1 MPa reported by Larson *et al.*⁽¹⁾ by 7 and Egan *et al.*⁽³⁾ by 15 J·K⁻¹·mol⁻¹. The pressure dependence of heat capacity was calculated using the relation

$$(\partial C_{p,\phi}^{\circ} / \partial p)_{T} = -T(\partial^2 V_{\phi}^{\circ} / \partial T^2)_{p} \quad (15)$$

where $(\partial^2 V_{\phi}^{\circ} / \partial T^2)$ was estimated from density results for H₃PO₄(aq) reported by Egan and Luff⁽²⁶⁾ from 289 to 345 K. The calculated difference in $C_{p,\phi}^{\circ}$ due to the difference in pressure is 12 ± 5 . The experimental and calculated pressure dependencies are in reasonable agreement considering the large uncertainty in $(\partial^2 V_{\phi}^{\circ} / \partial T^2)_{p}$.

For SO₂(aq), Barbero *et al.*⁽²⁾ reports $C_{p,\phi}^{\circ} = (195 \pm 6)$ corrected for dissociation at 298.15 K and 0.1 MPa, whereas we found $C_{p,\phi}^{\circ} = (146 \pm 12)$ at 303 K and 28 MPa. We could not calculate a correction for the pressure difference using Eq. (15), since the literature volumetric results for SO₂(aq) are only available at 298.15 K. However, the disagreement of 50 between the $C_{p,\phi}^{\circ}$ reported by Barbero *et al.*⁽²⁾ and our result is larger than one would expect, and it seems unlikely that it can be attributed solely to the pressure and temperature difference. However, the value of $C_{p,\phi}^{\text{exp}}$ from Barbero *et al.*⁽²⁾

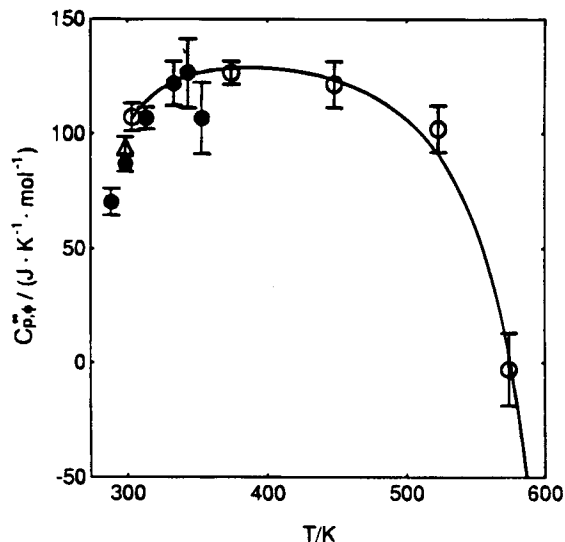


Fig. 2. Apparent molar heat capacity of $\text{H}_3\text{PO}_4(\text{aq})$ at infinite dilution $C_{p,\infty}$ as a function of temperature at different pressures. \circ , present results at $p = 28$ MPa; \bullet , Egan *et al.* at $p = 0.1$ MPa, Ref. 3; Δ , Larson *et al.* at $p = 0.1$ MPa, Ref. 1; —, Eq. (13) for the present results.

at a molality close to our experimental molality is only 10 higher than ours. Consequently, the disagreement is mostly due to the difference in calculated corrections and uncertainty of the extrapolating of our results for $\text{SO}_2(\text{aq})$ at 303 K to infinite dilution, as discussed in the previous section.

Finally, it is hoped that current results for heat capacities of $\text{H}_3\text{PO}_4(\text{aq})$ and $\text{SO}_2(\text{aq})$ at high temperatures and pressures will encourage further investigations of other important thermodynamic properties (densities, enthalpies of dilution, electrical conductances, *etc.*) for these substances.

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REFERENCES

1. J. W. Larson, K. G. Zeeb, and L. G. Hepler, *Can. J. Chem.* **60**, 2141 (1982).
2. J. A. Barbero, L. G. Hepler, K. G. McCurdy, and P. R. Tremaine, *Can. J. Chem.* **61**, 2509 (1983).

3. E. P. Egan, Jr., B. B. Luff, and Z. T. Wakefield, *J. Phys. Chem.* **62**, 1091 (1958).
4. Z. T. Wakefield, B. B. Luff, and R. B. Reed, *J. Chem. Eng. Data* **17**, 420 (1972).
5. R. W. Carter and R. H. Wood, *J. Chem. Thermodyn.* **23**, 1037 (1991).
6. A. V. Sharygin and R. H. Wood, *J. Chem. Thermodyn.* **28**, 851 (1996).
7. A. Inglese and R. H. Wood, *J. Chem. Thermodyn.* **28**, 1059 (1996).
8. P. G. Hill, *J. Phys. Chem. Ref. Data* **19**, 1233 (1990).
9. V. Majer, R. Crovetto, and R. H. Wood, *J. Chem. Thermodyn.* **23**, 333 (1991).
10. J. H. Christensen and R. B. Reed, *Ind. Eng. Chem.* **47**, 1277 (1955).
11. A. Lo Surdo, K. Bernstrom, C.-A. Jonsson, and F. J. Millero, *J. Phys. Chem.* **83**, 1255 (1979).
12. D. G. Archer, *J. Phys. Chem. Ref. Data* **21**, 793 (1992).
13. K. S. Pitzer, *J. Phys. Chem.* **77**, 268 (1973).
14. J. C. Tanger and H. C. Helgeson, *Am. J. Sci.* **288**, 19 (1988).
15. J. W. Johnson, E. H. Oelkers, and H. C. Helgeson, *Computers and Geosci.* **18**, 899 (1992).
16. A. Inglese, J. Šedlbauer, and R. H. Wood, *J. Solution Chem.* **25**, 847 (1996).
17. E. L. Shock, H. C. Helgeson, and D. A. Sverjensky, *Geochim. Cosmochim. Acta* **53**, 2157 (1989).
18. T. F. Young and M. B. Smith, *J. Phys. Chem.* **58**, 716 (1954).
19. A. V. Sharygin and R. H. Wood, *J. Chem. Thermodyn.* in press (1997).
20. R. E. Mesmer, W. L. Marshall, D. A. Palmer, J. M. Simonson, and H. F. Holmes, *J. Solution Chem.* **17**, 699 (1988).
21. D. G. Archer, P. Wang, *J. Phys. Chem. Ref. Data*, **19**, 371 (1990).
22. L. Hnědkovský, V. Majer, and R. H. Wood, *J. Chem. Thermodyn.* **27**, 801 (1995).
23. L. Hnědkovský and R. H. Wood, *J. Chem. Thermodyn.* in press (1997).
24. J. C. Wheeler, *Ber. Bunsenges. Phys. Chem.* **76**, 308 (1972).
25. J. M. H. Levelt Sengers, A. H. Harvey, R. Crovetto, and J. S. Gallagher, *Fluid Phase Equilibria* **81**, 85 (1992).
26. E. P. Egan, Jr. and B. B. Luff, *Ind. Eng. Chem.* **47**, 1280 (1955).