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Received for review September 22, 1987. Accepted February 11, 1988. Support of this research was provided by The National Science Foundation (Grant No. CBT-8514599). The apparatus used is part of the PVTx Laboratory at the University of Tulsa and was purchased with funds provided by several industries, The University of Tulsa, and a National Science Foundation specialized equipment grant (No. CPE-8104650).

Apparent Molar Heat Capacity and Other Thermodynamic Properties of Aqueous KCl Solutions to High Temperatures and Pressures

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Heat capacities of KCl solutions have been measured from 413 to 573 K at 200 bar over the molality range of 0.05-3.0 mol kg^{-1}. These were combined with literature data on volumes, heat capacities, enthalpies, and osmotic coefficients up to a temperature of 599 K and a pressure of 500 bar to yield comprehensive equations for the calculation of the thermodynamic properties of KCl(aq) to high temperatures and pressures by using the ion-interaction approach of Pitzer.

Introduction

Potassium chloride is an important electrolyte in many natural and industrial waters and its thermodynamic properties are of practical interest in industrial and geochemical applications. Heat capacities are particularly useful since these can be integrated to yield enthalpy and activity data by using integration constants evaluated from 298 K data available in the literature. Recent developments in flow calorimetry have minimized the experimental problems associated with determining heat capacities and have provided a useful tool for investigating the thermodynamic properties of electrolyte solutions to elevated conditions of temperature and pressure.

In this study we report our results for the heat capacity of KCl (aq) solutions at molalities from 0.05 to 3.0 mol kg^{-1} and temperatures from 413 to 573 K at a pressure of 200 bar. These values are combined with literature data on heat capacities, osmotic coefficients, and volumes to get a comprehensive set of equations for describing the thermodynamic properties of KCl (aq) to high temperatures and pressures.

Experimental Section

The heat capacity of KCl solutions were measured with a flow calorimeter described in detail by Rogers and Pitzer (*1*) and modified by Phutela and Pitzer (*2*). This high-temperature flow calorimeter is an adaptation of the design used by Picker et al. (*3*).

Briefly, the system consists of two flow calorimetric cells within the same thermostat plus two liquid-chromatography pumps (Kratos Spectroflow 400). In normal operations only one pump is used, and the flow is in series through the two cells. In calibration runs water flows through both cells. For solution measurements one has an exactly equal volumetric flow rate of water to one cell, and solution to the other. With both the sample solution and pure water flowing in the calorimeter, the electrical power necessary to equalize the temperature rise in both sides of the calorimeter is measured. The specific heat capacity of the solution at constant pressure, $c_{p,s}$, is then given by

$$c_{p,s}/c_{p,w} = \{1 + f(P_s - P_w)/P_w\}\rho_{w,298K}/\rho_{s,298K} \quad (11)$$

where $c_{p,s}$ and $c_{p,w}$ are the specific heat capacities of the solution and of pure water, respectively, f is the heat-loss correction factor, P_s and P_w are the electrical powers for solution and water, respectively, and $\rho_{w,298K}$ and $\rho_{s,298K}$ are the densities at 298.15 K of water and solution, respectively.

The correction factors were evaluated at each temperature by using a method suggested by Picker et al. (*3*) and used by Fortier et al. (*4*) and Smith-Magowan and Wood (*5*), with water flowing through both sides of the calorimeter and mimicking a change in the heat capacity on the working side by adding an increment of water flow through that side. For this purpose the second Spectroflow 400 pump was connected to the working side of our calorimeter.

The apparent molar heat capacity, ${}^{\phi}C_p$, can be calculated from the equation

$${}^{\phi}C_p = c_{p,s}M_2 + 1000(c_{p,s} - c_{p,w})/m \quad (12)$$

where m and M_2 are the molality and molecular weight of KCl, respectively.

The solutions used in this study were made up by mass from Baker reagent-grade KCl, which was dried overnight at 473 K and cooled in a vacuum desiccator.

Experimental Results

The results of the heat capacity measurements on KCl solutions are given in Table I. All of the present results are for 200 bar. Water properties used in the calculations were derived from the equation of state of Haar et al. (*6*), while the densities of KCl solutions at 298.15 K and 200 bar were obtained from the fit of Gates and Wood (*7*). The error estimates given in Table I were calculated from our sensitivity limit in determining P_s/P_w, typically ±0.000 15, and an accuracy of ±1% in the measurement of $(P_s - P_w)/P_w$ and of the correction factor, f.

Calculations

Review of Equations. One of our goals is to generate a comprehensive set of equations which describe the thermodynamic properties of aqueous KCl from these heat capacities and other appropriate data. The system of equations chosen

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Table I. Experimental Heat Capacity of Aqueous KCl Solutions at 200 bar Pressure

m	P_s/P_w	$C_{p,s}$, J g^{-1} K^{-1}	$^{\phi}C_p$, J mol^{-1} K^{-1}	δ^a
		T = 412.99 K; f = 1.02		
0.0500	0.9974	4.2133	−103	15
0.1010	0.9949	4.1928	−96.4	8.9
0.2540	0.9879	4.1344	−84.40	5.08
0.5004	0.9771	4.0448	−76.90	3.88
1.0000	0.9569	3.8794	−65.64	3.22
1.5006	0.9387	3.7318	−56.54	2.94
1.9988	0.9234	3.6044	−46.35	2.74
3.000	0.8928	3.3703	−36.67	2.56
		T = 423.87 K; f = 1.02		
0.0500	0.9973	4.2335	−117	16
0.1010	0.9946	4.2122	−111	9
0.2540	0.9871	4.1514	−98.90	5.29
0.5004	0.9758	4.0592	−88.91	4.06
1.0000	0.9560	3.8947	−70.01	3.29
1.5006	0.9374	3.7450	−60.72	3.01
1.9988	0.9206	3.6113	−52.88	2.84
3.0000	0.8905	3.3779	−40.57	2.62
		T = 472.31 K; f = 1.02		
0.0500	0.9967	4.3656	−172	17
0.1010	0.9935	4.3414	−162	10
0.2540	0.9848	4.2732	−143.4	6.0
0.5004	0.9720	4.1717	−126.1	4.7
1.0000	0.9483	3.9855	−107.9	3.9
1.5006	0.9284	3.8263	−90.71	3.51
1.9988	0.9090	3.6779	−82.29	3.32
3.0000	0.8781	3.4360	−62.01	2.99
		T = 522.70 K; f = 1.00		
0.0500	0.9954	4.6387	−298	19
0.1010	0.9903	4.6042	−317.3	12.3
0.2540	0.9785	4.5184	−263.6	7.9
0.5004	0.9616	4.3936	−226.6	6.2
1.0000	0.9308	4.1663	−193.8	5.2
1.5006	0.9062	3.9794	−164.17	4.67
1.9988	0.8861	3.8219	−139.84	4.27
3.0000	0.8495	3.5461	−110.56	3.81
		T = 572.50 K; f = 1.06		
0.0501	0.9906	5.2329	−909.5	29.4
0.1001	0.9842	5.1851	−739.8	19.5
0.2540	0.9630	5.0319	−672.1	14.2
0.5004	0.9360	4.8303	−574.4	11.6
1.0000	0.8945	4.5091	−452.6	9.3
1.5006	0.8605	4.2440	−385.9	8.1
1.9988	0.8330	4.0262	−336.1	7.4
3.0010	0.7942	3.7018	−255.9	6.2

[a] The uncertainty of each $^{\phi}C_p$ value was estimated assuming absolute errors of ±0.000 15 in P_s/P_w and relative errors of 1% in $\Delta P/P$ and in the correction factor, f.

for this purpose was developed by Pitzer (16) and are summarized in Table II. Here $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and C_{MX} are the virial coefficients related to short-range interionic forces. The temperature dependence of these coefficients is determined from the heat capacity data.

Heat capacities of KCl solutions at various temperatures are available from several sources (*8*–*15*). Experimental values are generally at 1 bar or saturation pressure, except for the data from Gates (*10*) (between 160 and 180 bar) and from this study (200 bar). Comparison of isothermal heat capacities between different data sets are, in many cases, meaningful only on an isobaric basis since the pressure dependency of heat capacities is quite significant. For example, Figure 1 compares apparent molar heat capacities at 298 K and 1 bar measured by several workers (*9*, *12*, *14*, *15*) with values from Gates (*10*) at the same temperature and 170 bar. As shown, there is a difference of about 20% in apparent molar heat capacities between 1 and 170 bar. This pressure dependence decreases to a minimum at some higher temperature (for NaCl (aq), this minimum is at around 353 K (*17*)), but increases again with a further increase in temperature and becomes substantial above 473 K.

Table II. Pitzer Equations for the Thermodynamic Properties of 1:1 Aqueous Electrolyte Solutions[a]

Osmotic Coefficient

(1a) $\phi - 1 = -A_{\phi}I^{1/2}/(1 + bI^{1/2}) + mB^{\phi}_{MX} + 2m^2C_{MX}$

(1b) $B^{\phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\exp(-\alpha I^{1/2})$

Activity Coefficient

(2a) $\ln \gamma_{\pm} = -A_{\phi}[I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})] + mB^{\gamma}_{MX} + 3m^2C_{MX}$

(2b) $B^{\gamma}_{MX} = B_{MX} + B^{\phi}_{MX}$
$= 2\beta^{(0)}_{MX} + (2\beta^{(1)}_{MX}/\alpha^2 I)[1 - (1 + \alpha I^{1/2} - \alpha^2 I/2)\exp(-\alpha I^{1/2})]$

Apparent Molar Enthalpy

(3a) $^{\phi}L = A_H \ln(1 + bI^{1/2})/b - 2RT^2[mB^L_{MX} + m^2C^L_{MX}]$

(3b) $B^L_{MX} = (\partial B_{MX}/\partial T)_{p,I}$
$= \beta^{(0)}_{MX}L + \beta^{(1)}_{MX}L\,(2/\alpha^2 I)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]$

(3c) $\beta^{(0)}_{MX}L = (\partial\beta^{(0)}_{MX}/\partial T)_p$

(3d) $\beta^{(1)}_{MX}L = (\partial\beta^{(1)}_{MX}/\partial T)_p$

(3e) $C^L_{MX} = (\partial C_{MX}/\partial T)_p$

Apparent Molar Heat Capacity

(4a) $^{\phi}C_p = \bar{C}^{\circ}{}_{p,2} + A_J \ln(1 + bI^{1/2})/b - 2RT^2[mB^J_{MX} + m^2C^J_{MX}]$

(4b) $B^J_{MX} = (\partial B^L_{MX}/\partial T)_{p,I} + (2/T)B^L_{MX}$
$= \beta^{(0)J}_{MX} + \beta^{(1)J}_{MX}(2/\alpha^2 I)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]$

(4c) $\beta^{(0)J}_{MX} = (\partial\beta^{(0)L}_{MX}/\partial T)_p + (2/T)\beta^{(0)L}_{MX}$

(4d) $\beta^{(1)J}_{MX} = (\partial\beta^{(1)L}_{MX}/\partial T)_p + (2/T)\beta^{(1)L}_{MX}$

(4e) $C^J_{MX} = (\partial C^L_{MX}/\partial T)_p + (2/T)C^L_{MX}$

Apparent Molar Volume

(5a) $^{\phi}V = \bar{V}^{\circ}{}_2 + A_V \ln(1 + bI^{1/2})/b + 2RT[mB^V_{MX} + m^2C^V_{MX}]$

(5b) $B^V_{MX} = (\partial B_{MX}/\partial P)_{T,I}$
$= (\partial\beta^{(0)}_{MX}/\partial P)_T + (\partial\beta^{(1)}_{MX}/\partial P)_T(2/\alpha^2 I)[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]$

(5c) $C^V_{MX} = (\partial C_{MX}/\partial P)_T$

Debye–Hückel Slopes

(6a) $A_{\phi} = {}^1/_3(2\pi N_0 d_w/1000)^{1/2}[e^2(DkT)]^{3/2}$

(6b) $A_H = 4RT^2(\partial A_{\phi}/\partial T)_p$

(6c) $A_J = (\partial A_H/\partial T)_p$

(6d) $A_V = -4RT(\partial A_{\phi}/\partial P)_T$

[a] Definition of symbols: b = a general constant with a value of 1.2 kg$^{1/2}$ mol$^{-1/2}$; α = 2.0 kg$^{1/2}$ mol$^{-1/2}$; β's and C are ion-interaction parameters specific to each solute MX; m = molality of the solute; I = ionic strength; $\bar{C}^{\circ}{}_{p,2}$ = apparent molar heat capacity of the solute at infinite dilution; $\bar{V}^{\circ}{}_2$ = apparent molar volume of the solute at infinite dilution; D = dielectric constant of water; d_w = density of pure water; the quantity C^{ϕ}_{MX}, which is reported occasionally, is $2C_{MX}$ for a 1:1 salt.

In order to compare heat capacity data at different pressures and to describe the pressure dependency of various quantities, volumetric data on KCl solutions were evaluated and were used to fit eq 5 at various temperatures and pressures. From the volumetric fit, one can obtain the pressure dependence of the Gibbs energy (G), enthalpy (H), and heat capacity (C_p) using the following relations:

$$(\partial G/\partial P)_T = V \tag{13}$$

$$(\partial H/\partial P)_T = V - T(\partial V/\partial T)_P \tag{14}$$

$$(\partial C_P/\partial P)_T = -T(\partial^2 V/\partial T^2)_P \tag{15}$$

The pressure dependencies of the Pitzer equations have been derived by Rogers and Pitzer (*18*) and are summarized in Table III.

Table III. Equations for the Pressure Dependence of Thermodynamic Properties of 1:1 Electrolytes

Osmotic Coefficient

$$\phi(P_2) - \phi(P_1) = -[A_\phi(P_2) - A_\phi(P_1)]\frac{I^{1/2}}{1 + bI^{1/2}} + \int_{P_1}^{P_2}\left\{m\left(\frac{\partial\beta^{(0)}_{\mathrm{MX}}}{\partial P}\right)_T + m\left(\frac{\partial\beta^{(1)}_{\mathrm{MX}}}{\partial P}\right)_T \exp(-\alpha I^{1/2}) + 2m^2\left(\frac{\partial C_{\mathrm{MX}}}{\partial P}\right)_T\right\} \mathrm{d}P \tag{7}$$

Activity Coefficient

$$\ln \gamma_\pm(P_2) - \ln \gamma_\pm(P_1) = -[A_\phi(P_2) - A_\phi(P_1)]\left(\frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b}\ln(1 + bI^{1/2})\right) + \int_{P_1}^{P_2}\left\{2m\left(\frac{\partial\beta^{(0)}_{\mathrm{MX}}}{\partial P}\right)_T + \frac{2m}{\alpha^2 I}\left(\frac{\partial\beta^{(1)}_{\mathrm{MX}}}{\partial P}\right)_T\left[1 - \left(1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2}\right)\exp(-\alpha I^{1/2})\right] + 3m^2\left(\frac{\partial C_{\mathrm{MX}}}{\partial P}\right)_T\right\} \mathrm{d}P \tag{8}$$

Apparent Molar Enthalpy

$$^{\phi}L(P_2) - {}^{\phi}L(P_1) = [A_H(P_2) - A_H(P_1)]\frac{\ln(1 + bI^{1/2})}{b} - 2RT^2\int_{P_1}^{P_2}\left\{m\left(\frac{\partial B^V_{\mathrm{MX}}}{\partial T}\right)_{p,I} + m^2\left(\frac{\partial C^V_{\mathrm{MX}}}{\partial T}\right)_p\right\} \mathrm{d}P \tag{9}$$

Apparent Molar Heat Capacity

$$^{\phi}C_p(P_2) - {}^{\phi}C_p(P_1) = [A_J(P_2) - A_J(P_1)]\frac{\ln(1 + bI^{1/2})}{b} - \int_{P_1}^{P_2} T\left(\frac{\partial^2 \bar{V}^{\circ}{}_2}{\partial T^2}\right)_p \mathrm{d}P - 2RT^2\int_{P_1}^{P_2}\left\{m\left[\left(\frac{\partial^2 B^V_{\mathrm{MX}}}{\partial T^2}\right)_{p,I} + \frac{2}{T}\left(\frac{\partial B^V_{\mathrm{MX}}}{\partial T}\right)_{p,I}\right] + m^2\left[\left(\frac{\partial^2 C^V_{\mathrm{MX}}}{\partial T^2}\right)_p + \frac{2}{T}\left(\frac{\partial C^V_{\mathrm{MX}}}{\partial T}\right)_p\right]\right\} \mathrm{d}P \tag{10}$$

Table IV. Literature Sources for Apparent Molar Volumes of Aqueous KCl Solutions

reference	temp range, K	press. range, bar	composn range, m	quantity meaSd or tabulated	estd std error, cm^3 mol^{-1}	std dev of fit, cm^3 mol^{-1}
Chen et al. (*20*)	273-323	1-1000	0.17-1.0	$^{\phi}V$	0.03-0.1	0.50
Egorov et al. (*21*)	298-623	98-1471	0.27-4.5	ρ	1.3-24.7	2.4
Ellis (*22*)	298-473	20	0.1-1.0	ρ	0.05-0.7	1.0
Firth and Tyrrell (*23*)	308-318	1	0.05-4.6	ρ	0.12-11.3	0.59
Gates and Wood (*7*)	298.15	1-400	0.06-3.0	$\Delta\rho$	0.038-0.047	0.10
Goncalves and Kestin (*24*)	298-323	1	0.33-4.6	ρ	0.011-0.15	0.29
Gucker et al. (*26*)	298.15	1	0.27-4.0	ρ	0.012-0.19	0.19
Isono (*27*)	288-328	1	0.05-4.0	ρ	0.012-1.0	0.39
Khaibullin and Borisov (*28*)	373-653	P_{sat}	0.14-3.4	ρ	0.3-14	3.3
Korosi and Fabuss (*29*)	298-453	P_{sat}	0.1-3.6	ρ	0.06-2.1	0.97
Olofsson (*12*)	298.15	1	0.05-2.0	$^{\phi}V$	0.01	0.16
Pepinov et al. (*30*)	298-623	20-300	0.7-3.4	ρ	0.1-3.0	1.4
Rodnyanskii et al. (*31*)	298-613	P_{sat}	0.25-3.0	$1/\rho$	0.4-10	4.5
Romankiw and Chou (*32*)	298-318	1	0.5-4.5	ρ	0.01-0.1	0.38
Sandor et al. (*33*)	283-313	1	0.1-4.7	ρ	0.1-5.1	0.45
Spedding et al. (*34*)	298.15	1	0.007-0.20	ρ	0.01	0.13
Stakhanova et al. (*14*)	298.15	1	0.5-4.5	ρ	0.01-0.1	0.19
Vaslow (*35*)	298.15	1	0.05-2.5	$^{\phi}V$	0.01	0.03

Literature Volumetric Data. There is a fair number of literature sources of volumetric data on KCl solutions (*7*, *19–35*), most of which are listed in Table IV. Column 5 in this table gives the quantities measured or tabulated in the references from which the apparent molar volumes, $^{\phi}V$, were calculated by using the equation

$$^{\phi}V = 1000(\rho_{\mathrm{w}} - \rho_{\mathrm{s}})/\rho_{\mathrm{w}}\rho_{\mathrm{s}}m + M_2/\rho_{\mathrm{s}} \tag{16}$$

where the ρ's now refer to the densities of water and solution at the temperature and pressure of interest. The estimated precision of the reported quantities was taken as stated by the original investigators or as estimated by us in some cases. Estimated errors in the apparent molar volumes, which increase with a decrease in molality, were derived from the propagation of these uncertainties in the reported quantities.

The consistency of experimental data from different sources was checked by plotting isothermal-isobaric apparent molar volumes as a function of molality. The volumes at 298 K are well-determined from various sources, including at high pressures from Chen et al. (*20*) and Gates and Wood (*7*). Up to 323 K the data at 1 bar from different references are quite consistent, but at higher pressures the values of Egorov et al. (*21*) and Pepinov et al. (*30*) at low molalities are inconsistent with the values of Chen et al. (*20*). Above 323 K there are relatively good data at or near saturation pressures to 423 K and 3.6 m KCl from Korosi and Fabuss (*29*) and to 473 K and 1 m from Ellis (*22*), although Korosi's data below 1 m are a bit inconsistent with those of Ellis. Additional data at or near saturation pressures up to 653 K are availabe from Khaibullin and Borisov (*28*), Pepinov et al. (*30*), and Rodnyanskii et al. (*31*), although of much poorer quality, particularly at the low concentration end of the data sets. Bell et al. (*19*) also have data at saturation pressure to 643 K and 1 m, but with insufficient precision to calculate apparent molar volumes.

At high pressures above 323 K, the data were mostly from Egorov et al. (*21*) and Pepinov et al. (*30*). Apparent molar volumes calculated from Pepinov et al.'s data are higher than those from Egorov's values, and frequently show incorrect

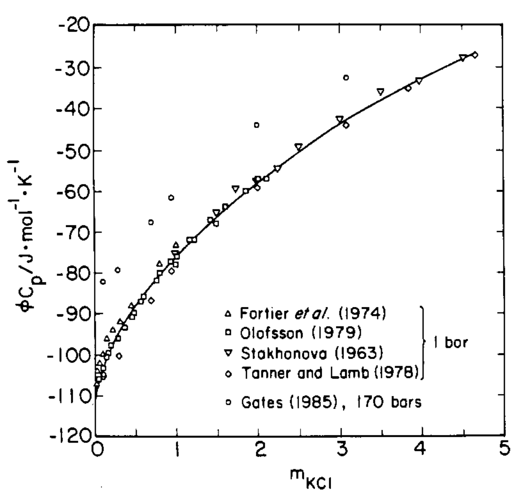

Figure 1. Apparent molar heat capacities, ${}^{\phi}C_p$, at 298.15 K at pressures of 1 and 170 bar. The solid line is calculated from the equations and parameters of this study.

Table V. Parameters for Eq 17 for the Apparent Molar Volume of KCl Solutions[a]

parameter	$\bar{V}°_2$, cm^3 mol^{-1}	B^V_{KCl}, kg mol^{-1} bar^{-1}
q_1	1.56152E03	0.0
q_2	-1.69234E05	0.0
q_3	-4.29918E00	9.45015E-08
q_4	4.59233E-03	-2.90741E-10
q_5	-3.25686E04	3.26205E-03
q_6	-6.86887E00	8.39662E-07
q_7	7.35220E02	0.0
q_8	2.02245E-02	-4.41638E-09
q_9	-2.15779E-05	6.71235E-12
q_{10}	1.03212E02	-4.42327E-05
q_{11}	5.34941E-03	-7.97437E-10
q_{12}	-5.73121E-01	0.0
q_{13}	-1.57862E-05	4.12771E-12
q_{14}	1.66987E-08	-6.24996E-15
q_{15}	-7.22012E-02	4.16221E-08

[a] 1.00E$-x$ = 1.000 × 10^{-x}. 1.000E0x = 1.000 × 10^{x}.

trends with concentration. These values were given significantly lower weights in the regression than those of Egorov et al. Also, apparent molar volumes calculated from Egorov et al.'s densities show incorrect negative pressure dependence at certain temperatures. Additional data are available from Gorbachev et al. (*25*) at 101 bar up to 553 K and 1.5 *m*, but their values are significantly lower than those from other sources and are not precise enough below 0.1 *m* to calculate apparent molar volumes. Their data were therefore excluded from the regression.

There are clearly large differences in precision of the volumetric data sets, as well as in data coverage of temperature, pressure, and concentration, and these proved to be troublesome in getting an overall fit of the volumetric data. The poor quality of the low concentration data above 473 K at saturation pressure and above 323 K at higher pressures prevents extrapolation of apparent molar volumes to infinite dilution to get accurate values of standard-state volumes from which the pressure dependencies of the other standard-state properties can be derived. When we attempted to get an overall fit to within experimental uncertainty of the more precise data sets, we obtained incorrect trends of calculated apparent molar volumes with pressure and/or molality at certain temperatures. Since our concern was in generating equations to describe the pressure dependencies of various thermodynamic properties, particularly the second temperature derivatives of the volumes required for heat capacity calculations, we have accepted lower fit criteria for those espeically precise data. Because uncertainties in available volumetric data become much larger above 573 K at all pressures, and above 500 bar at temperatures above 298 K where the only available measurements are those of Egorov et al. (*21*), the regression was limited to data up to 573 K and 500 bar. In addition, we have included in the data set standard-state volumes of KCl(aq) at various temperatures and pressures calculated from the equations of Tanger and Helgeson (*36*), in order to guide the regression to give correct temperature and pressure trends of the standard-state volumes.

Regression of Volumetric Data. Equation 5 gives the concentration dependence of the apparent molar volume in terms of the standard-state partial molar volume of the solute, $\bar{V}°_2$, and the pressure derivatives of $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and C_{MX} at a single temperature and pressure. As in the case of NaCl(aq) (*17*) and NaOH(aq) (*37*), it was found in preliminary calculations that the pressure dependence of $\beta^{(1)}_{MX}$ could not be determined from the apparent molar volumes because of the generally poor data at low molalities where $\beta^{(1)}_{MX}$ is important. In addition, volumetric data for KCl solutions at high temperatures and pressures extend only to 3.4 *m*, except Egorov et al.'s (*21*) data which go up to 4.5 *m*. Thus, we have found it unnecessary to include the pressure dependency of C_{MX}, which is important only at high concentrations. Therefore, $(\partial\beta^{(1)}_{MX}/\partial P)_T = 0$ and $B^V_{MX} = (\partial\beta^{(0)}_{MX}/\partial P)_T$, and $(\partial C_{MX}/\partial P)_T = 0$. That is, $\beta^{(0)}_{MX}$ will depend on both temperature and pressure in the final equation of state, whereas $\beta^{(1)}_{MX}$ and C_{MX} will depend only on temperature.

In order to fit the volumetric data at all *T*, *P*, and *m* simultaneously, equations describing the *T* and *P* dependence of $\bar{V}°_2$ and B^V_{MX} are needed. The basic form of the equations is essentially that used by Rogers and Pitzer (*18*) for NaCl (aq) with a few modifications and is

$$f_V(T,P) = q_1 + q_2/T + q_3T + q_4T^2 + q_5/(647 - T) + P[q_6 + q_7/T + q_8T + q_9T^2 + q_{10}/(647 - T)] + P^2[q_{11} + q_{12}/T + q_{13}T + q_{14}T^2 + q_{15}/(647 - T)] \quad (17)$$

where the *q*'s are determined by a least-squares fit of eq 17 to experimental data, *P* is the pressure of interest, and 647 K approximates the critical point of water. The equations for $\bar{V}°_2$ and B^V_{MX} were optimized by repeated least-squares regression to eliminate redundant parameters. Values of the *q*'s for $\bar{V}°_2$ and B^V_{MX} are given in Table V, and the standard deviations of fit for the apparent molar volumes for each data set are given in column 7 of Table IV. The pressure dependencies of the various thermodynamic properties can be calculated from these parameters, eq 17, and the equations in Table III.

Regression of Heat Capacities and Other Data. From the equations and parameters for the pressure dependence eval-

Table VI. Literature Sources for Apparent Molar Heat Capacities of Aqueous KCl Solutions

reference	temp range, K	press. range, bar	composn range, *m*	quantity measd or tabulated	estd std error, J mol^{-1} K^{-1}	std dev of fit, J mol^{-1} K^{-1}
Conti et al. (*8*)	333–493	P_{sat}	0.8–9.1	$C_{p,s}$	5–21	7.2
Fortier et al. (*9*)	298.15	1	0.02–1.0	${}^{\phi}C_p$	3.0	3.0
Gates (*10*)	298–599	164–179	0.1–3.0	${}^{\phi}C_p$	3–48	5.3
Likke and Bromley (*11*)	353–473	P_{sat}	0.28–1.5	$C_{p,s}$	1–46	13
Olofsson (*12*)	298.15	1	0.05–2.1	${}^{\phi}C_p$	3.0	0.9
Rüterjans et al. (*13*)	303–403	P_{sat}	0.51–1.8	${}^{\phi}C_p$	3.0	2.3
Stakhanova et al. (*14*)	298.15	1	0.5–4.5	$C_{p,s}$	0.5–4.2	1.0
Tanner and Lamb (*15*)	278–358	1	0.1–4.7	${}^{\phi}C_p$	3.0	1.9

uated above, experimental data for heat capacities of KCl solutions from various sources listed in Table VI can be recalculated to a single reference pressure for evaluation. The reference pressure chosen for our calculations is 179 bar, which is where most of the high-pressure measurements of Gates (*10*) were made, and which is close enough to the pressure of our experiments (200 bar) to minimize the effect of uncertainties in our pressure-dependency equations. By this procedure, our equations for properties at 179 bar can be combined, with minimum uncertainty, with an improved equation for pressure dependency based on new and more precise volumetric data.

In order to obtain an overall fit of the isobaric set of apparent molar heat capacities, equations for the temperature dependence of $\bar{C}^{\circ}_{p,2}$, $\beta^{(0)J}_{MX}$, $\beta^{(1)J}_{MX}$, and C^{J}_{MX} are needed. The basic form of the equations is slightly modified from that used by Pitzer et al. (*17*) for NaCl (aq) and is given

$$f_{C_p}(T,P_r) = u_1 + u_2/T + u_3 \ln T + u_4T + u_5T^2 + u_6/(T - 227) + u_7/(647 - T)^2 \quad (18)$$

where the u's are determined from a least-squares regression of eq 18 to the isobaric heat capacity data and P_r is the reference pressure of 179 bar.

Recalling the relationships between heat capacity, enthalpy, and osmotic or activity coefficients, and between the ion-interaction parameters for these quantities as given in Table II, the temperature-dependent equations (at pressure P_r) for enthalpy parameters $\beta^{(0)L}_{MX}$, $\beta^{(1)L}_{MX}$, and C^{L}_{MX}, and osmotic/activity coefficient parameters $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and C_{MX} are given as follows:

$$\begin{aligned} f_L(T,P_r) = {} & u_1T/3 + u_2/2 + u_3T(\ln T - \tfrac{1}{3})/3 + \\ & u_4T^2/4 + u_5T^3/5 + (u_6/T^2)[(T - 227)^2/2 + \\ & 454\,(T - 227) + (227)^2 \ln (T - 227)] + \\ & (u_7/T^2)[-(647 - T) + 1294 \ln (647 - T) + \\ & 647^2/(647 - T)] + K_1/T^2 + f_L(T_r,P_r)(T_r^{\,2}/T^2) \quad (19) \end{aligned}$$

$$\begin{aligned} f_G(T,P_r) = {} & u_1T^2/6 + u_2T/2 + u_3T^2(\ln T/2 - \tfrac{5}{12})/3 + \\ & u_4T^3/12 + u_5T^4/20 + u_6[T/2 + 3(227)^2/2T + \\ & 227(T - 227) \ln (T - 227)/T] - \\ & u_7[2(647 - T) \ln (647 - T)/T + \ln (647 - T)] - \\ & K_1/T - f_L(T_r,P_r)(T_r^{\,2}/T) + K_2 + f_G(T_r,P_r) \quad (20) \end{aligned}$$

where K_1 and K_2 are integration constants evaluated at the reference temperature, T_r, of 298.15 K, and $f_L(T_r,P_r)$ and $f_G(T_r,P_r)$ are values of the ion-interaction parameters for enthalpy and osmotic/activity coefficients, respectively, at the reference temperature and reference pressure. For our calculations, values of $\beta^{(0)L}_{MX}$, $\beta^{(1)L}_{MX}$, and C^{L}_{MX} at T_r and 1 bar were derived from fitting eq 3 to KCl(aq) enthalpy values tabulated in Wagman et al. (*38*), and values of $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and C_{mX} were taken from Holmes and Mesmer (*39*). These parameters were then recalculated to 179 bar from the pressure-dependency equations discussed above.

In general, the fits obtained with the KCl(aq) heat capacity data are quite good, as shown by comparisons of experimental and calculated values at 179 bar at various temperatures in Figure 1–3, and by the standard deviations of fit of each data set listed in Table VI. Although Likke and Bromley's (*11*) data show a bit of scatter, the fit to their values is within their stated experimental uncertainty of 0.013 J g^{-1} K^{-1} in specific heats. Conti et al.'s (*8*) values tend to be more negative than our calculated values, and are significantly more negative than those from other data sets up to 373 K, but are more consistent with Likke and Bromley's values above 373 K. The fit to Rüterjans et al.'s (*13*) data is very good to 363 K, with a standard deviation of 2.3 J mol^{-1} K^{-1}, but their values are significantly lower than ours and those of Conti et al. and Likke and Bromley above this temperature, with an overall standard deviation for all their data to 403 K of 9.0 J mol^{-1} K^{-1}.

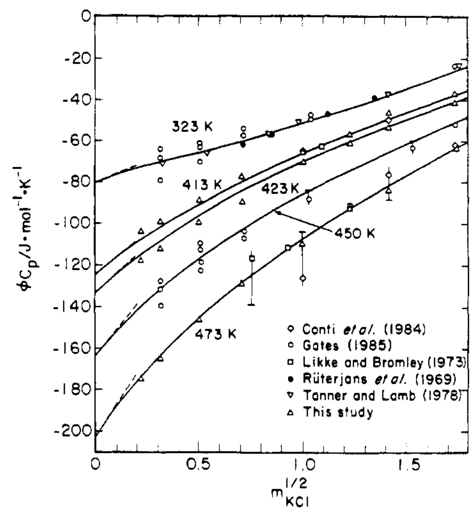

Figure 2. Apparent molar heat capacities, $^{\phi}C_p$, at 179 bar at temperatures of 323, 413, 423, 450, and 473 K. The solid curves are calculated from the equations and parameters of this study, and the dashed lines are the Debye–Hückel slopes. For clarity, not all experimental points at each temperature are shown.

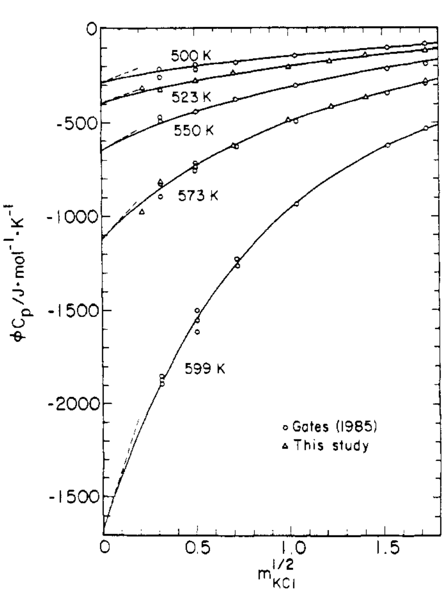

Figure 3. Apparent molar heat capacities, $^{\phi}C_p$, at 179 bar at temperatures of 500, 523, 550, 573, and 599 K. The solid curves are calculated from the equations and parameters of this study, and the dashed lines are the Debye–Hückel slopes.

Using eq 1–10 and the parameters evaluated from volumetric and heat capacity data, it is possible to calculate various thermodynamic properties at T and P. Initial comparison of calculated osmotic and activity coefficients with the values tabulated by Holmes and Mesmer (Table XI–XII, supplement to ref 43 to 523 K and 6 m KCl at saturation pressure indicated good agreement to 3 m, which is the highest molality of most heat capacity measurements, but it was clear that osmotic data at higher concentrations could contribute to an improved general equation. Consequently, a comprehensive regression was done including Holmes and Mesmer's tabulated values of osmotic coefficients to 6 m and 523 K (recalculated to 179 bar). The resulting parameters are given in Table VII. The standard deviation of fit for the osmotic coefficient data of Holmes and Mesmer is 0.003.

Calculation of Other Thermodynamic Properties. Apparent molar enthalpies have been determined for KCl solutions from

Table VII. Parameters for Eq 18, 19, and 20 for the Apparent Molar Heat Capacity, Apparent Molar Enthalpy, and Osmotic/Activity Coefficient[a]

parameter	$\bar{C}^\circ_{p,2}$, J mol^{-1} K^{-1}	$\beta^{(0)J}_{MX}$, kg mol^{-1} K^{-2} $\beta^{(0)L}_{MX}$, kg mol^{-1} K^{-1} $\beta^{(0)}_{MX}$, kg mol^{-1}	$\beta^{(1)J}_{MX}$, kg mol^{-1} K^{-2} $\beta^{(1)L}_{MX}$, kg mol^{-1} K^{-1} $\beta^{(1)}_{MX}$, kg mol^{-1}	C^J_{MX}, kg^2 mol^{-2} K^{-2} C^L_{MX}, kg^2 mol^{-2} K^{-1} C_{MX}, kg^2 mol^{-2}
u_1	3.71110E04	-2.10289E-02	2.20813E-01	0.0
u_2	0.0	6.03967E-01	-4.61849	7.64891E-04
u_3	-7.90247E03	3.67768E-03	-4.10116E-02	0.0
u_4	3.30367E01	-7.05537E-06	1.10445E-04	-1.12131E-08
u_5	-1.76733E-02	1.97968E-09	-4.73196E-08	1.72256E-11
u_6	-2.91950E04	-2.47588E-03	-2.74120E-02	0.0
u_7	-5.92362E06	1.44160E-01	3.32883E-01	-5.71188E-03
$f_L(T_r,1\text{ bar})$		6.77136E-04	9.67854E-04	-4.12364E-05
$f_L(T_r,P_r)$		6.56838E-04	9.67854E-04	-4.12364E-05
$f_G(T_r,1\text{ bar})$		4.8080E-02	2.18752E-01	-3.94E-04
$f_G(T_r,P_r)$		5.0038E-02	2.18752E-01	-3.94E-04
K_1		-2931.268116	6353.355434	28.172180
K_2		-33.953143	193.004059	-0.125567

[a] 1.000E-0x = 1 × 10^{-x}; 1.000E0x = 1 × 10^{x}.

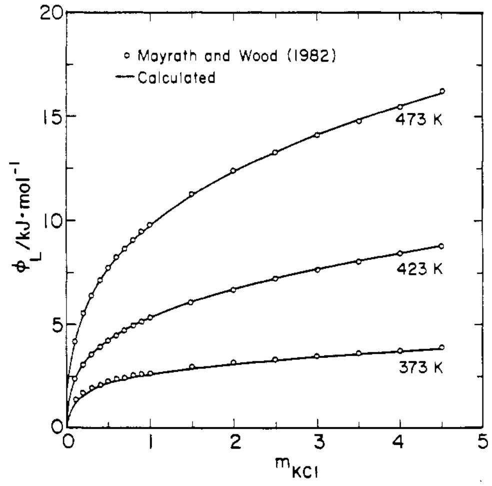

Figure 4. Calculated relative apparent molar enthalpies, $^{\phi}L$, at saturation pressure and at temperatures of 373, 423, and 473 K, compared with experimental values from Mayrath and Wood (*40*).

heat of dilution measurements by Mayrath and Wood (*40*) at 373, 423, and 473 K. These data were not included in a comprehensive fit of the Pitzer equations, hence it is worthwhile to compare our calculated values with their data. This comparison is shown in Figure 4, which indicates good agreement between experimental and calculated values to within 0.2 kJ mol^{-1}.

Up to 523 K, osmotic and activity coefficients at 1 bar or saturated pressure calculated from our equations are constrained by the inclusion of osmotic coefficient values from Holmes and Mesmer (*39*) in the overall regression. Above this temperature the only constraint is the second temperature derivative of the excess Gibbs energies evaluated from the heat capacity data. Although vapor pressures of KCl solutions at these temperatures have been measured by Wood et al. (*41*) and Zarembo et al. (*42*) from which osmotic and activity coefficients can be calculated, these were not included in the regression and can be used to check our calculated values at these higher temperatures. These comparisons at various temperatures are shown in Figure 5 in terms of vapor pressure lowering for KCl solutions as a function of molality. Osmotic coefficients, ϕ, calculated from our equations were converted to vapor pressures using the equation

$$\phi = (1000/2)mM_1RT\left[RT\ln(p^0/p) - \int_p^{p^0}(RT/P - V^\circ_1(\mathrm{g}))\,dP - \int_p^{p^0}\bar{V}^\circ_1(\mathrm{l})\,dP\right] \quad (21)$$

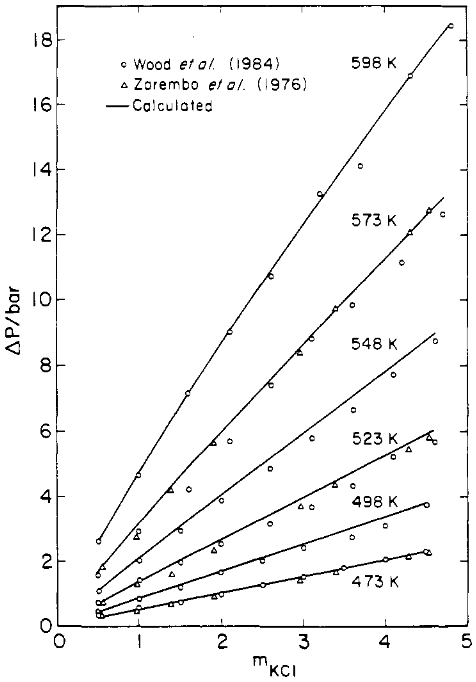

Figure 5. Calculated vapor pressure depressions, ΔP (vapor pressure of pure water – vapor pressure of solution), for KCl solutions compared with experimental data from Wood et al. (*41*) and Zarembo et al. (*42*).

where p^0 and p are the vapor pressures of pure water and the solution, respectively, M_1 is the molecular weight of water, $V^\circ_1(\mathrm{g})$ is the molar volume of water vapor at T and p, $\bar{V}^\circ_1(\mathrm{l})$ is the partial molar volume of water in the solution, which can be approximated by the molar volume of pure water. Figure 5 shows there is good agreement between measured and calculated vapor pressures to 598 K.

Discussion

The equations and parameters evaluated above permit the calculation of volumetric, activity, and thermal properties of KCl solutions to high temperatures and pressures. Because the volumetric data used to fit the Pitzer equations extend only to a temperature of 573 K, pressure of 500 bar, and molality equal to 4.5, the equations and parameters for apparent molar volumes and pressure dependencies are strictly valid only to those limits. Thus our calculations at higher temperatures and molalities (up to 600 K and 6 m KCl at pressures less than or equal to 200 bar) represent extrapolations of those equations, and calculations at still higher values may give incorrect volumes

Table VIII. Apparent Molar Heat Capacity for KCl(aq) Solutions, J (mol/K)$^{-1}$[a]

	temperature, °C							
molality	25.0	50.0	100.0	150.0	200.0	250.0	300.0	325.0
0.00	-114.0	-93.1	-105.1	-144.3	-245.9	-540.7	-1639	-3656
0.10	-103.2	-82.9	-88.3	-116.4	-197.7	-432.5	-1243	-2613
0.30	-94.6	-76.8	-78.4	-100.2	-171.3	-373.5	-1030	-2070
0.50	-88.3	-72.4	-72.0	-90.4	-155.6	-338.5	-908.1	-1767
1.00	-76.0	-63.5	-60.7	-74.4	-130.3	-282.1	-720.9	-1323
1.50	-66.1	-55.9	-52.2	-63.5	-113.0	-243.4	-602.1	-1057
2.00	-57.6	-49.1	-45.0	-54.9	-99.4	-212.9	-514.6	-873.0
3.00	-43.5	-37.3	-33.3	-41.8	-78.0	-165.0	-388.0	-627.8
4.00	-32.6	-27.8	-23.8	-31.6	-61.1	-126.6	-295.6	-466.9
5.00		-20.3	-16.1	-23.3	-46.7	-93.7	-221.3	-348.2
6.00			-9.9	-16.3	-34.0	-64.4	-157.3	-251.1

[a] Pressure = 1 bar at $T < 100$ °C, or P_{sat} above.

Table IX. Apparent Molar Enthalpy for KCl(aq) Solutions, kJ mol^{-1}[a]

	temperature, °C							
molality	25.0	50.0	100.0	150.0	200.0	250.0	300.0	325.0
0.10	0.34	0.59	1.24	2.34	4.15	7.62	17.20	31.11
0.30	0.33	0.75	1.78	3.52	6.36	11.72	26.48	47.66
0.50	0.24	0.79	2.07	4.21	7.65	14.14	31.91	57.15
1.00	-0.06	0.74	2.51	5.33	9.75	18.05	40.56	71.80
1.50	-0.37	0.64	2.80	6.10	11.20	20.75	46.37	81.24
2.00	-0.67	0.53	3.03	6.72	12.33	22.88	50.87	88.29
3.00	-1.21	0.30	3.38	7.68	14.11	26.23	57.80	98.69
4.00	-1.65	0.11	3.66	8.44	15.50	28.89	63.21	106.5
5.00		-0.04	3.90	9.06	16.66	31.13	67.75	112.8
6.00			4.10	9.59	17.64	33.09	71.73	118.3

[a] Pressure = 1 bar at $T < 100$ °C, or P_{sat} above.

Table X. Osmotic Coefficients for KCl(aq) Solutions[a]

	temperature, °C							
molality	25.0	50.0	100.0	150.0	200.0	250.0	300.0	325.0
0.10	0.927	0.925	0.918	0.905	0.887	0.860	0.817	0.781
0.30	0.907	0.907	0.900	0.883	0.857	0.819	0.759	0.710
0.50	0.901	0.903	0.896	0.877	0.847	0.803	0.733	0.678
1.00	0.899	0.905	0.899	0.877	0.840	0.786	0.701	0.636
1.50	0.905	0.914	0.910	0.884	0.842	0.781	0.685	0.614
2.00	0.914	0.926	0.923	0.894	0.849	0.782	0.677	0.602
3.00	0.937	0.954	0.951	0.919	0.868	0.792	0.673	0.590
4.00	0.965	0.983	0.980	0.946	0.890	0.807	0.676	0.588
5.00		1.012	1.007	0.971	0.913	0.824	0.682	0.587
6.00			1.030	0.993	0.933	0.840	0.688	0.585

[a] Pressure = 1.0 bar at $T < 100$ °C, or P_{sat} above.

or pressure dependencies, particularly for heat capacities which depend on the second temperature derivative of the volumes.

The evaluation of available volumetric data for KCl solutions indicated that the volumetric equations can be improved by new and more precise high-temperature data at saturation pressure and above. The effect of uncertainties in apparent molar volumes on the accumulated error in the pressure corrections to the various thermodynamic properties is difficult to determine because of the number of steps needed in the calculations. The estimated error for heat capacity corrections will be largest since those require information on the second derivative of the volume with respect to temperature. The minimum uncertainty for these corrections can be estimated by comparing experimental heat capacities obtained at saturation pressure (*8*, *9*, *11–15*) with those obtained at 164–179 bar by Gates (*10*) and at 200 bar in this study, with all values recalculated to a common pressure. Comparison of these data to 473 K indicated that the corrected values are in agreement within the scatter of the measured heat capacities. The same is true for data at 573 K, where pressure effects are much greater, using data at 179 bar from Gates (*10*) and at 200 bar from our experimental results. A value of 20% for the estimated error in pressure correction gives an uncertainty in recalculating apparent molar heat capacities from saturation pressure to 200 bar of the same magnitude as the uncertainty in experimental heat capacities, and can be used as the approximate error in the pressure corrections for apparent molar heat capacities. For corrections over larger pressure intervals, the percent uncertainty should remain roughly the same, although the absolute error will be larger. The pressure correction for enthalpy, which requires information on the first temperature derivative of the volume, will have about the same amount of uncertainty, while for osmotic or activity coefficients, which only need terms describing the pressure dependence of apparent molar volumes, the estimated uncertainty in the pressure corrections will be smaller, about 10%, resulting in a maximum error of ±0.007 in adjusting the value of an osmotic coefficient at 573 K from saturation pressure to 500 bar.

Extensive tables of the various functions seem unnecessary since the equations can be easily programmed into a small computer. For the convenience of users, however, we include in Tables VIII–XI values of apparent molar heat capacity, apparent molar enthalpy, and osmotic and activity coefficients over the range to 598 K and to 6 mol kg^{-1} or saturation molality at 1 bar or saturation pressure.

From the evaluation of available experimental data it is apparent that additional volumetric measurements are needed at saturation pressure at temperatures above 373 K, and at higher

Table XI. Activity Coefficients for KCl(aq) Solutions

	temperature, °C							
molality	25.0	50.0	100.0	150.0	200.0	250.0	300.0	325.0
0.10	0.768	0.761	0.740	0.707	0.662	0.603	0.520	0.460
0.30	0.687	0.681	0.656	0.615	0.558	0.486	0.389	0.324
0.50	0.650	0.646	0.620	0.575	0.513	0.434	0.333	0.268
1.00	0.605	0.605	0.580	0.528	0.456	0.370	0.265	0.203
1.50	0.584	0.589	0.563	0.506	0.429	0.337	0.230	0.170
2.00	0.574	0.582	0.557	0.495	0.413	0.317	0.208	0.150
3.00	0.570	0.584	0.558	0.489	0.397	0.293	0.182	0.126
4.00	0.578	0.596	0.569	0.492	0.392	0.281	0.166	0.112
5.00		0.613	0.584	0.500	0.392	0.274	0.156	0.102
6.00			0.599	0.510	0.395	0.270	0.148	0.094

[a] Pressure = 1.0 bar at $T < 100$ °C, or P_{sat} above.

pressures at temperatures greater than 323 K. Precise measurements at low concentrations are particularly important in order to determine the standard-state volumes of KCl (aq) and the pressure dependencies of other standard-state properties. Although KCl becomes more soluble with increasing temperature (reaching 10.8 m at 473 K and 18.8 m at 623 K (*43*)), experimental data on KCl (aq) properties extend only to less than 5 m, except for the isopiestic work of Holmes and Mesmer (*39*) and the heat capacity data of Conti et al. (*8*). Thus experiments at higher concentrations, particularly volumetric measurements, would be useful.

Glossary

A_ϕ, A_H, A_J, A_V	Debye–Hückel slopes for the osmotic coefficient, enthalpy, heat capacity, and volume
b	"ion-size" parameter in Pitzer's equations, $b = 1.2$ kg$^{1/2}$ mol$^{-1/2}$
B_{MX}, B_{MX}^{ϕ}	parameters in Pitzer's equations
B_{MX}^{V}	pressure derivative of B_{MX}
C_{MX}, C_{MX}^{ϕ}	parameters in Pitzer's equations
C_{MX}^{L}, C_{MX}^{J}	temperature derivatives of C_{MX}
C_{MX}^{V}	pressure derivative of C_{MX}
$c_{p,w}$, $c_{p,s}$	specific heat capacities of water and solution at constant pressure
$\bar{C}^\circ_{p,2}$	partial molar heat capacity of the solute at infinite dilution at constant pressure
$^{\phi}C_p$	apparent molar heat capacity at constant pressure
D	dielectric constant of pure water
d_w	density of pure water
e	electronic charge
f	heat-loss correction factor
f_{C_p}	temperature function for $\bar{C}^\circ_{p,2}$, $\beta_{MX}^{(0)J}$, $\beta_{MX}^{(1)J}$, and C_{MX}^{J}
f_G	temperature function for $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, and C_{MX}
f_L	temperature function for $\beta_{MX}^{(0)L}$, $\beta_{MX}^{(1)L}$, and C_{MX}^{L}
f_V	temperature and pressure function for $\bar{V}^\circ_2$ and B_{MX}^{V}
G	total Gibbs energy of the solution
H	total enthalpy of the solution
I	ionic strength
k	Boltzmann's constant
K_1, K_2	integration constants for eq 19 and 20
$^{\phi}L$	apparent molar enthalpy
M_1, M_2	molecular weight of water and solute
m	molality, mol kg^{-1}
N_0	Avogadro's number
p^0, p	vapor pressure of pure water and solution
P	pressure
P_r	reference pressure, $P_r = 179$ bar
P_w, P_s	electrical powers for water and solution
q_1–q_{15}	adjustable constants for $f_V(T,P)$
R	gas constant
T	temperature, kelvin
T_r	reference temperature, $T_r = 298.15$ K
u_1–u_7	adjustable constants for $f_{C_p}(T)$, $f_G(T)$, and $f_L(T)$
V	total volume of the solution
V°_1	molar volume of water
$\bar{V}^\circ_1$, $\bar{V}^\circ_2$	partial molar volume of water and solute at infinite dilution
$^{\phi}V$	apparent molar volume
α	ionic strength dependence parameter in Pitzer's equations; $\alpha = 2$ kg$^{1/2}$ mol$^{-1/2}$
$\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$	pairwise ion-interaction parameters in Pitzer's equations
$\beta_{MX}^{(0)L}$, $\beta_{MX}^{(0)J}$	temperature derivatives of $\beta_{MX}^{(0)}$
$\beta_{MX}^{(1)L}$, $\beta_{MX}^{(1)J}$	temperature derivatives of $\beta_{MX}^{(1)}$
$\gamma_\pm$	mean ionic activity coefficient
ϕ	osmotic coefficient
δ	estimated uncertainty in $^{\phi}C_p$

Registry No. KCl, 7447-40-7.

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Received for review October 6, 1987. Accepted February 9, 1988. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Engineering, and Geosciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Mutual Diffusivity, Thermal Conductivity, and Heat of Transport in Binary Liquid Mixtures of Alkanes in Chloroform

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Thermal conductivities, mutual diffusivities, and heats of transport have been measured as a function of composition in six binary systems of six- to eight-carbon alkanes in chloroform at 30 °C and ambient pressure. The measurement methods and the accuracy of the measured values are (a) Taylor dispersion method for diffusivities with 2% accuracy, (b) transient hot-wire method for thermal conductivities with 2% accuracy, and (c) Dufour effect method for heats of transport with about 4% accuracy. Results indicate that increased chain length decreases the diffusivity and heat of transport but has only a small increasing effect on thermal conductivity. Higher branching of the alkane chain tends to increase the diffusivity, slightly lower the heat of transport, and significantly lower the thermal conductivity.

Introduction

In a binary system, the heat and mass flux equations may be written as

$$-\mathbf{q} = k\nabla T + \rho D Q_1^* \nabla w_1 \tag{1}$$

$$-\mathbf{j}_1 = \rho D_T \nabla \ln T + \rho D \nabla w_1 \tag{2}$$

where $\mathbf{q}$ is heat flux, $\mathbf{j}_1$ is mass flux relative to the center of mass, k is thermal conductivity, ρ is density, D is mutual diffusivity, Q_1^* is heat of transport, D_T is the thermal diffusion coefficient, T is temperature, and w_1 is mass fraction of component 1. Onsager (*1*) derived a relationship between the cross transport coefficients D_T and Q_1^* which has been verified experimentally by Rowley and Horne (*2*). Thus, only three independent transport coefficients need to be measured in a binary nonelectrolyte mixture.

Because transport properties are often studied separately in different laboratories, there are few binary systems for which all three coefficients have been measured. Often engineering calculations require combinations of these coefficients in dimensionless groups, making data gaps bothersome. More importantly, most theories of transport properties employ analogous mechanisms and/or the same parameters for more than one transport coefficient. For example, all three properties depend upon the intermolecular potential parameters in the Enskog theory. If the model is consistent, values of the potential parameters fitted from one property could be used to predict the others.

For these reasons, and others, measurement of a complete set of transport properties for binary mixtures is important. In this paper we report measurements made in this laboratory for the diffusion coefficient, thermal conductivity, and the heat of transport on binary mixtures of *n*-hexane, *n*-heptane, *n*-octane, 3-methylpentane, 2,3-dimethylpentane, and 2,2,4-trimethylpentane in chloroform. This not only provides new experimental data for the purposes described above, but also permits qualitative examination of chain length, solute, and branching effects upon these properties. Similar studies were reported recently for the same alkanes with carbon tetrachloride (*3*).

Diffusion Coefficient Measurements

Diffusion coefficients were measured in a Taylor dispersion apparatus. Construction of the apparatus was made in accordance with well-known design parameters (*4*–*7*) to allow determination of diffusivities with an accuracy of better than 2.0%. Details of the theory and analysis techniques of the Taylor dispersion method are readily available, and our apparatus (*3*) was similar in design to that used by others (*7*–*10*). Specific details unique to this apparatus are described below. The diffusion tube, manufactured by Accu Tube Corp., consisted of a 16.684-m length of 0.052 ± 0.001-in.-o.d. and 0.031 ± 0.001-in.-i.d., 316-stainless steel tubing, tempered in a 9-in. coil. This design is consistent with the criteria derived by Aris (*4*) and Nunge et al. (*11*) for a coiled-tube dispersion apparatus. The injection valve was a Valco 6-way, zero-dead-volume valve which allowed replacement of 85 μL of carrier fluid with an equal volume of test fluid. The tubing, valve body, and injection sample loop were immersed in a Neslab-Tamson (Model TCV 70) 70-L visibility bath maintained at 30.00 ± 0.01 °C for these experiments. Temperatures were monitored with an HP 2804A quartz thermometer.

An ISCO high-pressure pump was used to provide constant, pulse-free, laminar flow at a rate of 7.937 mL/h. The pump was calibrated with water by using a measuring buret at 22 °C. All of the measurements performed in this study were made at ambient pressure and low flow rates. Thus, the pump served

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