J. Chem. Eng. Data **2001,** *46,* 331−332

Partial Molar Volumes of 13 Gases in Water at 298.15 K and 303.15 K

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The partial molar volumes of N_2, O_2, He, Ar, H_2, CH_4, C_3H_8, *n*-C_4H_{10}, *i*-C_4H_{10}, CCl_2F_2, and $CClF_3$ were determined in water at 298.15 K and 303.15 K and 1.013 bar. The measurements were made using a vibrating tube densimeter.

Introduction

The partial molar volumes of gases in liquids are significant for both practical and theoretical reasons. The partial molar volume, for example, appears in the Poynting correction for the effect of pressure on the Henry's law constant for solubility. The pressure dependence of the partial molar Gibbs energy at constant temperature is the partial molar volume. The partial molar volumes of gases in water are of interest in limnology and oceanography, and appear in a number of theories of solutions. For example, they can be calculated from scaled particle theory.

For simplicity we cite just the early extensive paper of Horiuti[1] and the two review articles by Handa et al.[2,3] This work follows the procedures developed by Moore et al.[4] Complete details are in Zhou's thesis.[5] This paper reports on the partial molar volumes of 13 gases (N_2, O_2, He, Ar, H_2, CH_4, C_2H_6, C_2H_4, C_3H_8, *n*-C_4H_{10}, *i*-C_4H_{10}, CCl_2F_2, $CClF_3$) in pure liquid water at 298.15 K and 303.15 K at 1.013 bar.

Experimental Section

O_2, N_2, H_2, CCl_2F_2, and $CClF_3$ were obtained from Airco and were all of purity of 99.0% or better. The remaining gases were obtained from Matheson, and all were of 99.0% purity or better except for CH_4 (98.0%) and C_2H_6 (95.0%). The distilled water used in this work was also processed through research-grade ion exchangers and had a resistivity greater than 5×10^4 μm.

The experimental procedure was the same as that of Moore et al.;[4] also see ref 5. Density measurements were made using a model O2D Sodev vibrating tube densimeter with a reproducibility of $\pm 0.000\,001$ g cm^{-3}. The water circulated through the densimeter was controlled to ± 0.0002 K for any given set of measurements. All of the critical components were housed in an air thermostat controlled to ± 0.1 K. Temperature measurements were made using a calibrated Leeds and Northrup knife blade platinum resistance thermometer on IPTS-68. For a vibrating tube densimeter the density, d, is related to the period, τ, by $d = a + b\tau^2$, where a and b are empirically determined constants. The a and b values were evaluated using the known densities of pure water and pure dry nitrogen gas, with all appropriate corrections.

Basically, the procedure involved alternating density measurements on pure degassed (Battino et al.[6]) liquid water and gas-saturated water. The temperature and barometric pressure (with corrections) were known for each measurement. The reported values are the average of many measurements.

The partial molar volume at infinite dilution is defined as

$$V_2^{\infty} = (\partial V/\partial n_2)_{T,P} \qquad (1)$$

Although the measurements were carried out at approximately atmospheric pressure, the experimental value of V_2 (x_2) is effectively V_2^{∞}, since the mole fraction solubilities of the gases for the systems studied are generally less than 10^{-4}. The partial molar volume at infinite dilution is calculated from

$$V_2^{\infty} = d_1^{-1} d_s^{-1}[M_1(d_s - d_1)(1 - 1/x_2) + M_2 d_1] \qquad (2)$$

where M_1 and M_2 are the molar masses of water and the gaseous solute, respectively, d_1 is the density of gas-free water, and d_s is the density of the gas-saturated water. The mole fraction x_2 of the solute was calculated from literature values[7] at the actual partial gas pressure of the measurement by applying Henry's law, which is accurate at these pressures and small pressure variations.

Results

Experimental results are given in Table 1 with the standard deviation for the multiple measurements for each system at 298.15 K and 303.15 K. The repeatability and uncertainty of the results are estimated to be about ± 1.5 cm^3 mol^{-1} and $\pm$1.5−4%. Some literature values are given at 298.15 K for comparison.

Discussion

We tested our data against three empirical correlations. The first involves the reduced density of the solvent and the relative molecular sizes of the solute and solvent.[11] The correlation is

$$V_2^{\infty}/\beta_{T,1}RT = 1 - C_{12}^{\infty} \qquad (3)$$

$$\ln[-C_{12}^{\infty}(V_1^{*}/V_2^{*})^{0.62}] = -2.4467 + 2.12074\rho_1 \qquad (4)$$

where $\beta_{T,1}$ is the isothermal compressibility of the solvent, ρ_1 is the reduced molar density ($=V_1^{*}/V_1$, where V_1 is the molar volume of the solvent and V_1^{*} is the reducing volume and is 46.4 cm^3 mol^{-1} from ref 12), V_2^{*} is the solute molar critical volume or $V_{c,2}$, and C_{12}^{∞} is the volume integral of the molecular direct correlation function between the two species. For 11 gases, omitting CCl_2F_2 and $CClF_3$, this

10.1021/je000215o CCC: \$20.00

Table 1. Partial Molar Volume at Infinite Dilution of Gases in Pure Liquid Water

	V_2^∞/cm^3 mol^{-1}	V_2^∞(lit)/cm^3 mol^{-1}	V_2^∞/cm^3 mol^{-1}
gas	$T = 298.15$ K	$T = 298.15$ K	$T = 303.15$ K
H_2	23.1 ± 1.1	25.2[a]	
O_2	32.1 ± 0.1	32.1,[b] 31.10[e]	28.6 ± 1.2
N_2	33.1 ± 1.6	32.8,[c] 34.29[e]	32.5 ± 0.8
Ar	32.7 ± 0.4	32.2,[b] 31.00[e]	28.7 ± 0.1
He	24.6 ± 3.0		
CH_4	32.0 ± 2.0	37.4[a]	25.3 ± 1.5
C_2H_6	49.6 ± 1.7	53.3[a]	47.7 ± 0.6
C_2H_4	45.4 ± 1.3		43.0 ± 0.8
C_3H_8	75.0 ± 3.1	66.6[d]	66.3 ± 2.9
n-C_4H_{10}	74.5 ± 2.0		77.5 ± 3.2
i-C_4H_{10}	74.9 ± 0.5		80.1 ± 4.0
CCl_2F_2	88.3 ± 3.1		86.5 ± 4.7
$CClF_3$	80.7 ± 3.0		98.3 ± 3.5

[a] Reference 8. [b] Reference 9. [c] Reference 10. [d] Reference 11. [e] Reference 12.

correlation predicts V_2^∞ with an average deviation of 4.9 cm^3 mol^{-1} at 298.15 K.

A second correlation taken from Moore et al.[4] involves the gas molar critical volume $V_{c,2}$ and is

$$V_2^\infty = 10.74\ \mathrm{cm}^3\ \mathrm{mol}^{-1} + 0.2683 V_{c,2} \tag{5}$$

For the 11 gases used in the previous correlation the average deviation was 3.6 cm^3 mol^{-1} at 298.15 K.

The third correlation taken from Moore et al.[4] uses a molar volume based on the van der Waals radius of the gas, V_{vdw}, and is

$$V_2^\infty = 16.0\ \mathrm{cm}^3\ \mathrm{mol}^{-1} + 1.27 V_{vdw} \tag{6}$$

For the same 11 gases at 298.15 K the average deviation was 3.4 cm^3 mol^{-1}.

In conclusion, this paper reports experimental partial molar volumes of 13 gases in water at two temperatures.

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Received for review July 17, 2000. Accepted November 23, 2000.

JE000215O