Diffusion Coefficients for Hydrogen Sulfide, Carbon Dioxide, and Nitrous Oxide in Water over the Temperature Range 293–368 K

A. Tamimi, Edward B. Rinker, and Orville C. Sandall*

Chemical and Nuclear Engineering Department, University of California, Santa Barbara, California 93106

A wetted-sphere absorption apparatus was used to measure the liquid-phase diffusion coefficients for hydrogen sulfide, carbon dioxide, and nitrous oxide over the temperature range 293–368 K. The experimental results obtained in this work are compared with values in the literature and with predictions from the Wilke–Chang equation. The data presented here extend the temperature range of reported diffusivities for these gases in water.

Introduction

Acid gases such as H_2S and CO_2 are generally removed from natural gas, biogas, synthetic natural gas, and other process gas streams by means of absorption into aqueous alkanolamine solutions. A key parameter needed to model this diffusion with chemical reaction process in the liquid phase is the diffusion coefficient. Because of the similarity in molecular properties for CO_2 and N_2O, the "N_2O analogy method" is often used to estimate the diffusivity of CO_2 for solutions in which CO_2 reacts chemically (Clark (*1*)). To apply this analogy method, the diffusion coefficients for the gases in the pure solvent (water) are needed. In the work reported here, the diffusion coefficients for CO_2, H_2S, and N_2O in water are measured over the temperature range 293–368 K. A wetted-sphere absorber was used for these measurements.

Experimental Apparatus and Procedure

The wetted-sphere apparatus used in these experiments is described in detail by Al-Ghawas et al. (*2*). A schematic drawing of the apparatus is given in Figure 1. The gases used in this work had purities of 99.8, 99.99, and 99.5 mol % for CO_2, N_2O, and H_2S, respectively. The water used in the experiments was deionized and distilled.

Before an experimental run, the water was degassed by heating to its boiling point under a vacuum. After degassing, the water was transferred to the water feed tank using helium gas to prevent any absorption of atmospheric air. The water feed tank and the inlet gas saturator were held in a thermostated water bath. The water and gas passed through coils embedded in the water jacket surrounding the wetted-sphere absorber before entering the absorber. The gas line between the gas saturator and the wetted-sphere apparatus was kept as short as possible and was insulated to prevent water vapor condensation at the higher operating temperatures. Before starting the water flow, the gas was allowed to run through the system for a time equal to five residence times in order to sufficiently flush the system of any air and fill the system with the gas being absorbed.

Degassed water was pumped through a rotameter and then through a surge tank blanketed with helium gas in order to damp any small oscillations in the liquid flow rate before entering the liquid distributor at the inlet of the absorber. Initially, the water was pumped at a high flow rate of about 20 $cm^3 \cdot s^{-1}$ to ensure complete wetting of the sphere. The flow rate was then reduced to a value in the range 0.15–3.0 $cm^3 \cdot s^{-1}$.

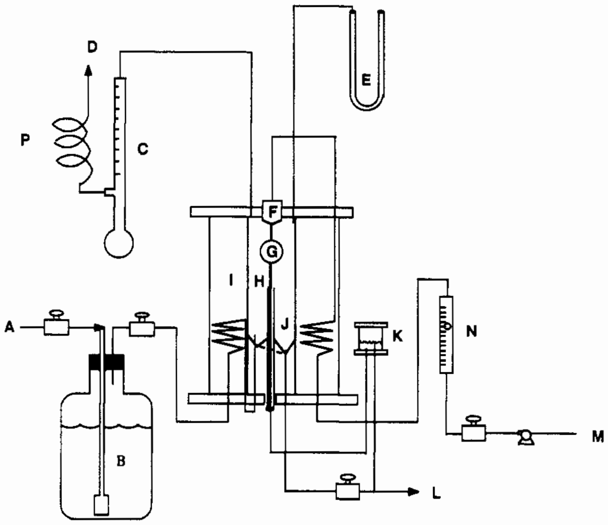

Figure 1. Schematic drawing of the wetted-sphere apparatus: (A) from gas supply; (B) saturator; (C) soap bubble meter; (D) to fume hood; (E) manometer; (F) liquid distributor; (G) wetted sphere; (H) absorption chamber; (I) water jacket; (J) receiver tube; (K) level adjustment; (L) to drainage; (M) from water feed tank; (N) rotameter; (P) long exit tube.

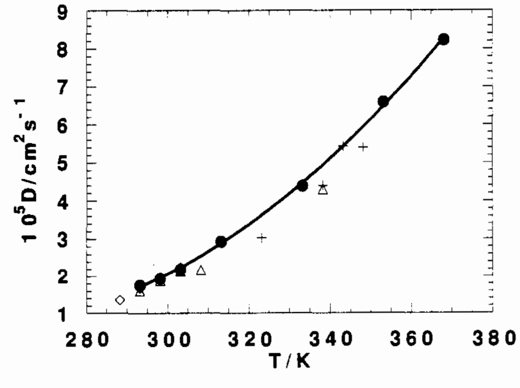

Figure 2. Diffusivity of CO_2 in water: (●) this work; (△) Himmelblau (*10*); (◇) Davidson and Cullen (*9*); (+) Thomas and Adams (*11*).

The temperatures of the gas and liquid were measured to within ±0.3 K using thermocouples located in the gas space surrounding the sphere and the liquid inlet to the sphere.

When the system reached the steady state, the gas from the cylinder was turned off while the liquid film was kept flowing steadily. The gas in the long gas exit tube (12 m long,

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* To whom correspondence should be addressed.

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Table 1. Experimental Diffusivities

	$10^5D(CO_2)/(cm^2{\cdot}s^{-1})$				$10^5D(N_2O)/(cm^2{\cdot}s^{-1})$			$10^5D(H_2S)/(cm^2{\cdot}s^{-1})$			
temperature/K	this work	Davidson and Cullen (*9*)	Himmelblau (*10*)	Thomas and Adams (*11*)	this work	Versteeg and van Swaaij (*5*)	Davidson and Cullen (*9*)	this work	Haimour and Sandall (*12*)	Tavares and Danckwerts (*13*)	Arnold (*14*)
288		1.37					1.50		1.53		
293	1.76	1.68	1.60		1.84	1.55		1.75	1.75	1.34	1.41
298	1.94	1.98	1.88	1.950	1.88	1.84	2.25	1.93	1.89	1.48	
303	2.20	2.25	2.15		1.93	2.27	2.55	2.07			
308			2.18			2.34			2.32		
313	2.93				2.61	2.58		2.55			
318						3.17					
323				3.03							
333	4.38				4.51			3.87			
338			4.30	4.40							
343											
348				5.40							
353	6.58				6.50	6.32		4.62			
368	8.20				7.30			5.49			

Table 2. Comparison between the Experimental Diffusivities and Predictions from the Wilke–Chang Equation (Calcd)

	$10^5D(H_2S)/(cm^2{\cdot}s^{-1})$			$10^5D(CO^2)/(cm^2{\cdot}s^{-1})$			$10^5D(N_2O)/(cm^2{\cdot}s^{-1})$		
T/K	exptl	calcd	% dev	exptl	calcd	% dev	exptl	calcd	% dev
293	1.75	1.74	−0.6	1.76	1.70	−3.4	1.84	1.63	−11.4
298	1.93	1.95	+1.0	1.94	1.92	−1.0	1.88	1.84	−2.1
303	2.07	2.22	+7.3	2.20	2.18	−0.9	1.93	2.09	+8.3
313	2.55	2.75	+7.8	2.93	2.69	−8.2	2.61	2.58	−1.1
333	3.87	4.23	+9.3	4.38	4.15	−5.3	4.51	3.98	−11.8
353	4.62	6.24	+35.1	6.58	6.12	−7.0	6.50	5.88	−9.5
368	5.49	7.9	+43.9	8.20	7.75	−5.5	7.30	7.44	+1.9

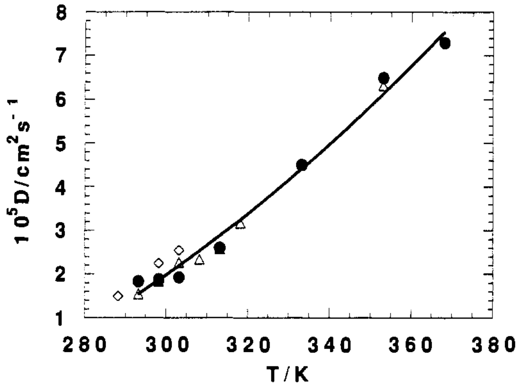

Figure 3. Diffusivity of N_2O in water: (●) this work; (◇) Davidson and Cullen (*9*); (△) Versteeg and van Swaaij (*5*).

5-mm i.d.) started to flow back into the absorber under atmospheric pressure due to the gas absorption. The volumetric gas absorption rate was measured using a soap bubble meter with a resolution of 0.01 $cm^3{\cdot}min^{-1}$. Each run was repeated at least three times.

Results

The diffusivities of the gases in water were determined using the Olbrich and Wild (*3*) equation for the physical absorption of a gas into a liquid

$$G/(\mathrm{mol{\cdot}s^{-1}}) = \frac{\{p/\mathrm{atm}\}\{L/(\mathrm{cm^3{\cdot}s^{-1}})\}\{1 - \sum_i b_i \exp[\lambda_i \epsilon]\}}{H/(\mathrm{atm{\cdot}cm^3{\cdot}mol^{-1}})} \quad (1)$$

where

$$\epsilon = 13.5D/(\mathrm{cm^2{\cdot}s^{-1}})\left[\frac{\{g/(\mathrm{cm{\cdot}s^{-2}})\}\{r_s/\mathrm{cm}\}^7}{\{\nu/(\mathrm{cm^2{\cdot}s^{-1}})\}\{L/(\mathrm{cm^3{\cdot}s^{-1}})\}^4}\right]^{1/3} \quad (2)$$

and G = molar gas absorption rate, p = gas partial pressure, L = liquid flow rate, b_i, λ_i = constants, H = Henry's law constant, r_s = radius of the sphere, and ν = kinematic viscosity. Equation 1 was solved using an iteration technique to give the diffusion coefficient, D. The solubility data needed for these calculations (in the form of the Henry's law constant, H) were taken from the *International Critical Tables* (*4*) for the case of N_2O and CO_2, except the solubility data for N_2O at temperatures of 80 °C and above were obtained from the paper of Versteeg and van Swaaij (*5*). Solubility data for H_2S in water were obtained from Wright and Maass (*6*). The viscosity of water was taken from the *Chemical Engineers' Handbook* (*7*).

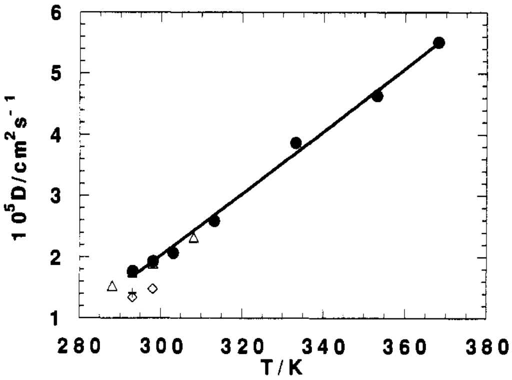

Figure 4. Diffusivity for H_2S in water: (●) this work; (◇) Tavares and Danckwerts (*13*; (△) Haimour and Sandall (*12*); (+) Arnold (*14*).

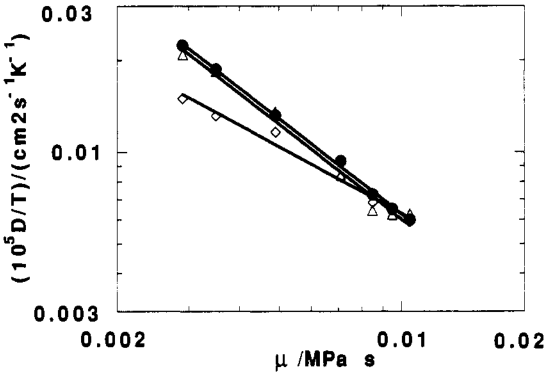

Figure 5. Diffusivity correlation: (●) CO_2; (△) N_2O; (◇) H_2S.

The experimental values obtained for the diffusion coefficients are shown in Table 1. Each entry in Table 1 represents the average of at least three measurements. The average standard deviations in the reported experimental diffusivity values is 0.0071×10^{-5}, 0.0024×10^{-5}, and 0.0161×10^{-5} $cm^2{\cdot}s^{-1}$ for the gases CO_2, N_2O, and H_2S, respectively. The estimated error in these experimental diffusivity values is thought to be less than 3%. Table 1 also compares the results obtained in this work with literature values. These data are shown in Figures 2–4. Table 2 compares the experimentally determined diffusion coefficients with predictions from the Wilke–Chang equation (*8*).

The diffusivity data were fitted to a modified form of the Stokes–Einstein equation using a nonlinear least-squares procedure to give

$$CO_2: \{D/(\mathrm{cm^2 \cdot s^{-1}})\}\{\mu/(10^{-3}\ \mathrm{Pa \cdot s})\}^{1.035}/\{T/\mathrm{K}\} = 5.35 \times 10^{-10} \quad (3)$$

$$N_2O: \{D/(\mathrm{cm^2 \cdot s^{-1}})\}\{\mu/(10^{-3}\ \mathrm{Pa \cdot s})\}^{1.034}/\{T/\mathrm{K}\} = 5.17 \times 10^{-10} \quad (4)$$

$$H_2S: \{D/(\mathrm{cm^2 \cdot s^{-1}})\}\{\mu/(10^{-3}\ \mathrm{Pa \cdot s})\}^{0.725}/\{T/\mathrm{K}\} = 22.4 \times 10^{-10} \quad (5)$$

where μ = dynamic viscosity and T = temperature. The results are shown plotted according to these correlations in Figure 5. The similarity in the exponents on the viscosity for CO_2 and N_2O is not surprising in view of the similarity in molecular properties for these two gases.

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