Acknowledgment

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Glossary

α, β, A, B, C	constants
B_i	second virial coefficient, cm^3/mol
n	number of experimental points
P	overall pressure, mmHg
P_i°	vapor pressure of pure component i, mmHg
R	gas constant
rmsd	root-mean-square deviation $(\sum(T_{\text{exptl}} - T_{\text{calcd}})^2/n)^{1/2}$
t	temperature, °C
T	temperature, K
T_i°	boiling point of pure component, K
v_i^L	molar volume of pure liquid component, cm^3/mol
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases
γ_i	activity coefficients

Subscripts

exptl	experimental
calcd	calculated
i	component i

Registry No. Propyl bromide, 106-94-5; methyl butyrate, 623-42-7.

Literature Cited

(1) Boublikova, L.; Lu, B. C. Y. *J. Appl. Chem.* **1969**, *19*, 89.
(2) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1975**, *20*, 168.
(3) TRC Tables, "Selected Values of Properties of Chemical Compounds"; Thermodynamics Research Center Data Project: College Station, TX, 1974.
(4) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(5) Tsonopoulos, C. *AIChE J.* **1975**, *21*, 827.
(6) Wisniak, J.; Tamir, A. *Chem. Eng. Sci.* **1975**, *30*, 335.
(7) Tamir, A. *Chem. Eng. Sci.* **1981**, *36*, 1453.
(8) Wisniak, J. *J. Phys. Chem.*, submitted.

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Molecular Diffusivity of Hydrogen Sulfide in Water

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The molecular diffusivity of hydrogen sulfide in pure water was measured at different temperatures and under atmospheric pressure by using a laminar jet. Experimental results are compared with those available in the literature and with the Stokes–Einstein relation. The diffusivity was found to vary from 1.53 × 10^{-5} cm^2/s at 15 °C to 2.32 × 10^{-5} cm^2/s at 35 °C.

Introduction

Hydrogen sulfide is one of the constituents of natural gas and refinery gas. It is usually required to remove H_2S to improve the quality of fuel gas, to decrease the poisoning rate of catalysts used in ammonia production, or to obtain pure sulfur after further processing in the Claus process. Data on the physical properties of hydrogen sulfide are important for absorber design for the sweetening process of natural and refinery gases.

The diffusivity of hydrogen sulfide gas has been investigated by a few workers (*1–5*); however, there is disagreement in the literature on the values of the diffusivity, and the values available do not cover a wide range of temperature. In the work reported here a laminar jet apparatus is used to determine the molecular diffusivity of hydrogen sulfide in water at temperatures from 15 to 35 °C.

The laminar jet apparatus used in this work has several advantages compared to other laboratory absorbers. Its fluid dynamics are fairly well-known, and it is very versatile since the contact time and surface area can be easily varied by changing the jet length and liquid flow rate. The absorption rate into a laminar jet usually shows good agreement with the Higbie penetration theory.

Experimental Apparatus and Procedure

The experimental apparatus is shown schematically in Figure 1. The jet chamber consists of a 25.0 cm long, 4.4 cm i.d. glass tube. It is enclosed by a constant-temperature jacket which is constructed from a 25.0 cm long, 12.5 cm i.d. Plexiglas tube. The jet nozzle is a square-edged orifice, 0.051 cm in diameter, drilled in a 0.008 cm thick stainless steel sheet. The downstream face of the nozzle was coated with a thin layer of grease to prevent wetting. The solution is fed through the nozzle from a 1.9 cm i.d. glass tube. The nozzle is supported by a Teflon plate and fastened to a Teflon collar using two O rings and can be adjusted vertically. The receiver is a capillary tube of 0.1-cm i.d. and is fitted into a funnel-shaped Teflon base. A hole in the base allows draining of any liquid overflow. The jet is centered by three screws with rubber stoppers at their ends and surrounding the intake tube. A reservoir with a weir is used to keep the level constant in the capillary tube without an over- or underflow. The reservoir can be adjusted in the vertical direction. The length of the jet is measured by a precision vernier caliper with an accuracy of 0.0025 cm mounted on the top of the apparatus. The temperatures of the jet chamber and the water jacket were measured by a digital thermometer with ±0.1 °C accuracy. The apparatus was checked under 20 psi pressure and no leakage was detected.

Solutions used were deionized water. The H_2S used was CP grade from the Union Carbide Co. with a purity of 99.5%. Water was pumped by a constant-flow pump and its rate was measured by a calibrated rotameter. The gas stream was saturated with water after leaving the gas cylinder. Both water and gas streams were passed through separate coils maintained in the water jacket before entering the jet chamber.

Initially, air was removed from the jet chamber by displacement with water. H_2S gas was then introduced to the jet chamber while water was drained. Then the solution flow rate was fixed followed by adjustment of the liquid level in the capillary receiver. H_2S gas was allowed to flow into the jet chamber for a sufficient time until the required constant temperature was reached. Between experiments, the jet chamber was sealed off to prevent introducing air, and the chamber was purged again with H_2S at the beginning of each new experi-

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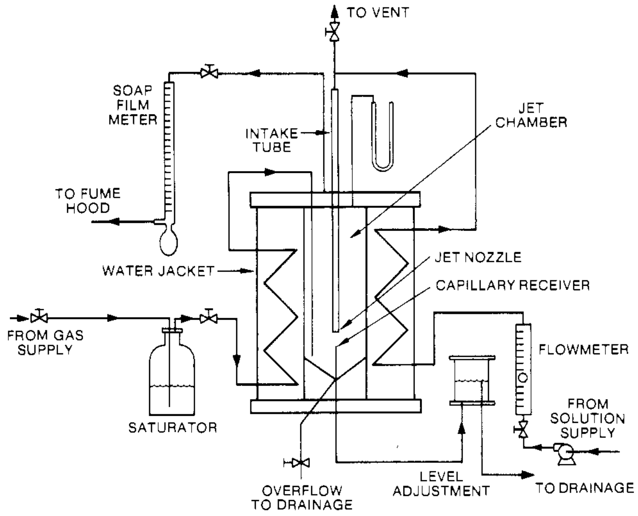

Figure 1. Schematic diagram of the apparatus.

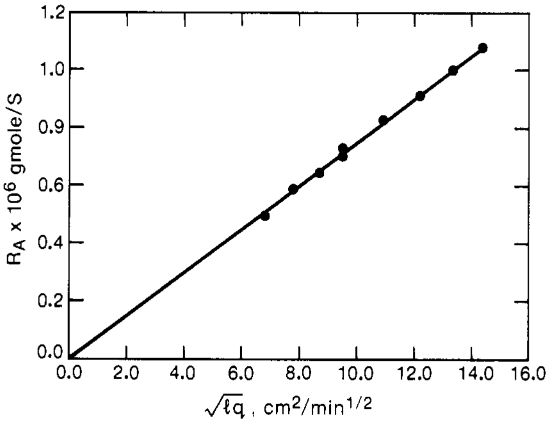

Figure 2. Rate of absorption of CO_2 into water at 25 °C and 1 atm vs. $(lq)^{1/2}$.

ment. The reproducibility of the results obtained gives confidence that all air had been purged from the chamber. After conditions had stabilized, the gas inlet was closed, and the rate of gas entering the jet chamber was determined by measuring the time needed for a soap film to travel through a certain volume. Under these conditions, the rate of gas entering is equal to the rate of absorption. Experiments were repeated several times and an average was taken. The maximum deviation between readings was less than 2%.

Carbon dioxide was used to check the accuracy and the hydrodynamics of the apparatus at different rates of flow and different jet lengths. The carbon dioxide used was a bone-dry grade from Union Carbide Co. with a purity of 99.8%.

Results and Discussion

According to the penetration theory for a laminar jet, the diffusivity of a gas absorbed in a solution without a chemical reaction is given by

$$D_A = R_A^2/(16lqC_A^{*2}) \tag{1}$$

Thus, a plot of R_A vs. $(lq)^{1/2}$ at a constant temperature and pressure should give a straight line which passes through the origin and having a slope $4C_A^*D_A^{1/2}$.

For CO_2 at 25 °C and 1 atm, such a plot is shown in Figure 2. The solubility of CO_2 at 25 °C and 1 atm was taken as 3.29 × 10^{-5} g-mol/cm³ (*6*). The product $C_A^*D_A^{1/2}$ was found to be 1.445 × 10^{-7} g-mol/(cm² s$^{1/2}$). Hence, the diffusivity of CO_2 is 1.93 × 10^{-5} cm²/s with a standard deviation of 3.3% and an estimated maximum experimental error of ±5%. This result is in good agreement with values available in the literature (*7–10*) as shown in Table I.

Table I. Diffusivities of CO_2 in Water at 25 °C

$10^5 D_A$, cm²/s	ref	$10^5 D_A$, cm²/s	ref
1.92	*8*	1.98	*7*
2.00	*10*	1.93	this work
1.95	*9*		

Table II. Henry's Law Constant and Solubility of H_2S at Different Temperatures and 1 atm[a]

T, °C	He°, L atm/g-mol	C_A*, g-mol/L	T, °C	He°, L atm/g-mol	C_A*, g-mol/L
15.0	7.58	0.1320	25.0	10.04	0.0996
20.0	8.60	0.1162	35.0	12.05	0.0830

[a] From Wright and Maass (*11*).

Table III. Experimental Data and Diffusivity for Absorption of H_2S into Water

T, °C	l, cm	q, cm³/min	$10^6 R_A$, g-mol/s	$10^5 D_A$, cm²/s
15.1	1.074	30.1	1.531	1.56
15.0	1.074	39.9	1.774	1.58
15.0	1.074	49.7	1.994	1.60
15.0	1.074	59.5	2.198	1.63
15.0	1.074	69.3	2.392	1.66
15.2	2.131	30.1	2.067	1.43
15.0	2.131	39.9	2.452	1.52
15.0	2.131	49.7	2.735	1.52
14.9	2.131	59.5	3.011	1.54
14.9	2.131	69.3	3.236	1.53
20.0	1.956	30.1	1.878	1.66
20.0	1.956	39.9	2.201	1.72
20.0	1.956	49.7	2.494	1.78
20.0	1.956	59.5	2.711	1.75
25.0	1.161	30.1	1.366	1.90
25.0	1.161	39.9	1.534	1.81
25.0	1.161	49.7	1.725	1.83
25.0	1.161	59.5	1.917	1.89
25.0	1.161	69.3	2.093	1.94
25.0	1.956	30.1	1.747	1.84
25.0	1.956	39.9	2.013	1.85
25.0	1.956	49.7	2.529	1.87
25.0	1.956	59.5	2.521	1.94
24.9	2.664	30.1	2.056	1.88
25.0	2.664	39.9	2.376	1.89
25.0	2.664	49.7	2.656	1.89
25.0	2.664	59.5	2.925	1.92
35.0	1.074	30.1	1.131	2.16
35.0	1.074	39.9	1.376	2.41
35.0	1.074	49.7	1.511	2.31
35.0	1.074	59.5	1.682	2.41
35.0	2.131	30.1	1.615	2.21
35.1	2.131	39.9	1.896	2.30
35.0	2.131	49.7	2.112	2.29
34.9	2.131	59.5	2.242	2.16

Table IV. Diffusivity of H_2S in Water

ref	T, °C	$10^5 D_A$, cm²/s	ref	T, °C	$10^5 D_A$, cm²/s
1	20.0	1.63	*3*	16.0	1.77
4	20.0	1.63	this work	15.0	1.53
2	20.0	1.98	this work	20.0	1.75
5	20.0	1.34	this work	25.0	1.89
5	25.0	1.48	this work	35.0	2.32

For hydrogen sulfide, the experimental work covered the temperature range 15.0–35.0 °C. The solubility of H_2S at different temperatures was calculated from Wright and Maass (*11*). The estimated accuracy of the solubility results according to these authors is 0.1%. An error of 0.1% in gas solubility results in a 0.2% error in diffusivity. The solubility data are

Table V. Comparison of Diffusivity of H_2S in Water Obtained by Calculated and Experimental Methods

	$10^5 D_A$, cm²/s								
		Wilke-Chang (*13*)		Scheibel (*14*)		Othmer-Thaker (*15*)		Akgermann-Gainer (*16*)	
T, °C	exptl	calcd	% dev	calcd	% dev	calcd	% dev	calcd	% dev
15.0	1.53	1.57	2.6	1.49	−2.6	1.49	−2.6	1.71	11.8
20.0	1.75	1.82	4.0	1.73	−1.1	1.72	−1.7	1.96	12.0
25.0	1.89	2.08	10.1	1.97	4.2	1.96	3.7	2.24	18.5
35.0	2.32	2.66	14.7	2.53	9.1	2.47	6.5	2.83	22.0

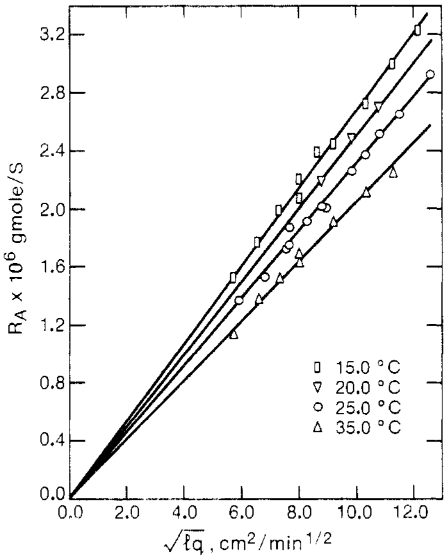

Figure 3. Rate of absorption of H_2S into water at different temperatures and 1 atm vs. $(lq)^{1/2}$.

shown in Table II. The experimental data for the H_2S absorption are shown in Table III. The values of the diffusivity for H_2S at different temperatures were calculated from eq 1 by plotting R_A against $(lq)^{1/2}$ as shown in Figure 3. The maximum standard deviation for the diffusivity was found to be 4.3% compared with an estimated maximum experimental error of ±5%.

The values of the diffusivity for H_2S from this work and from other researchers are shown in Tables III and IV. It should be pointed out that both Tavares da Silva and Danckwerts (*5*) and Perry and Chilton (*12*) edited the value given by Arnold (*1*) by mistake, since units in the original paper of Arnold (*1*) are in cm²/day and not in cm²/s.

Our results show that the Stokes-Einstein relation ($D\mu/T$ = a constant) is not strictly followed. A plot of log D_A/T vs. log μ as shown in Figure 4 gives a straight line with a slope of −0.74 for the range of 15–35 °C. Thus, the data obtained in this work are described by eq 2 with a maximum deviation of 1.4%.

$$D_A\mu^{0.74}/T = 1.91 \times 10^{-9} \qquad (2)$$

Table V gives a comparison of the experimental values of the diffusivity of hydrogen sulfide in water with those obtained from the correlations of Wilke and Chang (*13*), Scheibel (*14*), Othmer and Thakar (*15*), and Akgermann and Gainer (*16*). The percent deviation in Table V is defined as

$$\% \text{ dev} = 100(\text{calcd} - \text{exptl})/\text{exptl}$$

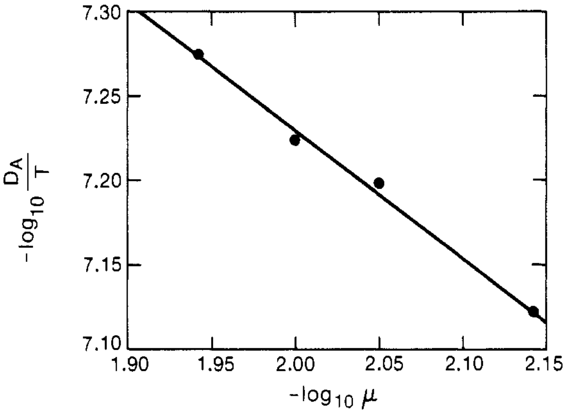

Figure 4. Effect of μ on D_A/T for H_2S.

It is found that the correlation of Othmer and Thakar best predicts the experimental results.

Glossary

C_A^*	equilibrium concentrations of A, g-mole/L
D_A	diffusivity of solute A, cm²/s
He°	Henry's law constant, L atm/g-mol
l	jet length, cm
q	liquid flow rate, cm³/s
R_A	rate of absorption of solute A, g-mol/s
T	temperature, K
μ	viscosity of solution, poise

Literature Cited

(1) Arnold, J. *J. Am. Chem. Soc.* **1930**, *52*, 3937.
(2) Hagenbach, D. M. *Chem. Rev.* **1898**, *65*, 673.
(3) Himmelblau, D. M. *Chem. Rev.* **1964**, *64*, 527.
(4) Hüfner, G. *Z. Phys. Chem.* **1898**, *27*, 227.
(5) Tavares da Silva, A.; Danckwerts, P. V. *I. Chem. E. Symp. Ser.* **1988**, *No. 28*, 48.
(6) Danckwerts, P. V.; Sharma, M. M. *Chem. Eng.* **1966**, *10*, 244.
(7) Perez, J. F.; Sandall, O. C. *AIChE J.* **1973**, *19*, 5.
(8) Ratcliff, G. A.; Holdcraft, J. G. *Trans. Inst. Chem. Eng.* **1963**, *41*, 315.
(9) Thomas, W. J.; Adams, M. J. *AIChE J.* **1965**, *61*, 668.
(10) Vivian, J. E.; King, C. J. *AIChE J.* **1964**, *10*, 220.
(11) Wright, R. H.; Maass, O. *Can. J. Res.* **1932**, *6*, 94.
(12) Perry, R. H.; Chilton, C. H. "Chemical Engineer's Handbook", 4th ed.; McGraw-Hill: New York, 1963; pp 3-225.
(13) Wilke, C. R.; Chang, P. *AIChE J.* **1955**, *1*, 264.
(14) Scheibel, E. G. *Ind. Eng. Chem.* **1954**, *46*, 2007.
(15) Othmer, D. F.; Thakar, M. S. *Ind. Eng. Chem.* **1953**, *45*, 589.
(16) Akgermann, A.; Gainer, J. L. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 373.

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