

Diffusion Coefficients of CO₂, C₂H₄, C₃H₆, and C₄H₈ in Water from 6° to 65° C.

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Absorption of gas by a liquid jet was used to measure the diffusivities of carbon dioxide, ethylene, propene, and butene-1 in pure water at various temperatures and at atmospheric pressure. Diffusivities for the latter three gases are reported for the first time. As a first step, the coefficients of diffusion of carbon dioxide in pure water at various temperatures were determined and compared with values reported by previous investigators and with values predicted theoretically. The agreement between the CO₂ diffusivities measured in this study, and other studies and the theoretical predictions, was quite satisfactory. Then the coefficients of diffusion were determined for C₂H₄, C₃H₆, and C₄H₈ (butene-1) in pure water at temperatures from 6° to 65° C. The agreement between the experimental and theoretically predicted diffusivities was good for CO₂ but not for the other gases.

DIFFUSIVITY IS ONE of the controlling factors in interphase mass transfer in gas-liquid systems. Measurement of diffusivities is also of interest in developing and evaluating models of the liquid state. This study presents new data for the diffusion coefficients of C₂H₄, C₃H₆, and C₄H₈ (butene-1) in water from 6.5° to 65° C., and also compares the diffusion coefficients of CO₂ obtained in an identical way with the values reported by other investigators.

Reliable and accurate values of diffusivity for gas-liquid systems are not easy to obtain because of numerous experimental problems. Weissberger (42) Crank (6), Johnson and Babb (17), and Jost (18) among others discuss the use of diaphragm cells, capillary tubes, refractive index, radioactivity, etc. to make the measurements required to calculate diffusion coefficients. A simple experimental method is to absorb solute gas in a laminar flowing solvent in known geometry, and from the observed adsorption rate calculate the diffusion coefficient. Various experimental devices based on this procedure have been described. For example, Davidson and Cullen (8) measured the diffusivity of carbon dioxide by passing a liquid layer over a sphere. Danckwerts and Kennedy (7) used a rotating drum to measure gas absorption, and various investigators have employed wetted wall columns (11, 21, 26, 40). Other methods include the use of disc columns (41) and packed columns (33). Several studies have been made using horizontal ducts (35, 43).

Probably the most successful technique is to absorb gas in a laminar falling jet (4, 5, 9, 19, 22-24, 27, 31, 37, 39); this was the method employed in this study. Jets have the definite advantage of simple mathematical analysis, freedom from surface ripples, and absence of surface active agents at the interface.

THEORY

In the mathematical derivation the following assumptions have been made:

At the moment of contact between the liquid and gas equilibrium exists at the interface.

Diffusion in the direction of the liquid flow can be disregarded, that is, the problem is one of one dimensional diffusion.

The thickness of the surface film for penetration by gas is very much less than the radius of the jet. D_s is constant at any one temperature and independent of concentration.

Then the diffusion equation for the jet can be written as:

$$v_s \frac{\partial c}{\partial z} = D_s \frac{\partial^2 c}{\partial x^2} \quad (1)$$

The boundary conditions are:

$$c = C_0 = 0 \quad \text{at} \quad z = 0 \quad (2)$$

$$c = C_0 = 0 \quad \text{as} \quad x \rightarrow \infty \quad (3)$$

$$c = C^* \quad \text{at} \quad x = 0 \quad (4)$$

To integrate Equation 1 the following additional assumptions are made:

The surface velocity, v_s , is constant.

The surface velocity v_s is equal to the average velocity of flow \bar{v} , where:

$$\bar{v} = \frac{F}{\pi(d^2/4)} \quad (5)$$

The sixth assumption made above is justified, since a so-called "bell-shaped nozzle" was used. This type of a nozzle eliminates the initial parabolic velocity profile obtained from a jet of constant radius, and gives a flat velocity profile at the nozzle tip. Also, the small effect of the acceleration of fluid is counteracted by the small change in the surface area of the jet.

The total moles of gas transferred per unit time into the jet are:

$$N = \pi d \int_0^L N_z \Big|_{x=0} dz = 4C^*(D_s FL)^{1/2} \quad (6)$$

where

$$N_z \Big|_{x=0} = -D_s \left(\frac{\partial c}{\partial x} \right) \Big|_{x=0} = C^*(D_s v_s / \pi z)^{1/2} \quad (7)$$

A slight correction is necessary to adjust the diffusivity for some of the assumptions made in deriving Equation 6.

Since the jet occupies only a finite region and the diffusion is not exactly one dimensional, some error is introduced. Tang (36) analyzed this problem, and noted that the exact solution of the basic diffusion equation could be obtained in an infinite series form:

$$N = \frac{\pi d^2 v_i C^*}{4} \left[1 - 4 \sum_{n=1}^{\infty} \frac{\exp[-\lambda_n^2 (Gz)]}{\lambda_n^2} \right] \quad (8)$$

where Gz is the Graetz number of diffusion:

$$Gz = (4DL/d^2 v_i) \quad (9)$$

The series in the exact solution converged very slowly when the Gz value was large, requiring 2500 terms when $Gz = 10^6$. If K is defined as the correction factor by which the diffusivity, as computed by Equation 7, should be multiplied to give the exact value of the diffusion coefficient, D , the following values show that the correction is small; however, the correction was applied in this work:

Gz	K
10^2	1.095
10^3	1.028
10^4	1.009
10^5	1.003

EXPERIMENTAL

The apparatus used in carrying out the measurements was similar to that used by Onda, Okamoto, and Yamaji (24). The major parts of the apparatus were: a constant head water reservoir, a thermostatic bath, and an absorption chamber. Various valves and rotameters were used to control the gas and liquid flows, to regulate the pressure in the absorption chamber, and to maintain a constant liquid level in the absorption chamber.

Water flowed from the constant head reservoir into coils in the thermostatic bath, through a rotameter, and into the bell-shaped (converging) nozzle placed in a thermostated absorption chamber. (To attain temperatures below room temperature ice was manually fed into the thermostatic bath.) Four different nozzles with inner diameters at the tip of 0.05715 cm., 0.08382 cm., 0.1092 cm., and 0.1702 cm. were fabricated of brass. Water from the nozzle formed a laminar jet which dropped into a glass jet receiver. The centerline of the stem of the jet receiver could be adjusted to coincide exactly with the centerline of the nozzle, so that the jet on leaving the nozzle did not hit the side of the receiver. In this way a cylindrical column with a well defined length was formed since the level of the water in the jet receiver could be closely adjusted by means of an exterior level control.

The gas to be absorbed was first bubbled through water to saturate it with water vapor, brought to the proper temperature, and used to flush the absorption chamber. In taking the data, gas was transferred from a volumetric gas burette by raising a mercury reservoir driven by a constant speed motor. After some adjustments, the rate of transfer from the gas burette became equal to the rate of absorption by the jet, and the pressure in the absorption chamber remained constant. The details of the apparatus and procedure can be found in reference (38).

CALCULATIONS AND RESULTS

Taking logarithms of both sides of Equation 6 gives

$$\log N = \log [4C^*(D_e)^{1/2}] + \frac{1}{2} \log (FL) \quad (10)$$

This is the equation of a straight line with a slope of $\frac{1}{2}$ and an intercept of $\log [(4C^*(D_e)^{1/2})]$. That the slope was $\frac{1}{2}$ was verified experimentally. The gas phase was assumed to obey

the ideal gas law. The volume of gas absorbed was corrected for absorption at zero jet length:

$$V^* = V' - V_0 \quad (11)$$

where V_0 was the arithmetic average of the two volumetric rates of gas absorbed at zero jet length as measured before and after each experimental run.

Since N and FL were known, D_e could be calculated from Equation 10 if C^* , the saturated concentration of gas in water was known. The C^* values can be calculated from the Henry's law constant, H . Values of the diffusivities are quite sensitive to the solubility data used. An error of 1% in the value of C^* causes an error of about 2% in D_e , hence very accurate solubility data are needed to get accurate values of D_e . Table I, which lists the values of D obtained in this study, includes the values of C^* employed in the calculations so that as more accurate values of C^* become available, it will be possible to revise the tabulated values of D . The precision in the values of N was $\pm 1\%$ and that of FL was $\pm 2\%$. No estimate of the error in D can be given since the error in C^* was not known. The correction factors used were:

CO_2 :	$K = 1.009$
C_2H_4 :	$K = 1.009$
C_3H_6 :	$K = 1.009$
C_4H_8 :	$K = 1.028$

DISCUSSION

By using Othmer reference substance plots (25), the diffusivity vs. temperature curves are essentially linearized; this facilitates evaluation of the data. The coefficients of diffusion for CO_2 calculated in this study are compared in Figure 1 with those of other investigators. There seems to be general agreement between the measurements made in this study and the others. It is not possible to compare the diffusivities of C_2H_4 , C_3H_6 , and C_4H_8 measured in this work with other investigations, because no diffusivity values are reported in the literature for these three gases.

Various semi-empirical methods have been proposed to predict diffusivities as a function of temperature (1, 8, 12, 13, 15, 20, 24, 30, 44). The methods of Wilke and Chang

Table I. Calculated Corrected Diffusion Coefficients^a
($D = KD_e$)

t (°C.)	$C^* \times 10^6$ (Gram Mole/Cm. ³)	$D \times 10^5$ (Cm. ² /Sec.)
CO_2		
6.5	56.0	1.145
25.0	31.2	1.850
35.0	23.8	2.179
52.0	15.2	3.613
65.0	10.7	4.296
C_2H_4		
6.7	8.20	0.682
25.4	4.51	1.085
35.0	3.53	1.396
52.0	2.61	2.020
65.0	2.15	2.579
C_3H_6		
7.0	13.1	0.376
25.0	6.26	0.681
35.0	4.33	0.895
53.0	2.29	1.373
65.0	1.51	1.868
C_4H_8		
7.0	4.20	5.157
25.0	3.09	6.612
40.0	2.32	9.485
60.0	1.96	12.48

^aSources of solubility data: CO_2 (32); C_2H_4 (32); C_3H_6 (2, 32); C_4H_8 (3).

(45) and of Othmer and Thakar (25), appear to us to more closely represent the over-all experimental results for CO₂ than any of the other proposed methods. Wilke and Chang developed the following expression:

$$D = \frac{7.4 \times 10^{-8} (2.6M)^{1/2} T}{\mu V_m^{0.6}} \quad (12)$$

while Othmer and Thakar predicted

$$D = \frac{14.0 \times 10^{-5}}{\mu^{1.1} V_m^{0.6}} \quad (13)$$

The molal volume of the solute, V_m , was obtained from the Le Bas values of atomic volumes (28).

Figures 1 through 4 compare the predicted and experimental values of D for the four gases. Equation 13 predicts the diffusivities satisfactorily only for CO₂. The Le Bas volumes are not satisfactory for the unsaturated hydrocarbons, or, from another view, Equations 12 and 13 are not satisfactory as correlating relations for the diffusivity of these gases in water. Use of V_m to a different power, say $\frac{3}{4}$, would improve the predictive ability of both equations for the hydrocarbons.

In order to provide a convenient means of calculating D , a quadratic equation was also used to correlate the diffusivities:

$$D = (A + Bt + Ct^2) 10^{-5} \quad (14)$$

The constants A , B , and C were calculated statistically, using the least square method:

Gas	A	B × 10 ²	C × 10 ⁴
CO ₂	0.95893	2.4161	3.9813
C ₂ H ₄	0.53615	1.4781	2.5657
C ₃ H ₆	0.29773	0.8086	2.4837
C ₄ H ₈	4.79791	12.5610	3.9235

Equation 14 can be used, together with the empirically determined constants given in the above table, to calculate the diffusivities of CO₂, C₂H₄, C₃H₆, and C₄H₈ in water for the temperature range from 6° to 65° C. The diffusivities computed in this manner are all within ±11% of the experimentally measured diffusivities.

In analyzing the homologous series C₂H₄, C₃H₆, and C₄H₈ it was hoped that it would be possible to get some insight into the effect of chemical structure on diffusion.

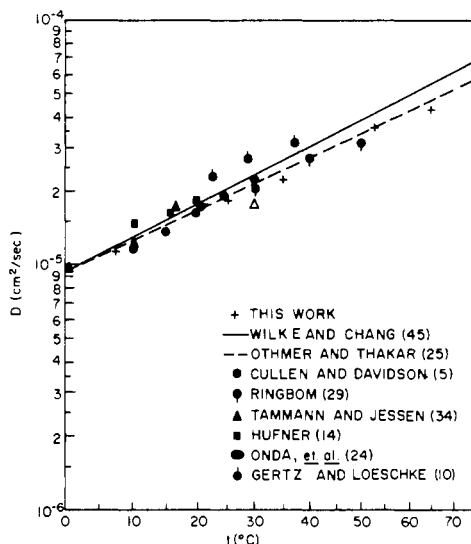


Figure 1. Experimental and theoretically predicted diffusivities for CO₂ in water

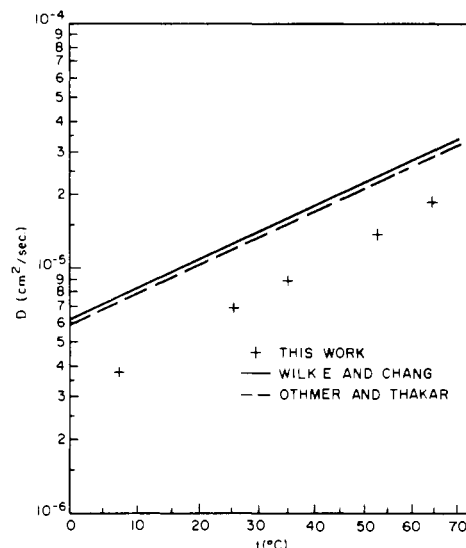


Figure 3. Experimental and theoretically predicted diffusivities for C₃H₆ in water

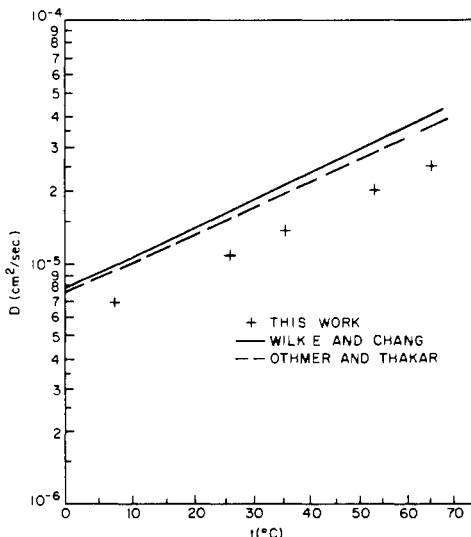


Figure 2. Experimental and theoretically predicted diffusivities for C₂H₄ in water

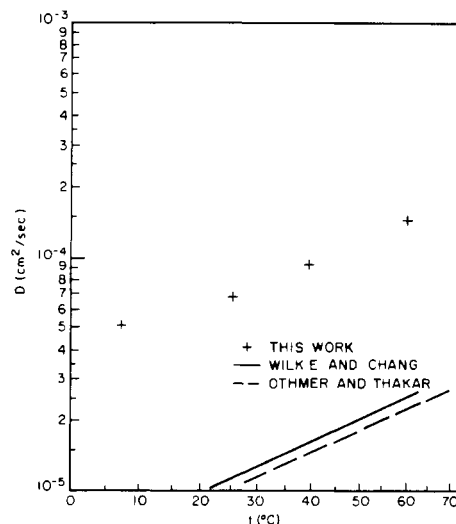


Figure 4. Experimental and theoretically predicted diffusivities for C₄H₈ in water

One might have expected the diffusivities to decrease with increasing molecular weight (I_6), but the diffusivities of C_4H_8 are actually higher than those of C_2H_4 and C_3H_6 at any one temperature. The experimental findings do not seem to indicate an apparent correlation between the chemical structure and the diffusivities for these three gases.

NOMENCLATURE

- A = empirical constant, $cm.^2/sec.$
 B = empirical constant, $cm.^2/(sec.)(t^\circ C.)$
 C = empirical constant, $cm.^2/(sec.)(t^\circ C.)^2$
 c = concentration of gas in water at any instant, (gram mole)/ $cm.^3$
 C_0 = initial concentration of gas in water, (gram mole)/ $cm.^3$
 C^* = saturated equilibrium concentration of gas in water, (gram mole)/ $cm.^3$
 d = diameter of jet, cm.
 D_e = diffusivities corrected for exact solution of the diffusion equation, $cm.^2/sec.$
 D = coefficient of diffusion, $cm.^2/sec.$
 F = water flow rate, $cm.^3/sec.$
 Gz = Graetz number of diffusion defined by Equation 9
 H = Henry's law constant, mm. Hg
 K = correction factor, unitless
 L = jet length, cm.
 M = molecular weight of solvent
 N = number of moles absorbed per unit of time, mole/sec.
 T = temperature, $^\circ K.$
 t = time, sec.; or temperature, $^\circ C.$, as indicated
 V_0 = average volume of gas absorbed at "zero" jet length, $cm.^3/sec.$
 V' = "gross" volume of gas absorbed, $cm.^3/sec.$
 V^* = "net" volume of gas absorbed, $cm.^3/sec.$
 V_m = molal volume of solute as a liquid at its normal boiling point, $cm.^3/mole$
 v_z = surface velocity of jet in the axial direction, $cm./sec.$
 \bar{v} = mean velocity of jet, $cm./sec.$
 x = distance measured from the surface of the jet toward the axis of the jet, cm.
 z = distance measured along the direction of flow, positive downwards, cm.
 π = numerical constant, 3.14159...
 μ = viscosity of solution at temperature t , centipoise
 λ = zeros of J_0

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