Diffusion Coefficients of Nitrogen and Oxygen in Water

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Measurements of laminar dispersion in a capillary have been used to determine the molecular diffusivities of O_2 and N_2 dissolved in water. Measurements made on the CO_2–H_2O system at 25° C., a system for which the diffusion coefficient was well known, indicated good agreement with the values reported by other investigators. No solubility data were required to determine the diffusion coefficient in this work and, in this aspect, the experimental method used offered a significant advantage over other techniques. Several correlations of diffusivity with temperature were tested and a new correlation is proposed.

EXPERIMENTAL determination of diffusion in liquids is inherently difficult because the diffusion process in liquids is so slow. This problem is magnified in the case of sparingly soluble gases because of difficulties in the accurate determination of trace quantities of dissolved gas. For example, the saturation concentration of nitrogen in water at standard conditions is less than one part in one hundred thousand on a mole basis.

Two of the more popular experimental methods used to evaluate dissolved gas diffusion coefficients have been the laminar liquid jet (*25, 35, 38*) and the diaphragm cell (*29, 32, 40*). An experimental run can be made in a relatively short time with a liquid jet apparatus; however, liquid jets are absorption devices that require an accurate knowledge of the absorbed gas solubility. The diaphragm cell is a relative device requiring calibration. Also, it requires a long time to obtain one diffusivity since transfer across the diaphragm occurs by diffusion only, and, consequently, several hours are needed to obtain a measurable concentration change.

The experimental method developed in this investigation has been adapted from the method developed originally by G. I. Taylor (*36, 37*). The technique, which is described in detail in (*9*), consisted of imposing a known concentration change of solute gas on a fluid in laminar flow passing through a long slender duct. The molecular diffusivity could be obtained from measurements of the concentration distribution downstream from the injection point. The time required to carry out an experimental run in such an apparatus, while not as short as in a liquid jet, was considerably less than for a diaphragm cell.

EXPERIMENTAL

The three significant advantages of the experimental method were:

No calibration was necessary.

Knowledge of the gas solubility was not required. (This feature was particularly advantageous since the error in the calculated diffusion coefficient due to the uncertainty in solubility values could easily exceed the error in the actual diffusion measurements.)

No gas-liquid interfaces were present.

The apparatus operated essentially as follows. A step change in the dissolved gas concentration was imposed by a rotating valve on water in laminar flow through a capillary 600 cm. in length and 0.202 cm. in diameter. The capillary as supplied by the manufacturer was made to the specifications of 0.080 ± 0.001-inch I.D. (0.203 ± 0.0025 cm.) and 0.120 inch O.D. with an eccentricity less than 10% of the wall thickness. The average inside diameter of the capillary was determined in the laboratory as 0.0795 inch (0.202 cm) by determining the volume of the capillary filled with water and subsequently displacing the water by an immiscible fluid into a calibrated container.

Fluid passed from the capillary exit through an expansion valve into a vacuum chamber, where the water vapor was selectively removed from the dissolved gas by low temperature condensation, before entering a mass spectrometer. The relative bulk average concentration of the dissolved gas was continuously measured by the mass spectrometer.

Considerable precaution was exercised in constructing the diffusion section of the apparatus to ensure that the capillary was straight and undisturbed by vibrations. The capillary was centered inside a hard drawn ¾ inch O.D. copper tube—which served as a thermostat by circulating water—by means of grooved supports at, approximately, 2-foot intervals. The copper tube in turn was supported at 2-foot intervals by metal blocks that were attached to a rigid metal frame. The frame in turn was supported by vibrationless mountings.

The sensitivity of the mass spectrometer was not nearly great enough to measure accurately the solute gas concentration from the expansion valve when mixed with the accompanying water vapor. Therefore, a high percentage of the water had to be removed without removing the solute gas. This selective removal was accomplished by passing the vapors from the expansion valve through cold traps. For all experimental runs, the outer surface of both traps was cooled by dry ice-acetone. When the solute gas was carbon dioxide, the inner wall of the downstream trap was cooled with a dry ice–acetone solution. For runs with nitrogen and oxygen, this inner surface was cooled with liquid nitrogen. Using liquid nitrogen, rather than a dry ice–acetone solution, to cool the inner wall of the downstream cold trap, decreased the amount of water vapor entering the mass spectrometer.

Conflicting design criteria were encountered in the design of the cold trap system. Long residence times and large surface area enhanced the removal of water vapor, but molecular mixing occurred in the vacuum system between the expansion valve and the mass spectrometer ionization chamber. If higher residence times were allowed, the concentration front of the solute would be altered significantly in passage from the expansion valve to the ionization chamber. Thus, the optimum design was one that combined minimum volume and maximum area, retaining a volume sufficiently large to prevent ice accumulation from plugging the flow path. To maintain the proper pressure at the inlet of the ionization chamber, a single-stage glass diffusion pump was inserted between the second trap and the mass spectrometer.

Brackman and Fite (2) discovered that trace amounts of permanent gases in water vapor were trapped, or occluded, on a cold surface by the condensing water vapor, particularly when the cold surface was at or below the normal boiling point of the permanent gas. To determine whether occlusion was occurring to an appreciable degree in the apparatus used in this study, water containing dissolved CO_2 was allowed to flow into the cold trap system through the expansion valve. A solution of dry ice-acetone was used to cool the trap surfaces. After several grams of water had collected in the cold traps, the expansion valve was closed, and the temperature of the cold surfaces was allowed to rise slowly. The amount of CO_2 downstream from the cold traps was monitored continuously by the mass spectrometer. No evidence of CO_2 having been trapped by the condensing water vapor was observed.

RESULTS

The experimental design and operation in this study were based on the constraints:

(1) τ = dimensionless time = $(Dt/R^2) > 2$

(2) Pe = Peclet number = $(2Ru/D) > 250$

For these values, it is shown in (9) that Equation 1 below holds. Diffusivities were determined from the following analytical approximate solution for Taylor diffusion in a capillary:

$$C = \frac{C_O}{2}\ erfc \left[\frac{L - u_{1/2}t}{(4k_{1/2}t)^{1/2}} \right] \tag{1}$$

where:

$u_{1/2} = L/t^{1/2}$; $k_{1/2} = R^2 u_{1/2}^2/48D$; C = bulk average concentration; C_O = step change in concentration of solute; L = length of capillary (600 cm.); D = diffusivity; t = time; R = capillary radius; and $t_{1/2}$ = time at which the experimental bulk average concentration was $C_O/2$.

Although the recorder response from the mass spectrometer was actually a measurement in millivolts, the response was directly proportional to the mass of solute gas in the ionization chamber at any given time. Consequently, the recorder response was proportional to the amount of solute gas dissolved in the liquid. Actual concentrations did not need to be determined in as much as the mathematical model, Equation 1, expresses the concentration relative to the step input, C_O. The use of a concentration scale relative to the step change in concentration is of value because, in contrast with gas absorption devices, the gas solubility is not involved in computing the diffusivity.

The final recorder response minus the background reading was taken as the measure of the concentration step change, C_O. In carrying out the least square fit of the concentration *vs.* time data, a large number of discreet values were selected from the recorder output between values 10 and 90 % of C_O. The reported values of diffusivities evolved from minimization of the sum of the squares of the relative per cent deviation of the difference $(C_{\text{exptl.}} - C_{\text{calcd.}})$, where $C_{\text{exptl.}}$ = experimental bulk average concentration at time t, and $C_{\text{calcd.}}$ = bulk average concentration calculated from Equation 1 at time t. The minimization was carried out on a digital computer employing the standard direct search procedures for nonlinear regression. Both the value of the diffusivity, D, and the concentration step change, C_O, were evaluated in the least square fit. The difference between C_O determined experimentally and that established by the minimization procedure was less than 2 %.

A test of the validity of the experimental apparatus and procedure was carried out by comparing the calculated diffusivities for CO_2 in H_2O with known values of other investigators. Six of the more recent literature values for the diffusivity of CO_2 in H_2O are shown in Table I, together with the average experimental value obtained from this study. The experimental standard deviation for CO_2-H_2O in the present study was 0.10×10^{-5} cm^2 per second. Previous experimental values shown in Table I differ from the mean value obtained in this study by less than one standard deviation; therefore, we felt that the factor of bias could be safely ignored.

The diffusion coefficient of both N_2 and O_2 was determined at 10°, 25°, 40°, and 55° C.; the average values and coefficients of variation—standard deviation of D divided by mean value of D—are listed in Table II.

COMPARISON WITH PREVIOUS WORK

There is a considerable discrepancy in the values of the diffusion coefficients reported in the literature as can be ascertained by reference to Figures 1 and 2. In these figures the diffusion coefficient is recorded on a logarithmic scale *vs.* the reciprocal absolute temperature.

Many of the values of the diffusion coefficient for N_2 and O_2 found in the literature were dependent, to some degree, on the value used for the solubility of the dissolved gas. A detailed explanation of the various experimental methods employed to obtain the diffusivity of sparingly soluble gases dissolved in liquids cannot be given here. [The interested reader is referred to a recent review by Himmelblau (12) or to the respective original articles.] However, Table III gives a summary of several techniques used to determine the diffusivity of gases dissolved in liquids according to rather general categories. Included in this table is the approximate dependence of the calculated value of the diffusion coefficient on the value used for the gas solubility. Of the experimental techniques listed in Table III, polarography or laminar liquid jets are generally considered to be the more precise experimental methods.

Table I. Diffusion Coefficient of Carbon Dioxide in Water at 25° C.

D (10^5) Cm.^{2}/ Sec.	Investigator	Method	Date
1.87	Scriven (32)	Diaphragm cell	1956
1.95	Woods (44)	Jet	1961
1.92	Tang and Himmelblau (35)	Jet	1964
2.00	Vivian and King (40)	Diaphragm cell	1964
1.85	Unver and Himmelblau (39)	Jet	1964
1.95	Thomas and Adams (38)	Jet	1965
1.92	This work		

Table II. Experimental Diffusion Coefficients

System	Temperature, ° C.	Number of Experimental Runs, n	Mean Value of Diffusion Coefficient, D (10^5) Cm.^{2}/Sec.	Coefficient of Variation, η
CO_2-H_2O	25	10	1.92	0.055
N_2-H_2O	10	5	1.29	0.091
	25	5	2.01	0.100
	40	5	2.83	0.038
	55	5	3.80	0.084
O_2-H_2O	10	6	1.54	0.066
	25	7	2.20	0.072
	40	8	3.33	0.125
	55	5	4.50	0.073

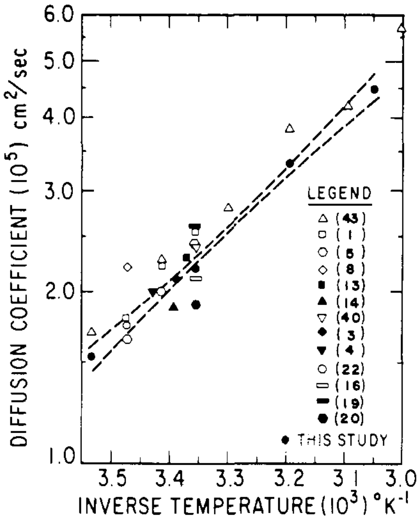

Figure 1. Experimental diffusion coefficients—oxygen in water

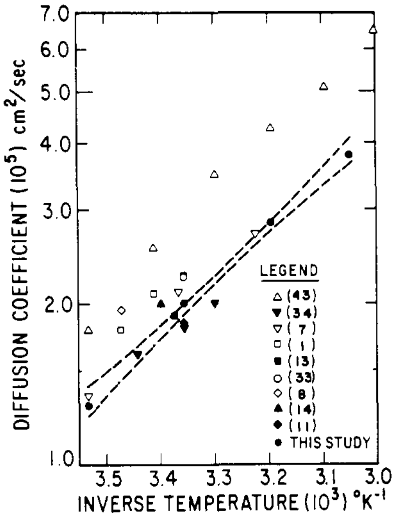

Figure 2. Experimental diffusion coefficients—nitrogen in water

Table III. Dependence of Calculated Diffusion Coefficient on Solubility

Investigator	Experimental Technique	Functional Dependence of D on Solubility, S
Davidson and Cullen (*5*); Baird and Davidson (*1*); Davies, Kilner, and Radcliff (*6*)	Wetted sphere, laminar liquid jets	$D \propto 1/S^2$
Houghton, Ritchie, and Thomson (*13*); Wise (*43*)	Dissolution of bubbles	$D \propto 1/S$
Brdicka and Wiesner (*3*); Jordan, Ackerman, and Berger (*16*); Kolthoff and Miller (*19*)	Polarography	$D \propto 1/S^2$
Carlson (*4*); Tammann and Jessen (*34*); Smith, Friess, and Morales (*33*)	Diffusion across plane, stagnant interface (gas-liquid or liquid-liquid)	$D \propto 1/S^2$

Polarographic measurements are reproducible to within approximately 4 % (*12*) while the precision of a liquid jet is about 2 % (*35*). However, the value of the diffusivity calculated from measurements with polarographic or liquid jet apparatus is highly dependent on the value of the solubility used in the calculation. Any error in the solubility data is magnified in the calculated diffusion coefficient. In addition, measurements of diffusion rates by polarographic techniques are limited to electro-reducible or electro-oxidizable substances.

CORRELATION OF DIFFUSIVITIES WITH TEMPERATURE

Reference to Figures 1 and 2 shows that the differences in the values of the diffusion coefficients determined by different techniques would preclude any conclusions as to the effect of temperature on a given gas-water system. Of the diffusion coefficient values shown in Figures 1 and 2, other than those from this study, only Tammann and Jessen (*34*) and Wise (*43*) have measured the diffusion rate over a temperature range greater than 13° C. However, the results both of Tammann and Jessen and of Wise are subject to question.

Tammann and Jessen used agar-agar in their liquid phase, but more recent studies (*10, 38*) have indicated that such gelatin-type materials will cause a significant change in the diffusion rate. Wise determined diffusivities by observing the rate of dissolution of stationary bubbles in a stagnant water media. The proper mathematical model for the system used by Wise is quite complex (*31, 43*), and apparently his model did not represent the measured data satisfactorily. Consequently, only the diffusivities obtained in this work were used to test various correlations.

Several semi-empirical models were tested by fitting them to the diffusivities listed in Table II. The Stokes-Einstein (or Sutherland) equation

$$\frac{D\mu}{T} = \frac{k'}{6\pi a} \tag{2}$$

where

k' = Boltzmann constant; T = absolute temperature; a = radius of solute molecule; μ = viscosity of the solvent;

which indicates that for a given solvent $D\mu/T$ should be constant, was fit by the least-square method. The ratio of the variance owing to regression, s_2^2, and the variance owing to experimental error, s_1^2, is shown in Table IV. A comparison of the variance ratio with the statistic F indicated that the fit was acceptable for the N_2-H_2O and O_2-H_2O systems.

The relations developed by Eyring and various co-workers (*18, 30*), as well as other investigators (*24, 26, 28, 41*), also indicate the same dependence of the diffusion coefficient on temperature, i.e., that $D\mu/T$ = constant, for a common solvent, and hence represented the diffusivities.

Neither the relations of McCall and co-workers (*23*) nor those of Kamal and Canjar (*17*) were tested. The expression developed by Kamal and Canjar for binary liquids involved a temperature dependent parameter that has no physical basis in dissolved gas systems, namely the latent heat of vaporization of the solute at the temperature of diffusion. Wise has adequately demonstrated elsewhere (*43*) that the theoretical model of Longuet-Higgins and Pople (*21*) does

Table IV. Comparison of Equation 2 with Experimental Data

Temperature, °C.	$D\mu/T$ (10^9) $\frac{(G.)(Cm.)}{(Sec.^2)(°K.)}$ N_2-H_2O	O_2-H_2O
10	0.596	0.711
25	0.602	0.659
40	0.593	0.698
55	0.586	0.695
s_2^2/s_1^2	0.10	0.87
F(90%)	2.46	2.35

not correctly predict the variation of the diffusion coefficient with temperature, because the increase in the diffusion coefficient with increasing temperature as predicted by the Longuet-Higgins and Pople model is only about 10% of that observed experimentally. Panchenkov (*27*) has shown that Eyring's equation may, with little error, be written:

$$D = A_2 \exp.\left(-\frac{B}{R_1 T}\right) \qquad (3)$$

where both A_2 and B are independent of temperature. The natural logarithm of Equation 3 may be written:

$$Y = \ln A_2 - \frac{B}{R_1} Z \qquad (4)$$

where:

$$Y = \ln D$$

$$Z = \frac{1}{T}$$

which is the equation of a straight line with a slope of $-B/R_1$ and an intercept of $\ln A_2$. Equation 4 also proved to be a good fit to the values in Table II, as shown in Table V.

One should not conclude from Table V that B is the same for all gas-liquid systems—around 4500 cal. per gram mole—since H_2 and He give smaller values.

Because of the agreement between Equation 3 and the experimentally determined temperature dependence of the diffusivity, the possibility of interpreting the constants A_2 and B of Equation 3 in terms of temperature independent molecular properties was examined. Unfortunately, the diffusion coefficient predicted by an equation of the form of Equation 3 is greatly dependent on the value of the constant, B, in the exponential. For example, consider the N_2–H_2O system at 25° C. If the estimated value of B were in error by 5%, the predicted value of the diffusion coefficient would be in error by approximately 45%. Because of this sensitivity of the diffusion coefficient to the value of the parameter in the exponential, we concluded that the exponential form of Equation 3 was not suitable for the development of a semi-empirical or empirical correlation.

Ferrell (*9*) proposed a correlation based on activated rate theory which is an extension of Wilke and Chang's (*42*) equation

$$D = \frac{4.8 \times 10^{-7} T}{\mu^{\alpha}} \left[\frac{1 + \lambda^{*2}}{V_m}\right]^{0.6} \qquad (5)$$

The parameters of Equation 5 are based on the following units of the physical parameters:

Table V. Comparison of Equation 3 with Experimental Data

	N_2–H_2O	O_2–H_2O
$A_2(10^5)$ (cm.^{2}/sec.)	$3412 \pm {}^{3906}_{1821}$	$4286 \pm {}^{4838}_{2274}$
B (cal./g. mole)	4422 ± 461	4470 ± 457
s_2^2/s_1^2	0.54	0.57
F(90%)	2.67	2.56

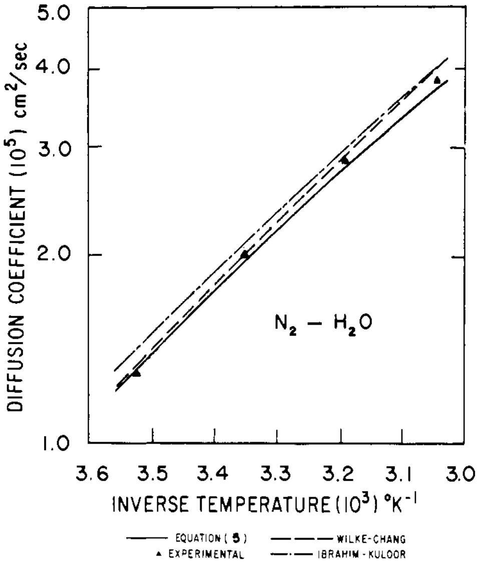

Figure 3. Comparison of experimental and predicted diffusion coefficients

T = °K; μ = viscosity of solvent (centipoise); V_m = molar volume of solute at its normal boiling point (cc. per gram-mole); λ^* = quantum parameter of solute = $h/\sigma(m\epsilon)^{1/2}$ (dimensionless); D = mutual diffusion coefficient (cm.^{2}/second); m = mass of the molecule; and h = Planck constant.

The exponent α is

$$\alpha = \frac{\sigma}{\left(\frac{V_m}{N}\right)^{1/3}}$$

ϵ, σ = force constants obtained from the temperature variation of the coefficient of viscosity of the molecules in the gas phase by the Lennard-Jones 6-12 potential; and N = Avogadro's number.

Equation 5 can be compared with the Wilke-Chang equation for water as a solvent and the Ibrahim and Kuloor (*15*) relation. Figure 3 shows the agreement is excellent for all three relations; the figure for O_2 is quite similar.

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Enthalpy, Heat Capacity, and Heat of Fusion of Aluminum from 366° to 1647° K.

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The enthalpy, $H_T - H_{298.15^\circ K.}$, of aluminum has been determined primarily to establish the heat capacity of liquid aluminum, which was essentially constant at 7.59 cal. per (mole deg.) from 933° to 1650° K. The heat of fusion was 2560 ± 50 cal. per mole. Smoothed values of enthalpy and heat capacity from 298° to 1700° K. are given.

THE LITERATURE on the enthalpy and heat capacity of aluminum has been well documented by Kelley (*8*), Stull and Sinke (*23*), and most recently by Hultgren and coworkers (*7*). While solid aluminum would not appear to need reinvestigating, the experimental data for liquid aluminum are not in good agreement and, for the most part, just begin to cover the liquid range.

The development of refractory materials more resistant to attack by molten aluminum has made the measurement of liquid aluminum enthalpy more practical and the work reported here was undertaken to obtain more definitive data in the liquid range. Observations were made also in the solid range as an internal check on the applied corrections.

EXPERIMENTAL

The aluminum was contained in a covered refractory crucible which was sealed in a platinum-10% rhodium alloy capsule by arc welding under a helium pressure of about 8 cm. mercury. High purity aluminum was purchased from the United Mineral and Chemical Corporation and was machined into cylinders to fit the crucibles. Spectrographic analysis detected 2.7 p.p.m. of Cu, 1.8 p.p.m. of Fe, and 2.0 p.p.m. of Si.

Crucibles of titanium diboride—National Carbon Co. Division of Union Carbide Corp.—and of boron nitride—Cerac, Inc.—were used. The reason for using two different crucibles will soon become evident. Titanium diboride was the only crystalline phase detected by x-ray diffraction in a sample of the titanium diboride. However, 0.02% Al, 3% Cr, 1.2% Fe, 0.07% Mo, and 0.04% V were found by spectrographic analysis.

Enthalpy, $H_T - H_{298.15^\circ K.}$, was measured in a copper block drop calorimeter already described (*12*), correcting for the heat content of the platinum-10% rhodium alloy capsule from previous empty capsule measurements.

A titanium diboride crucible with cover—8.736 grams—was sealed in a platinum-10% rhodium alloy capsule—15.029 grams—by arc welding under helium at about 8 cm. of mercury pressure. The enthalpy of the empty crucible was determined, but the top and bottom of the crucible stuck to the metal capsule and, therefore, was not used again. An aluminum cylinder—6.072 grams—was contained in a second titanium diboride crucible—12.554 grams—sealed in a platinum-10% rhodium capsule—14.406 grams—for the first series of measurements on aluminum. This series ended when the crucible cracked, apparently from the stress brought about by the rapid heating of the aluminum, allowing molten aluminum to attack the capsule, which then fell apart.

Additional titanium diboride crucibles could not be purchased, and boron nitride was selected as the crucible material for further experiments. Two crucibles were purchased.

A glaze was found on the first crucible after measuring its enthalpy. The glaze contained boric acid, identified by x-ray diffraction, and was soluble in methanol. Consultation with the manufacturer confirmed the presence of boron oxide as a constituent of a proprietary oxide binder.