Re_c = critical value of Re
$Re_{ic} = Re_c$ for $\bar{\xi} = \bar{\xi}_1$
$Re_{oc} = Re_c$ for $\bar{\xi} = \bar{\xi}_2$
v = axial velocity component
$\langle v \rangle$ = average of v
$\mathbf{v}$ = velocity vector

Greek Symbols

∇ = gradient operator
λ = value of ξ for which velocity is maximum
μ = viscosity
ξ = r/R_o
$\bar{\xi}$ = value of ξ at which K is maximum
$\bar{\xi}_1$ = value of $\bar{\xi}$ for $\sigma \leq \bar{\xi}_1 \leq \lambda$
$\bar{\xi}_2$ = value of $\bar{\xi}$ for $\lambda \leq \bar{\xi}_2 \leq 1$
ρ = density
σ = annulus aspect ratio, R_i/R_o
ϕ = $1 + \sigma^2 - 2\lambda^2$

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Diffusion Coefficients for Helium, Hydrogen, and Carbon Dioxide in Water at 25°C.

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Accurate values of the diffusivities of gases in liquids are useful in many different branches of research. Gas diffusivity data for sparingly soluble gases is of special interest since they are useful in testing the various theories of liquid phase diffusion for the case when the solute is of low molecular weight. In engineering, they are employed in investigations concerning the role of diffusion in interfacial mass transfer and as an aid in interpreting laboratory investigations, as well as for the design of mass transfer equipment. Moreover, they are frequently needed to interpret physiological studies.

A number of investigators have determined diffusivities of sparingly soluble gases such as helium and hydrogen in water, but because of a wide range of these values as shown in Table 2, their results are in need of confirmation. The main problem involved in these studies has been the difficulties associated with the accurate determination of trace quantities of dissolved gas.

The objective of this work was to determine the diffusion coefficients of two important slightly soluble gases, helium and hydrogen, in water. The method employed in this work requires no empirically determined parameters and has the advantage of being relatively fast. As a test of the reliability of this method, experiments were also carried out with carbon dioxide, a gas having a well-known diffusion coefficient. A wetted wall column technique was used with a relatively long (0.200 m) stainless steel tube as the wetted wall. Water was mixed with a small amount of a surface active agent to suppress surface ripples and give well-defined hydrodynamics. The apparatus and technique used were those employed by Perez and Sandall (1973) for diffusivity measurements in non-Newtonian liquids.

THEORY

A solution for the differential equation describing gas absorption into a liquid flowing in a falling film with a parabolic velocity profile was obtained by Pigford (1941). As a result of later research carried out by Emmert and Pigford (1954), it was concluded that for short contact times this solution reduces to the penetration theory prediction of Higbie (1935) which is based on the assumption of a uniform velocity.

Thus, for the short contact times of our experiments, an equation may be derived (Perez and Sandall, 1973) from penetration theory to relate the diffusivity to variables which can be measured or calculated:

$$D = \frac{\pi}{4} \frac{q^2}{U_s l} \left\{ \frac{r}{r+d} \right\}^2 \left[\frac{C_2 - C_1}{(C_s - C)_{lm}} \right]^2 \qquad (1)$$

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental apparatus was that used by Lamourelle and Sandall (1972) and is shown schematically in Figure 1. The apparatus consisted of absorption and desorption sections so that the water could be recycled. A laminar film of water was formed on the outside of a 0.0159 m diameter stainless steel tube. The length of the wetted wall was 0.200 m. Flow rates were determined using a rotameter, and the water temperature was measured by a chromel-constantan thermocouple. In the course of the experiment, a mixture of distilled water and 0.3 wt % Petrowet R was used. Petrowet R is a surface active agent manufactured by the Dupont Company.

The solution had to be stripped of the gas in the desorption section after every run so that the water could be recycled. The stripping process was carried out at an absolute pressure of 1.6×10^4 pascals which was created by a filter pump.

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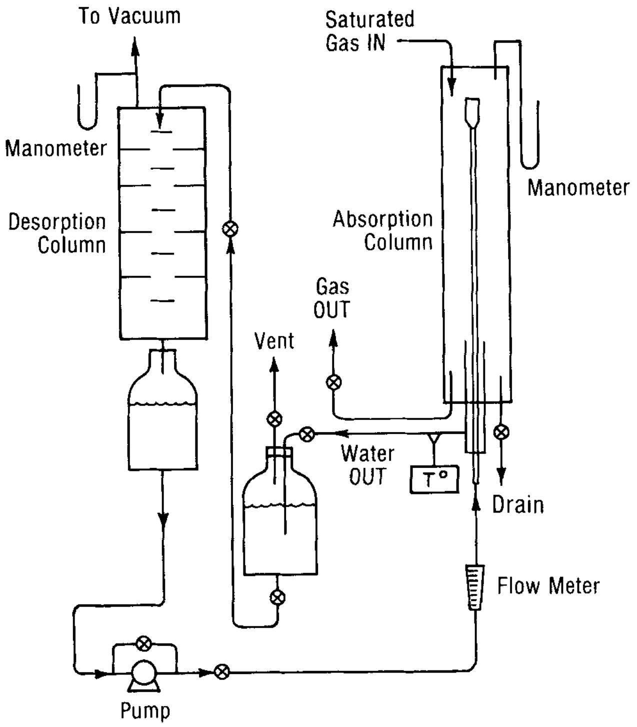

Figure 1. Schematic drawing of the experimental apparatus.

For each experiment, the pump was turned on, and the laminar film was formed on the wetted wall. Then, the water level in the receiver was held constant at the mark of 0.200 m. Next, the gas was introduced into the system and flowed out through a bottom flange. Liquid samples were withdrawn from the inlet and outlet after enough time was allowed for the water to fill the receiver three or four times. A duplicate set of samples was withdrawn after the same period of time as a check on the steady state operation.

To analyze the liquid samples for the concentration of helium or hydrogen, a Hewlett-Packard Chromatograph Model 5750 in conjunction with an Infotronic Integrator Model CRS-208 was used. Five milliliter samples were withdrawn into 30 ml glass syringes. Five milliliters of the carrier gas were added to the liquid sample in the syringe, and the tip of the needle was sealed with a piece of rubber. The plunger was pulled back to the 25 ml graduation to create a vacuum, and the contents of the syringe were shaken vigorously under vacuum. The plunger was then placed back on the 10 ml graduation, and the gaseous phase was injected into the chromatograph. The chromatograph column was a 6.35×10^{-3} m diameter, 3.66 m long column with 5A molecular sieve as the adsorbent. A precolumn containing calcium sulfate was provided to remove any moisture that might enter the column during sample injection.

A wet chemistry technique was used for the analysis of carbon dioxide in solution. The carbon dioxide was precipitated as barium carbonate from a solution of barium chloride and sodium hydroxide. The excess sodium hydroxide was titrated to a phenolphthalein end point with hydrochloric acid.

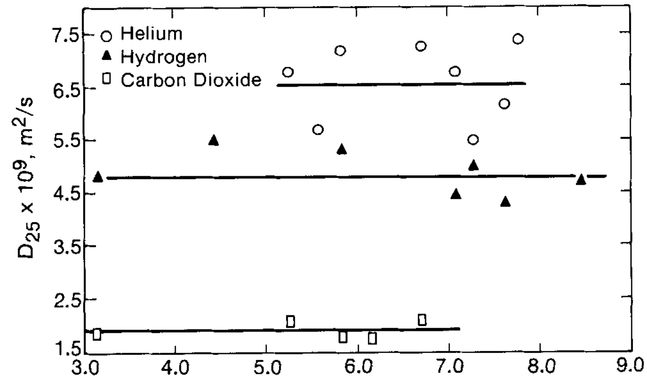

Figure 2. Diffusion coefficients at 25°C vs. flow rate.

Table 1. Average Diffusion Coefficients of Gases in Water at 25°C

Gas	$D \times 10^9$ (m^2/s)	% mean deviation	% standard deviation
CO_2	1.88	7.76	9.11
H_2	4.80	9.12	10.88
He	6.50	9.37	11.02

PRESENTATION AND DISCUSSION OF RESULTS

To calculate the diffusivities from Equation (1), the values of q, l, C_1, and C_2 are measured, and C_s is obtained from Henry's law:

$$C_s = P_A/H \tag{2}$$

The Henry coefficients H were obtained from the International Critical Tables. The surface velocity U_s and the film thickness d were calculated from equations derived for laminar film flow.

The results are shown in Figure 2 plotted against the water flow rate. Experimental temperatures varied from 22.5° to 26.0°C, and the diffusivities shown in Figure 2 were corrected to 25°C by holding the group $(D\mu/T)$ constant, as is suggested by the Stokes-Einstein theory. The experimental results show no trend with flow rate. The straight lines on the graph represent the average diffusivities for each gas.

The average values along with their percent mean deviations and percent standard deviations are listed in Table 1. The maximum experimental error is estimated to be about 10.8%, which may be compared with the deviations tabulated in Table 1.

Surface active agents used to suppress ripples were found by Emmert and Pigford (1954) to cause an interfacial resistance to mass transfer. In our study, 0.30 wt % Petrowet R was used. Even though this is the same concentration of the same agent as used by Emmert and Pigford, no interfacial resistance is evident from the results presented here. An explanation, as proposed by Perez and Sandall (1973), for this apparent discrepancy may be that a relatively long exposure time is required for there to be a sufficiently high concentration buildup of surface active agent at the surface to result in an interfacial resistance. That is, the column of Emmert and Pigford was 1.14 m long compared to a length of 0.20 m in this work. Therefore, for the same flow rate, the contact time is approximately six times shorter than that of the longer column. Furthermore, the data of Emmert and Pigford show closer agreement with penetration theory, assuming no interfacial resistance at high flow rates. Lynn, Straatmeier, and Kramers (1955) found good agreement with penetration theory for sulfur dioxide absorption in water using wetted wall columns of 0.12 to 0.22 m and for various surface active agent concentrations up to 0.80 wt %. Similarly, Perez and Sandall found no evidence of an interfacial mass transfer resistance for the system carbon dioxide in water and various aqueous polymer solutions.

Diffusivities reported by other investigators are listed in Table 2 for comparison with this work. The literature values chosen as the most reliable, in the case of helium and hydrogen, are the ones reported by Vivian and King (1964). This choice was based on the investigation and

TABLE 2. VALUES OF MOLECULAR DIFFUSION COEFFICIENTS FOR GASES IN WATER

Gas	$D \times 10^9$ (m^2/s)	Reference
CO_2	1.85	Unver and Himmelblau (1964)
	1.87	Davidson and Cullen (1957)
	1.88	Clark (1964)
	1.89	Tham et al. (1967)
	1.92	Ferrell and Himmelblau (1967); Tang and Himmelblau (1965)
	1.95	Emmert and Pigford (1954); Woods (1961)
	1.96	Thomas and Adams (1965)
	1.98	Duda and Vrentas (1968); Perez and Sandall (1973)
	2.00	Vivian and King (1964)
	1.88	This work
H_2	3.20*	Ipatieff and Teodorovich (1937)
	4.00	Tamman and Jessen (1929)
	4.10	Gertz and Loescheke (1954)
	4.50	Ferrel and Himmelblau (1967)
	4.80	Vivian and King (1964)
	4.95†	Houghton et al. (1962)
	5.26	Baird and Davidson (1962)
	6.30	Wise and Houghton (1966)
	7.20	Davidson and Cullen (1957)
	4.80	This work
HE	4.80	Gertz and Loescheke (1954)
	6.24**	Houghton et al. (1962)
	6.28	Ferrell and Himmelblau (1967)
	6.30	Vivian and King (1964)
	7.50	Wise and Houghton (1966)
	9.50	Baird and Davidson (1962)
	6.50	This work

* Corrected from 20°C.
† Corrected from 24.5°C.
** Corrected from 22.1°C.

comparison of diffusivity techniques and results performed by St-Denis and Fell (1971). They concluded that data obtained from Vivian and King's diaphragm cell technique were the most reliable for the following reasons: no interface was present, no gas solubilities were required, and the hydrodynamics were well defined. Comparison of the average diffusivities from this work and those of Vivian and King showed deviations of -5.85% for carbon dioxide and $+3.24\%$ for helium. Hydrogen showed negligible deviation.

CONCLUSIONS

This method has been used previously by Perez and Sandall (1973) for diffusion of gases in non-Newtonian liquids, and the results have been found to be satisfactory. In this work, the technique was used to measure diffusivities of slightly soluble gases in water, a rather difficult system to analyze owing to the small amounts of dissolved gas in the liquid. The results show good agreement with the literature. The technique has the advantages of being relatively fast and not having any empirically determined parameters, since all variables are directly measured.

NOTATION

C = bulk concentration, kg moles/m^3
C_1 = concentration at the inlet, kg moles/m^3
C_2 = concentration at the outlet, kg moles/m^3
C_s = surface concentration, kg moles/m^3
d = liquid film thickness, m
D = molecular diffusion coefficient, m^2/s
H = Henry's coefficient, pascal m^3/kg mole
l = height of the wetted wall column, m
P_A = partial pressure, pascal
q = flow rate per unit wetted perimeter, m^2/s
Q = liquid flow rate, m^3/s
r = wetted wall column radius, m
U_s = surface velocity, m/s
π = 3.14159 . . .

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Limits of the Chemical Method for the Determination of Physical Mass Transfer Parameters in Mechanically Agitated Gas-Liquid Reactors

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Interfacial parameters a and $k_L a$ in gas-liquid stirred tanks are generally determined in assuming the liquid phase perfectly mixed, which is most often realistic, and the gas phase either in piston flow (Cooper et al., 1944; Karwat, 1959; Yoshida et al., 1960; Liu et al., 1972) or perfectly mixed (Westerterp et al., 1963; Calderbank, 1958; Figueiredo and Calderbank, 1978; Sridharan, 1975). A comparison of the data obtained for both gas flows is sometimes proposed (Mehta and Sharma, 1971; Yagi and Yoshida, 1977). When the gas is dispersed into liquids that we term clean, the coalescence and redispersion due to bubble interaction either inside the dispersion or with the cavities behind the stirrer blades (Van't Riet and Smith, 1973) assure a perfect mixing of the gas phase. On the contrary, for liquids that we term polluted by the presence of dissolved electrolytes or surface active agents that diminish or nearly totally inhibit the coalescence, the piston flow model may not represent conveniently the behavior of the gas, even though the bubbles may be considered independent in a first approximation.

The aim of this communication is to propose a flow model for gas dispersion into liquids inhibiting coalescence that seems more realistic than the piston flow model. Then criteria will be deduced to insure, when the real behavior of the gas phase is ignored, the independence within 10% relatively to this behavior of the mass transfer parameter data measured in a laboratory scale well-stirred tank by the chemical method. First, the model is used to represent the behavior of the dispersion of not shrinking bubbles, that is, absorption of diluted gas. Then, by analogy with the work of Linek and Mayrhoferova (1969), the model is applied to the case of the dispersion of shrinking bubbles, that is, absorption of pure gas.

THEORY: CHARACTERISTIC DISTRIBUTIONS OF THE DISPERSION

The calculation scheme of the two considered cases is presented in Figure 1. Assumptions are either specific or common for both types of dispersion.

1. The bubbles originated by the distributor do not loose their identity up to the moment they leave the reactor or up to their complete dissolution inside the liquid bulk.
2. Each bubble is perfectly mixed except for instantaneous chemical regime.
3. Mass transfer resistance is located in the liquid phase, and the true liquid side mass transfer coefficient only depends on the bubble diameter δ_o as follows:

$$k_L = \overline{xk_L}\delta_o^{\mu} \tag{1}$$

The most frequent value proposed in literature is $\mu = 0.5$ (Levich, 1962; Akita and Yoshida, 1974).

4. For each bubble, the liquid phase composition is invariable; that is, the liquid evolution time is sufficiently slow to be neglected when compared to the residence time of a bubble inside the dispersion.

The assumptions for the dispersion of the nonshrinking bubbles are:

1. The distribution function $f(\delta_o)$ of the size of the bubbles is invariable in the dispersion and is represented by the Bayens (1967) distribution

$$f(\delta_o) = K\delta_o^2 \exp(-k^2\delta_o^2) \tag{2}$$

K and k are empirical constants. This distribution has been successfully used for gas-liquid dispersions (Padmanabhan and Gal-Or, 1968).

2. The reduced residence time of each bubble depends on the magnitude of its diameter as follows:

$$\theta_o = t_{\delta_o}/\tau_G = \lambda\delta_o^{-\nu} \tag{3}$$

The bubble diameter fraction δ_o, $\delta_o + d\delta_o$ in the dispersion occupies the gas volume fraction dV_o/V_o, and the corresponding volumetric flow rate is

$$\frac{dQ_o}{Q_o} = \frac{dV_o}{\theta_o V_o} = \frac{\delta_o^{\nu+3} f(\delta_o)\, d\delta_o}{\lambda \int_0^\infty \delta_o^3 f(\delta_o)\, d\delta_o} \tag{4}$$

Normation of Equation (4) leads to

$$\lambda = I_\nu/k^\nu = \frac{1}{2k^\nu}\int_0^\infty y^{\nu/2+2}\exp(-y)\,dy \tag{5}$$

and if we consider the relations (2), (3), (4), and (5), the outlet fraction of gas flow rate dQ_o/Q_o of age comprised between θ_o and $\theta_o + d\theta_o$ is

$$E(\theta_o) = \frac{1}{\nu} I_\nu^{6/\nu}\theta_o^{-(2+6/\nu)}\exp[-(I_\nu/\theta_o)^{2/\nu}] \tag{6}$$

Representative theoretical curves are shown in Figure 2. As the probability for the bubble to leave or to stay inside the dispersion depends on the competition between the drag force and the buoyancy force acting on it, this normally leads to $1 \leqq \nu \leqq 2$. It may be observed in Figure 2 that the distributions obtained for $1 \leqq \nu \leqq 2$ are

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