x_2 = length of bubble interface from $x = 0$
z = direction perpendicular to bubble surface measured from bubble surface

Greek Letters

α, β = constants
δ = water film thickness
μ = coefficient of shear viscosity
ν = kinematic viscosity (μ/ρ)
ρ = fluid density
σ = coefficient of interfacial tension

Subscript

av = average

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Diffusion Coefficients of Hydrogen and Helium in Water

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Measurements of laminar dispersion in a capillary have been used to determine the molecular diffusion coefficients of hydrogen and helium dissolved in water over the temperature range of 10° to 55°C. Literature correlations did not predict realistic values of the diffusivities for the hydrogen—water and helium—water binaries. A statistical analysis of the experimental diffusion coefficients indicated that they could be related to the absolute temperature by a semiempirical correlation, which may be considered an extension of the well-known Wilke-Chang correlation. This relation was based on the absolute reaction rate model of liquids.

Knowledge of molecular diffusion coefficients of sparingly soluble gases dissolved in liquids is important in many fields. The theorist employs these values in testing existing or proposed liquid state theories for low molecular weight solutes. The experimentalist often uses diffusion coefficients of dissolved gases as an aid in interpreting laboratory investigations. Finally, diffusion coefficients are useful to the engineer in his investigation and prediction of mass transfer.

With the exception of water as the liquid solvent, very little experimental data have been reported (*14*), and even for water, there is a wide range in the diffusivities for dissolved hydrogen and helium. In addition, in the majority of experiments the value of the diffusion coefficient has been obtained at only one temperature.

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 the difficulty in determining accurately trace quantities of dissolved gas (*18*). For example, the saturation concentration of helium in water at standard conditions is less than 1 p.p.m. on a mole basis.

The experimental method used in this investigation was adapted from that developed originally by Taylor (*24, 25*). The technique essentially consists of imposing a known concentration change of solute on a fluid in laminar flow passing through a long slender duct. The molecular diffusivity can 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.

MATHEMATICAL MODEL OF PHYSICAL SYSTEM

In dilute solutions of gases dissolved in liquids, the effect of gas concentration on the system density and viscosity is so small that these parameters can be assumed to be the same as those of the solvent. Consequently, in an isothermal laminar flow system, with no chemical reactions, with the diffusion path a cylindrical duct, and with a concentration distribution possessing axial symmetry, the mass balance for fully developed flow becomes

$$\frac{\partial c^+}{\partial t} + 2u\left[1 - \frac{r^2}{R^2}\right]\frac{\partial c^+}{\partial z} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c^+}{\partial r}\right) + \frac{\partial^2 c^+}{\partial z^2}\right] \quad (1)$$

For a step change in the input concentration imposed on the fluid, the initial and boundary conditions accompanying Equation (1) are

$$c^+(0, r, z) = 0, \quad z > 0 \tag{2a}$$

$$c^+(t, r, 0) = C_0, \quad t \geqq 0 \tag{2b}$$

$$\frac{\partial c^+}{\partial r}(t, R, z) = 0 \tag{2c}$$

$$\frac{\partial c^+}{\partial r}(t, 0, z) = 0 \tag{2d}$$

$$c^+(t, r, \infty) = 0 \tag{2e}$$

Conditions (2*a*) and 2*b*) are a formulation of the concentration step function at the duct inlet. Relation (2*c*) is the physical restriction of zero mass flux through the tube wall, and (2*d*) arises from the assumption of axial symmetry. Mathematically, (2*e*) implies a semi-infinite tube. Obviously, the tube in any experimental system must be finite. However, to impose the boundary condition of finite length on the mathematical model increases the complexity of an already complex model. Physically, (2*e*) may be interpreted as a requirement that the concentration profile not be disturbed by a physical boundary in the axial direction. Boundary condition (2*e*) is compatible with the physical boundary imposed by the valve.

It is generally agreed that Equation (1) subject to conditions (2) cannot be solved in terms of a closed-form analytical expression. Even if a complete solution were available, it would, in all probability, be so complex as to be of little practical use for experimental investigations. Because of this, the majority of investigations of solutions of Equations (1) and (2) have been directed toward simplified expressions that describe the concentration distribution in restricted regions of the independent variables.

Taylor concluded that, subject to certain restrictions, namely

$$\tau = \frac{Dt}{R^2} >> 0.007$$

$$N_{Pe} = \frac{2Ru}{D} >> 13.8$$

the solution of Equation (1) was given approximately by

$$c^+ = C_m + \frac{R^2u}{4D}\frac{\partial C_m}{\partial x_1}\left(-\frac{1}{3} + \frac{r^2}{R^2} - \frac{r^4}{2R^4}\right) \tag{3}$$

where the cross-sectional average concentration

$$C_m = \frac{2}{R^2}\int_0^R c^+ r\,dr$$

was to be determined from the differential equation

$$\frac{\partial C_m}{\partial t} = \tilde{k}\frac{\partial^2 C_m}{\partial x_1^2} \tag{4}$$

For a concentration change consistent with that shown in Equations (2*a*) and (2*b*), Taylor expressed the solution of Equation (4) as

$$C_m = \frac{C_0}{2}\,\mathrm{erfc}\left[\frac{x_1}{(4\tilde{k}t)^{1/2}}\right] \tag{5}$$

Aris (*4*) concluded that Equations (3) and (4) were essentially equivalent to Equation (1) for large values of τ and small values of N_{Pe} if the apparent dispersion coefficient $\tilde{k}$ were replaced by an effective dispersion coefficient *K*, namely

$$K = D + \tilde{k} = D\left(1 + \frac{N_{Pe}^2}{192}\right) \tag{6}$$

Inspection of Aris' work (*12*) has indicated that the time variable in Equation (4) was not equivalent to the time variable *t* defined in Equation (1) but rather that

$$t_T = t + f \tag{7}$$

where t_T is the proper time variable to use in Equation (4).

For an initially uniform solute distribution the correct function *f* can be shown to be

$$f \approx -\frac{R^2}{15D}$$

In addition to the analytical investigations just mentioned, several numerical studies have been carried out on the dispersion problem. One of the first investigations, that of Farrell and Leonard (*11*), which neglected axial diffusion and used the boundary conditions for an impulse input, concluded that the approximation shown in Equations (3) and (4) was acceptable for $\tau \geqq 0.8$ if $N_{Pe} > 100$.

Based on the above studies it appeared that for systems in which the Peclet number was greater than approximately 100, Equations (3) and (5), with t_T introduced for *t*, represented the solute gas concentration, subject to the initial step change in concentration for laminar flow in capillaries if the dimensionless time τ is reasonably large.

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

$$\tau \geqq 2$$
$$N_{Pe} \geqq 250$$

These values are two and one-half times the minimum values indicated by Ananthakarishnan and co-workers (2) for the acceptance of Equations (3) and (5) as a suitable approximation of Equations (1) and (2). Although these particular choices of τ and N_{Pe} were arbitrary, the extra margin in the minimum acceptable values of the dimensionless time and the Peclet number provided additional assurance that the approximate solution was an adequate representation of Equations (1) and (2).

The experimental apparatus used in this study measured the bulk average, or bucket mixing, concentration, and not C_m. For a cylindrical duct with axial symmetry, the bulk average concentration *C* is given by

$$C = \frac{4}{R^2}\int_0^R \left(1 - \frac{r^2}{R^2}\right) c^+ r\,dr \tag{8}$$

By substitution of Equation (5) into Equation (3) and replacement of *t* by t_T, one obtains

$$c^+ = \frac{C_0}{2}\left\{\mathrm{erfc}\left[\frac{z - ut_T}{(4\tilde{k}t_T)^{1/2}}\right] + \frac{3R^2}{\pi Dt_T}\left(\frac{1}{3} - \frac{r^2}{R^2} + \frac{r^4}{2R^4}\right)\exp\left[\frac{-(z - ut_T)^2}{4\tilde{k}t_T}\right]\right\} \tag{9}$$

Application of definition (8) together with Equation (9) gives the Taylor approximation to the bulk average concentration as

$$C = \frac{C_0}{2}\left\{\mathrm{erfc}\left[\frac{z - ut_T}{(4\tilde{k}t_T)^{1/2}}\right] + \left(\frac{R^2}{48\pi Dt_T}\right)^{1/2}\exp\left[\frac{-(z - ut_T)^2}{4\tilde{k}t_T}\right]\right\} \tag{10}$$

For the values of τ encountered in this study ($\tau > 2.2$), Equation (10) could be replaced by

$$C = \frac{C_0}{2}\,\text{erfc}\left[\frac{L - u_{1/2}t}{(4k_{1/2}t)^{1/2}}\right] \tag{11}$$

where

$$k_{1/2} = \frac{R^2 u_{1/2}^2}{48D}$$

L = length of capillary, fixed at 600 cm. in this study with little loss of accuracy if the velocity $u_{1/2}$ was evaluated from

$$u_{1/2} = \frac{L}{t_{1/2}} \tag{12}$$

where $t_{1/2}$ = time at which the experimental bulk average concentration became $C_0/2$.

The velocity calculated from Equation (12) is to be distinguished from the velocity u shown in Equation (1). As τ approaches infinity, $u_{1/2}$ would be identical to u. For finite values of τ, $u_{1/2}$ is always less than u; however, for $\tau > 2$, this difference was small, about 2 to 3%.

Since Equation (11) is simple, the calculation of diffusion coefficients from experimental concentration vs. time data was considerably simplified by using Equation (11) instead of Equation (10); the calculated D's agreed to within 2%. Also, for $N_{Pe} > 250$, the value of the diffusion coefficient calculated from the apparent dispersion coefficient $\tilde{k}$, may, with negligible error, be assumed to be equivalent to the value calculated from the effective dispersion coefficient K.

EXPERIMENTAL WORK

Figure 1 is a sketch of the experimental apparatus. The significant advantages of the experimental method were: (1) No calibration was required. (2) Knowledge of the hydrogen and helium solubility was not required. (This feature was particularly advantageous since the solubility in slightly soluble gas systems is not known accurately, and the error in the calculated diffusion coefficient due to uncertainty in solubility values could easily exceed the error in the actual diffusion measurements.) (3) No gas-liquid interfaces were present.

Two storage carboys were placed in a constant-temperature bath, one for solute-free degassed water and one for the water containing the hydrogen or helium. Rotameters, and for a portion of the experimental runs a specially designed and calibrated volume displacement meter, were installed between the carboy and the diffusion section to ensure constant volumetric flow.

The step change in dissolved gas concentration was attained by changing the fluid entering the section of capillary tubing from solute-free water to water containing the dissolved gas. Details of construction of the rotating valve can be found in reference *12* along with the other details of the experimental apparatus and procedure. The capillary in which the diffusion took place was a stainless steel tube 600 cm. (about 20 ft.) in length with an average inside diameter determined in the laboratory of 0.202 cm. (0.0795 in.). Considerable precautions were exercised in constructing the diffusion section of the apparatus to ensure that the capillary was straight and undisturbed by vibrations. Through the use of insulation and heaters the temperature of the capillary was maintained within ±0.5°C.

To detect the very small concentrations of dissolved gas, the analytical equipment consisted of an expansion valve, a system to trap selectively the water vapor, and a continuously recording mass spectrometer. The entire flow stream was drawn from the capillary exit into a vacuum chamber through an expansion valve. After the material was vaporized at the expansion valve, it passed through two cold traps in series, a single-stage diffusion pump, and a Consolidated Electrodynamics Corporation 21-620 mass spectrometer. The cold traps were needed because the sensitivity of the mass spectrometer was not nearly great enough to measure accurately the solute gas concentration after expansion when mixed with the carrier water vapor. It was necessary to remove a high percentage of the water in the traps without removing solute gas. Although Brackman and Fite (*7*) found that trace amounts of permanent gases in water vapor were trapped, or occluded, on a cold surface by condensing water vapor, particularly when the cold surface was at or below the normal boiling point of the permanent gas, tests made in this study showed that no such losses occurred.

To determine whether occlusion was occurring to an appreciable degree, water containing dissolved gas was allowed to flow into the cold trap system through the expansion value. After several grams of water had been 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 inert gas downstream from the cold traps was monitored continuously by the mass spectrometer. No evidence of gas having been trapped by the condensing water vapor was observed.

To reduce the time required for the vapors to flow from the expansion valve to the ionization chamber in the mass spectrometer, a single-stage glass diffusion pump with a pumping

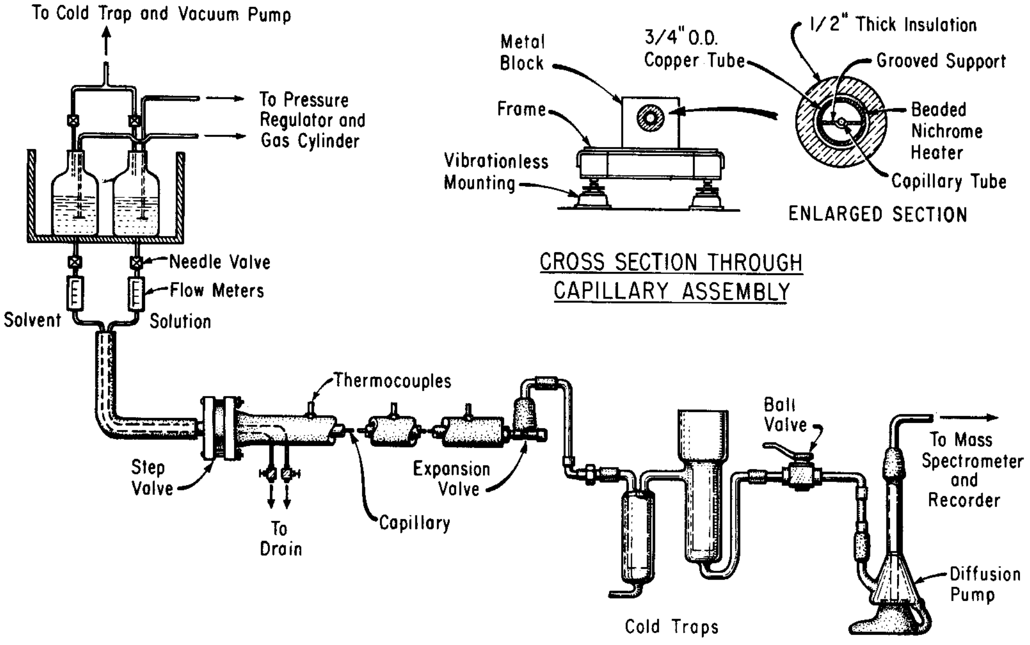

Fig. 1. Schematic flow diagram of experimental apparatus.

capacity of approximately 1 liter/sec. was installed between the downstream trap and the mass spectrometer inlet. Purified six-ring polyphenol ether was used as the diffusion pump oil; the mass spectrometer detected only trace amounts of decomposition products from this ether.

In the development of the mathematical model and the solution of the model, it was assumed that the bulk average concentration profile measured by the mass spectrometer would be equivalent to the profile at the end of the diffusion capillary; that is, it was assumed that mixing and holdup in the analytical section (expansion valve, cold traps, etc.) could be neglected. The relative effect of any mixing in the analytical section on the bulk average concentration profile would vary with the time required for the concentration at the expansion valve to increase from 0 to C_0. For an infinite time, the mixing due to the 10-sec. passage through the analytical section could be ignored, while for the opposite extreme a perfect step change in concentration at the expansion valve would be drastically altered on passage through the analytical section.

The time required for the bulk average concentration to increase from 10 to 90% of C_0 could be decreased by increasing the fluid velocity in the capillary $u_{1/2}$. Therefore, any effect of mixing in the analytical section would become evident as $u_{1/2}$ was increased, and Equation (11) would give an increasingly poor fit of the concentration profile as $u_{1/2}$ was increased. A series of runs was made for the hydrogen-water system at 25°C. in which the fluid velocity $u_{1/2}$ was varied from 0.17 to 0.59 cm./sec. The diffusivities calculated from Equation (11) varied in a random manner about their mean values with no evident dependence on the velocity $u_{1/2}$. Consequently, for the transition times used in the experimental apparatus, it was concluded that mixing and holdup in the analytical section could be neglected.

To initiate a run the process lines, containing solute-free water or solution, were flushed with 100 to 200 cc. of liquid from the carboys. An auxiliary vacuum pump was used to evacuate the cold-trap system. The expansion valve was adjusted to give the desired flow rate, as indicated by the flowmeter, and the expansion-valve heating element adjusted to the proper temperature. By adjusting the bypass needle valve, the flow of water containing solute gas was set at approximately the same flow rate as the degassed water. To attain steady state flow through the expansion valve, the system was allowed to operate 10 to 15 min.

After the flow had reached steady state conditions, the step valve was rotated to initiate flow of gas solution through the capillary, and the time was noted. A few minutes after the step valve was changed, the mass spectrometer recorder was placed in operation. A mass scan was made to determine the amount of extraneous gases present in the solute-free water. The mass spectrometer was then set to register the gas being tested, and, at suitable times, a scan was made of the extraneous gases present in the solution. These gases, notably nitrogen, oxygen, and water vapor, were always present to some degree.

RESULTS

Because the recorder response of the mass spectrometer was directly proportional to the amount of solute gas C, and because the solution of the mathematical model, Equation (11), expressed concentration relative to the step input C_0, the recorder response could be used as a measure of the solute gas concentration without reference to the actual solute gas concentration values. Therefore, the bulk average concentration C and the concentration step change C_0 could be stated in any arbitrary units as long as these units were consistent.

Statistical reduction of the experimental data was necessary to obtain the best calculated value of the diffusion coefficient. Equation (11) was fitted to the experimental concentration-time data by minimization of the sum of the squares of the relative percent deviation; that is, G was minimized where

$$G = \sum_{i=1}^{n} \left[\frac{(C_{\text{exp}})_i - (C_{\text{calc}})_i}{(C_{\text{calc}})_i} (100) \right]^2$$

The minimization was carried out on a digital computer with the Hooke and Jeeves direct search procedures as modified by Anthony and Himmelblau (3).

To find out if a significant bias existed in the diffusion coefficients determined as described above, a series of measurements was made for the carbon dioxide-water system at 25°C., a system which has been studied more extensively than any other dissolved gas system. Six of the more recent literature values for the diffusivity of carbon dioxide in water are listed in Table 1, together with the average experimental value obtained from ten runs in this study. The experimental standard deviation calculated for carbon dioxide in water was 0.10×10^{-5} sq.cm./sec. The values listed in Table 1 differ from 1.92 $\times 10^{-5}$ obtained in this study by less than one standard deviation.

Table 2 lists the mean values of the diffusion coefficients of hydrogen and helium in water as well as the coefficient of variation, that is, the standard deviation for D divided by the mean value of D. Figures 2 and 3 compare the diffusion coefficients listed in Table 2 with those of previous investigators. It is clear that there is considerable difference between the values reported here and most of the earlier work which is quite scattered.

Since gas solubility was not a factor in the calculations for D in this study, previously published values have not been adjusted to any specified set of solubility data but are those reported by the original experimentalist. The value of the diffusivity calculated from measurements with a polarographic or liquid jet apparatus is highly dependent on the value of the gas solubility used in the calculation. Any error in the solubility data is magnified in the calculated diffusion coefficient. The comments on solubility should not be taken as an implication that the discrepancies in the values of the diffusion coefficient

TABLE 1. DIFFUSION COEFFICIENT OF CARBON DIOXIDE IN WATER AT 25°C.

$D(10^5)$, sq. cm./sec.	Investigator	Method	Date
1.87	Scriven (*21*)	Diaphragm cell	1956
1.95	Woods (*31*)	Jet	1961
1.92	Tang and Himmelblau (*23*)	Jet	1964
2.00	Vivian and King (*28*)	Diaphragm cell	1964
1.85	Unver and Himmelblau (*27*)	Jet	1964
1.95	Thomas and Adams (*26*)	Jet	1965
1.92	This work		

TABLE 2. EXPERIMENTAL DIFFUSION COEFFICIENTS

System	Temperature, °C.	No. of experimental runs, n	Mean value of diffusion coefficient $D(10^5)$, sq. cm./sec.	Coefficient of variation, η
Hydrogen-water	10	5	3.19	0.067
	25	16	4.50	0.036
	40	5	5.91	0.015
	55	6	8.12	0.072
Helium-water	10	5	4.82	0.048
	25	5	6.28	0.026
	40	6	8.03	0.024
	55	5	10.46	0.050

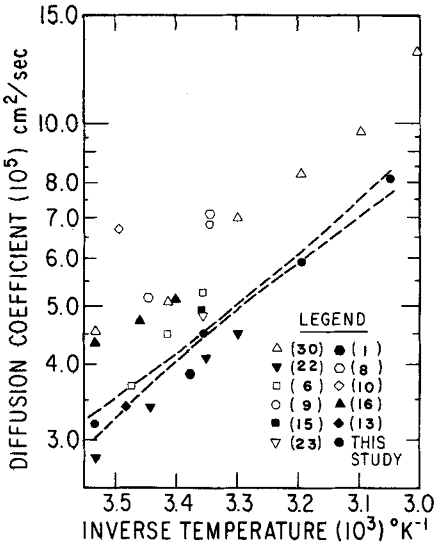

Fig. 2. Experimental diffusion coefficients; hydrogen in water.

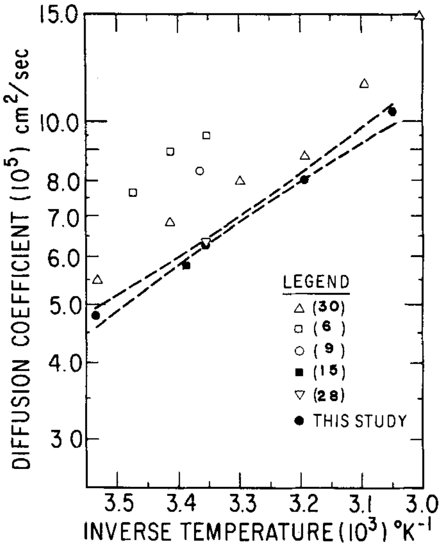

Fig. 3. Experimental diffusion coefficients; helium in water.

shown in Figures 2 and 3 are due to solubility alone; however, solubility is a factor that should not be disregarded.

One of the important objectives in gathering diffusivities is to determine the effect of temperature on the diffusion coefficient. Reference to Figures 2 and 3 shows that the discrepancy between the earlier values of the diffusion coefficient 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 2 and 3, other than those from this study, only Tammann and Jessen (*22*) and Wise (*30*) have measured the diffusion rate over a temperature range greater than 13°C. But the results of both Tammann and Jessen and of Wise are subject to question.

Tammann and Jessen determined diffusivities by measuring the volumetric rate of absorption of gas into a stagnant column of water. They added agar-agar, a form of gelatin, to the water to increase the viscosity and thereby to prevent convective mass transfer engendered by instability. The values of the diffusion coefficient determined by Tammann and Jessen for hydrogen in water, although lower, are in qualitative agreement with the values obtained in this study. However, more recent studies (*5, 27*) have indicated that the addition of gelatinous materials will cause a significant change in the diffusion rate. In addition, the viscosity of gelatin solutions is highly sensitive to temperature. Any change in the diffusion rate due to the presence of the agar in Tammann and Jessen's experimental measurements would not be expected to remain constant over a significant temperature range.

Wise determined the diffusion rate by observing the rate of dissolution of stationary bubbles of gas in a stagnant water system. Although the measurements were rapid, their precision was rather poor. The experimental coefficient of variation for the diffusion coefficients ranged from approximately 0.06 to 0.19 with an average of about 0.12. More important than lack of precision was the question of agreement between the mathematical model and the experimental system. An adequate mathematical description of the dynamics of bubbles has proven to be an exceedingly complex problem (*21, 30*). A complete review of the mathematics involved will not be given here; however, graphs of the square of the bubble diameter vs. *t* taken from Wise's experimental data did not produce straight lines as predicted by the mathematical relations, but instead consistently formed hyperbolic types of curves. Readjustment of the mathematical model would have yielded lower values of diffusivities.

In conclusion, it is believed the values reported in Table 2 represent realistic and reasonably accurate diffusivities for hydrogen and helium in water.

CORRELATION OF THE EFFECT OF TEMPERATURE ON DIFFUSION COEFFICIENTS

Present theoretical models of transport processes in the liquid state cannot, in general, be relied upon to predict quantitatively the value of the diffusion coefficient for sparingly soluble gases dissolved in water. Consequently one falls back on empirical and semiempirical correlations. Because of the unusual properties of water as compared with those of other liquids, the semiempirical relation developed here to predict the diffusion coefficient of dissolved hydrogen and helium in water should not be expected to predict correctly the corresponding diffusivities in all gas-liquid systems.

Some molecular models used to predict diffusivities were tested for the hydrogen and helium data listed in Table 2. Among them were

$$\text{Stokes-Einstein (Sutherland) equation} \quad \frac{D\mu}{T} = \frac{k}{6\pi r_1} \tag{13}$$

$$\text{Eyring} \quad \frac{D\mu}{T} = \frac{\lambda^2 k}{(\xi\lambda_1)(k''/k')} \frac{\partial \ln a}{\partial \ln c} \tag{14}$$

The development of and references for these equations can be found in reference *14*.

Equation (13) indicates that for a given solvent the value of the group $D\mu/T$ should be dependent on the size of the solute molecule but should be independent of temperature. In Equation (14), since the specific volume of a liquid does not change significantly with a change in temperature, the intermolecular spacing of the molecules may be taken as essentially independent of temperature. Therefore, the right-hand side of Equation (14) does not change with temperature in a given solvent. Consequently, Equations (13) and (14) both indicate the same dependence of the diffusion coefficient on temperature, that is, that $D\mu/T$ = constant. However, Equation (13) was developed on the postulate that the system was a binary

TABLE 3. COMPARISON OF $(D\mu/T)$ WITH EXPERIMENTAL DATA

Temperature, °C.	$D/\mu T$ (10^9) (g.)(cm.)/(sec.^{2})(°K.) Hydrogen-water	Helium-water
10	1.47	2.23
25	1.35	1.88
40	1.24	1.68
55	1.25	1.61
s^2_2/s^2_1	15.4	74.4
F(90%)	2.29	2.44

one and that the solute molecule was much larger than the surrounding solvent molecules. In contrast, Equation (14) was based on the postulate of self-diffusion; that is, the system be single component, which, in turn, implies that all molecules be identical in size.

From the experimental values of the diffusion coefficient together with tabulated values of water viscosity, the values of $D\mu/T$ were calculated for the hydrogen-water and helium-water systems and are listed in Table 3. For both helium-water and hydrogen-water the values of $D\mu/T$ tend to decrease with increasing temperature. From a statistical regression analysis for each gas, the hypothesis that $D\mu/T$ was constant was tested. The ratio of the variance due to regression, s_2^2, and the variance due to experimental error, s_1^2, is shown in Table 3. A comparison of the variance ratio with the Fisher F value indicated that the hypothesis had to be rejected.

The theory of absolute reaction rates can provide a molecular model to serve as a basis for correlation of diffusivities. The expression of Eyring for the molecular diffusion coefficient was written as

$$D = A_1 T \exp\left(-\frac{E_D}{RT}\right) \tag{15}$$

The natural logarithm was taken of Equation (15), and ln (D/T) was differentiated with respect to the absolute temperature to give

$$\frac{d}{dT}\left[\ln\left(\frac{D}{T}\right)\right] = \frac{E_D}{RT^2} \tag{16}$$

A similar treatment of the corresponding expression for viscosity yielded

$$\frac{d}{dT}[\ln(\mu)] = -\frac{E_\mu}{RT^2} \tag{17}$$

where E_μ = energy of activation for viscous flow. Equation (16) was divided into Equation (17) and integrated to give

$$\ln\left(\frac{D}{T}\right) = -\frac{E_D}{E_\mu}\ln(\mu) + \ln A_4 \tag{18}$$

where ln A_4 is the constant of integration. The parameter A_4 is independent of temperature but will be a function of the properties of the solvent and solute.

It was not unreasonable to assume that the change in E_D, and consequently E_D/E_μ, from one solute to another in a given solvent may be evaluated from the properties of the solute species rather than the properties of the mixture. A study of several systems indicated there was essentially an equality between the ratio E_D/E_μ and the quantity α, if α was computed from

$$\alpha = \frac{\sigma}{\left(\frac{V_m}{N}\right)^{1/3}} \tag{19}$$

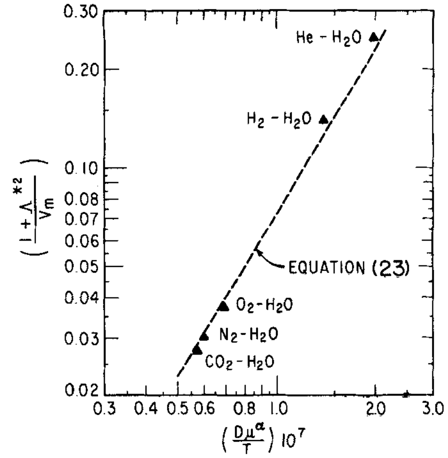

Fig. 4. $(D\mu^\alpha/T)$ vs. $(1 + \Lambda^{*2}/V_m)$.

Replacing E_D/E_μ by α and taking antilogarithms of (18) one gets

$$D = \frac{A_0 T}{\mu^\alpha} \tag{20}$$

A_0 would, in general, be a function of the properties of both the solvent and solute species, but since water was the only solvent studied, A_0 should only be dependent on the properties of the dissolved gases.

Nakanishi et al. *(19)* have proposed that quantum effects may be present in the diffusion of lighter gases, such as helium and hydrogen, dissolved in liquids with high internal pressures. To account for this quantum effect, Hildebrand and co-workers used the square of a dimensionless quantum parameter Λ^{*2} to correlate the diffusion coefficient of the lighter gases dissolved in organic liquids at 25°C. The dimensionless parameter Λ^{*2} is defined as

$$\Lambda^* = \frac{h}{\sigma(m\epsilon)^{1/2}} \tag{21}$$

It was postulated that for sparingly soluble gases dissolved in water the quantity A_0 in Equation (20) would be given by

$$A_0 = \bar{a}\left[\frac{1+\Lambda^{*2}}{V_m}\right]^b \tag{22}$$

The best values of the constants $\bar{a}$ and b were determined by linear regression analysis, after which Equation (20) could be written as

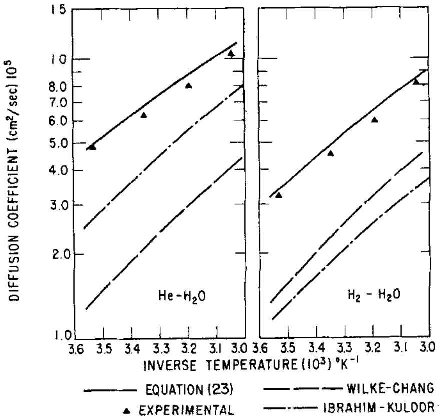

Fig. 5. Comparison of experimental and predicted diffusion coefficients.

$$D = \frac{4.8 \times 10^{-7}\, T}{\mu^{\alpha}} \left[\frac{1 + \Lambda^{*2}}{V_m} \right]^{0.6} \qquad (23)$$

The parameters of Equation (23) are based on the following units: T = °K.; μ = viscosity of solvent (centipoise); V_m = molar volume of solute (cc./g.-mole); Λ^* = quantum parameter of solute (dimensionless); D = mutual diffusion coefficient (sq.cm./sec.).

Figure 4 represents Equation (23) for hydrogen and helium and three additional gas-liquid systems for which reliable diffusivities are available. Equation (23) may be considered an extension of the correlation developed by Wilke and Chang (29). Figure 5 compares Equation (23) with the correlation of Wilke and Chang, and also with that of Ibrahim and Kuloor (*17*), and indicates the reasonably close agreement between experimental and predicted diffusivities.

NOTATION

a = activity
$\bar{a}, b$ = constants
A = constant
c = concentration
c^+ = mole fraction of solute gas in liquid phase
C = bulk average concentration
C_m = cross-sectional average concentration
C_0 = concentration of solute gas in step input
$(C_{\text{exp}})_i$ = experimental bulk average concentration at time $t = t_i$
$(C_{\text{calc}})_i$ = calculated bulk average concentration by Equation (11) at time $t = t_i$
D = molecular diffusion coefficient of solute gas in the liquid
E_D = energy of activation for diffusion
E_μ = energy of activation for viscous flow
f = $-R^2/15D$
F = Fisher variance ratio
G = sum of squares of deviations
h = Planck constant
$\tilde{k}$ = apparent diffusion coefficient = $(R^2u^2/48D)$
$k_{1/2}$ = $(R^2 u_{1/2}^2/48D)$
k = Boltzmann constant
k''/k' = ratio of diffusion velocity in solution to self diffusion
K = effective dispersion coefficient = $\tilde{k} + D$
L = duct length
m = mass of a molecule in Equation (21)
n = number of experimental concentration-time pairs for a given run
M_n = molecular weight of solute gas
N = Avogadro number
N_{Pe} = Peclet number = $2Ru/D$
r = radial coordinate
r_1 = molecular radius
R = radius of duct
R = gas constant
s^2 = variance
t = time
t_T = time variable defined by Equation (7) = $t + f$
$t_{1/2}$ = time at which the experimental bulk average concentration became $C_0/2$
T = absolute temperature
u = average velocity in axial direction
$u_{1/2}$ = $L/t_{1/2}$
V_m = M_n/ρ_n = molar volume of the solute gas at its normal boiling point
x_1 = $z - ut$
z = axial coordinate

Greek Letters

α defined by Equation (19) = $\dfrac{\sigma}{\left(\dfrac{V_m}{N}\right)^{1/3}}$
ϵ = force constant
η = coefficient of variation
λ = coordination number
λ_1 = distance between equilibrium jump positions of the diffusing molecule
Λ^* = quantum parameter as defined by Equation (21)
μ = viscosity of solution
ξ = average number of nearest neighbors
ρ_n = liquid density of solute gas at its normal boiling point
σ = force constant in Lennard-Jones 6-12 potential
τ = Dt/R^2

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