Dividing Equation (A6) by Equation (A7) and then using Equation (A9) to eliminate $(dy_{A_o}/dL)/(dT_o/dL)$ one gets

$$r_o x_o - (N_A)_{z=1} = \frac{q_w/\Delta H}{1 + \dfrac{1}{(\eta' - 1)}} \tag{A10}$$

Now in the absence of a heterogeneous reaction

$$-(N_A)_{z=1} = \bar{r}_F x_F \tag{A11}$$

where $\bar{r}_F$ is the average value of r in the film. Thus Equation (A10) can be written

$$\frac{\bar{r}_F x_F \Delta H}{q_w} + \left(\frac{r_o x_F \Delta H}{q_w}\right)\left(\frac{x_o}{x_F}\right) = \frac{1}{1 + \dfrac{1}{(\eta' - 1)}} \tag{A12}$$

There remains the problem of evaluating the first term in Equation (A12). This term is the ratio of the energy absorbed by the chemical reaction within the film to the wall heat flux, and it is given by

$$\frac{\bar{r}_F x_F \Delta H}{q_w} = 1 - \frac{(dT/dz)_{z=1}}{(dT/dz)_{z=0}} \tag{A13}$$

TABLE A1. STEADY STATE VALUES OF THE BULK REACTION RATE

$\eta = 11, \quad \eta' = 11$

$\sqrt{m}$	$\epsilon \equiv \dfrac{r_o x_F \Delta H}{q_w}$	
	$x_o/x_F = 100$	$x_o/x_F = 10$
0.15	0.008	0.075
0.3	0.006	0.055
0.9	0.0009	0.0087
1.66	0.000074	0.00074

when one assumes that the heterogeneous reaction rate is negligible. Evaluating the (dT/dz) terms in Equation (A13) by using Equation (A3) and then eliminating $(\bar{r}_F x_F \Delta H/q_w)$ by using Equation (A12) one gets

$$\frac{1}{\eta'} + \left(\frac{x_o}{x_F}\right)\epsilon = \frac{\dfrac{\phi}{\eta} + (1-\phi/\eta)\left(\dfrac{\sqrt{m\eta}}{\sinh\sqrt{m\eta}}\right) - \left(\dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}}\right)\left(1 - \dfrac{1}{\cosh\sqrt{m\eta}}\right)\left(\dfrac{\phi}{m\eta}\right)\epsilon}{\dfrac{\phi}{\eta} + (1-\phi/\eta)\left(\dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}}\right) + \left(\dfrac{\sqrt{m\eta}}{\tanh\sqrt{m\eta}}\right)\left(1 - \dfrac{1}{\cosh\sqrt{m\eta}}\right)\left(\dfrac{\phi}{m\eta}\right)\epsilon} \tag{A14}$$

For given values of (x_o/x_F), m, η, and η' Equation (A14) can be solved simultaneously with Figure A1 [or Equation (A5) with no heterogeneous reaction] to yield the value of ϵ.

For the simple case in which all binary-pair diffusion coefficients are equal

$$\eta' - 1 = (\eta - 1) N_{Le} \tag{A15}$$

With this simplification for $\eta = 11$ and $N_{Le} = 1$, $\eta' = 11$. The solution to Equation (A14) for this case is shown in Table A1.

When one compares Table A1 with Figure A1, it is clear that the assumption that $r_o = 0$ is an excellent one if

$$x_o/x_F > 10 \tag{A16}$$

If inequality (A16) did not hold, the basic notion of the film theory, that the film holdup is negligible, is open to serious question. Furthermore for most practical cases involving turbulent flow inequality (A16) should surely be satisfied.

The foregoing analysis leads to the conclusion that for cases of practical importance the steady state value of r_o required to account for the imbalance in heat transfer to the bulk and diffusion of reactants from the bulk is so small that it has a negligible effect upon the results as presented in Figure 1. It is also clear that if r_o is not equal to its steady state value at the leading edge of the wall (that is the inflow boundary condition), it will rapidly approach that steady state value as the gas flows down in the L direction. This basic conclusion is unaltered if the foregoing analysis is repeated for other values of η and for other values of the Lewis number.

On the other hand if the heterogeneous reaction is rapid enough to produce a large value of $(\phi - 1)$ while the homogeneous reaction is so slow that it would, in the absence of the heterogeneous reaction, produce a small value of $(\phi - 1)$, then clearly the assumption of chemical equilibrium in the bulk is not justified in general.

Binary Liquid Diffusion Coefficients

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The present work proposes a new approach for the calculation of the diffusion coefficients in binary liquid systems. The proposed equation is based on the results obtained by statistical mechanics of transport phenomena in dense media. It does not include viscosity explicitly, and the variables required for the calculation are fundamental in nature; these are the free volume of a molecule obtainable from physical measurements such as velocity of sound and the heat of vaporization of the solute. In spite of its theoretical background, the proposed correlation obtains results on fifty-six different solute-solvent systems with about 13% deviation from the experimental results. The effect of concentration on the diffusion coefficient is very easy to determine and is more in accord with experimental results than can be predicted by other available correlations.

The available correlations for the prediction of diffusion coefficients may be divided into two classes. In the first class theoretical correlations based on the works of Einstein (*11*), Eyring (*12, 14*) and Hill (*18, 19*) are included. Einstein's approach is based on the kinetic theory and Brownian motion. Eyring employs the hole theory for the liquid state and the activation energy consideration to obtain an

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expression for the diffusion coefficient. In Hill's approach hydrodynamics is employed in conjunction with a model for the liquid state suggested by Andrade (*1*). The diffusivities predicted by these theoretical correlations show high deviation from the experimentally determined diffusivities, which renders them of little use for engineering design purposes. The second class of correlations includes the empirical equations of Wilke and Chang (*39*) and Othmar and Thakar (*31*). Although these equations are empirical, they are correlations of significant properties that appear in the equations derived theoretically, especially those of Eyring. At the present time the best available correlation for the calculation of diffusion coefficients is that of Wilke and Chang (*39*). Their equation gives values for the diffusion coefficient with an average deviation of about 12% from the experimental values for some 132 systems.

In most of the available correlations the viscosity of the system is one of the important variables. This makes it necessary to have available viscosity data on the system for the calculation of the diffusion coefficient. Accordingly, any error that may occur in the determination of the viscosity will add to the uncertainty of the calculated diffusion coefficient. Besides, very little data are available on the viscosity of solutions, which makes it difficult to study the effect of concentration on the diffusion coefficient.

In accordance with Eyring's model of the liquid state, a liquid is treated as a disordered crystal lattice with holes floating in the liquid medium. In spite of its apparent theoretical arguments, this approach is basically empirical and suffers from some basic disagreements with experimental studies on the structure of the liquid state. A summary of such disagreements is presented by Hildebrand (*17*). Therefore it is assumed that the empirical equations mentioned above will suffer from the same complication.

The modern approach to the liquid state is based on statistical mechanics. By this method the distribution function describing the probability of one molecular arrangement is determined, and its variation with time is predicted. From a knowledge of the distribution function at one instant many of the properties of the system can be predicted, and a knowledge of the variation of the distribution function with time leads to an understanding of the transport phenomena. Diffusion according to this model is treated as a process controlled by random walk with very small steps. The application of statistical mechanics to the study of the gaseous state has proven to be successful as shown by the works of Chapman and Cowling (*7*) and Hirschfelder, Curtiss, and Bird (*20*). In order to apply this approach to the liquid state Kirkwood (*25*) formulated the theory of transport phenomena in dense media. This was followed by further treatment by Bearman and Kirkwood (*3*), Irving and Kirkwood (*22*), and Rice and co-workers (*35, 36, 37*). In these works the theory of the transport phenomena in liquids was developed to an extent which makes it possible to calculate many of the transport coefficients encountered by engineers.

EXTENSION OF STATISTICAL MECHANICAL RESULTS TO BINARY LIQUID DIFFUSION

Rice and co-workers (*35, 36, 37*) derived an equation for the self-diffusion coefficient in liquids. The diffusion coefficient was assumed of the form

$$D = \frac{kT}{\xi} \qquad (1)$$

In order to evaluate ξ they consider a pseudo two-component system consisting of two molecular species, 1 and 2, interacting with potentials of intermolecular force U_{11}, U_{12}, and U_{22}, which in a pure fluid will become $U(R)$, where R is a distance coordinate. It is also assumed that there are N_1 molecules of type 1 and N_2 molecules of type 2, and N_2 is allowed to approach zero. Species 2 may be considered as isotopically tagged molecules of 1.

Following statistical mechanical arguments one can obtain an expression for ξ

$$\xi^2 = \frac{Nm}{3V_o} \int \nabla^2_{R_{12}} U(R_{12}) g^{(2)} (R_{12}) d^3 R_{12} \qquad (2)$$

where R_{12} is the distance between molecules 1 and 2, and $g^{(2)}(R_{12})$ is a correlation factor obtained from the equation of state for the liquid:

$$\frac{pV_o}{NkT} = 1 - \frac{N}{\sigma V_o kT} \int R_{12}\, U\,(R_{12}) g^{(2)}(R_{12}) d^3(R_{12}) \qquad (3)$$

When one assumes the molecules to be rigid spheres, $g^{(2)}(R_{12})$ can be approximated by

$$g^{(2)}(R_{12}) = 1 + 2.5\left(\frac{v_o}{v}\right) + 4.5864\left(\frac{v_o}{v}\right)^2 \qquad (4)$$

It is also noted that ξ can be related to the intermolecular force contribution to shear viscosity by the equation

$$\eta_v = \frac{m}{30\xi}\left[12\left(\frac{NkT}{V_o} - P\right) + \frac{N(N-1)}{V_o^2} \int R^2_{12}\, \nabla^2 U(R_{12}) g^{(2)} (R_{12}) d^3 R_{12}\right] \qquad (5)$$

From (1), (2), and (5), and with the assumption that $U(R_{12})$ has the Lennard-Jones form, the self-diffusion coefficient is related to η_v by

$$D = \frac{5kTV_o\eta_v}{m}\left[\frac{1}{24L - 15pV_o - 15RT}\right] \qquad (6)$$

where L can be approximated by

$$L = \Delta H_{\text{vap}} - RT \qquad (7)$$

The expression for η_v has the form

$$\eta_v = \frac{5kT}{8\Omega}\left[\frac{4\pi\sigma^3}{15v} + \left(\frac{4\pi\sigma^3}{15v}\right)^2 g^{(2)}(\sigma)\right] \qquad (8)$$

where $g^{(2)}(\sigma)$ is $g^{(2)}(R_{12})$, for which an approximation is given in Equation (4), and

$$\Omega = \left(\frac{4\pi kT}{m}\right)^{1/2} \sigma^2 \qquad (9)$$

In accordance with Equation (6) D is more closely related to the intermolecular contribution to viscosity η_v rather than the total shear viscosity. By further manipulation Equation (6) can be reduced to

$$D = 1.2021 \times 10^{-8}\left(\frac{RT}{\pi M}\right)^{1/2} \frac{V_o^{1/3}}{(v_o/v)^{2/3}}\left[1.6\ \frac{v_o}{V} + 2.56\left(\frac{v_o}{v}\right)^2 g^{(2)}(\sigma)\right] \left[\frac{RT}{24L - 15pV_o - 15RT}\right] \qquad (10)$$

where $g^{(2)}(\sigma)$ is obtained from (4). It is recommended that the value (v_o/v) be calculated from the theoretical equation presented by Collins and Navidi (*8*) based on the velocity of sound measurements at low frequencies and on the free volume equation of state for liquids:

$$u_s = \frac{1 - \frac{2}{3}\left(\frac{v_o}{v}\right)^{1/3}}{1 - \left(\frac{v_o}{v}\right)^{1/3}} \left\{\frac{CpRT/M}{Cp\left[1 - \frac{2}{3}\left(\frac{v_o}{v}\right)^{1/3}\right] - R}\right\}^{1/2} \qquad (11)$$

Collins and Navidi show that this equation gives comparable results to those obtained by Kincaid and Eyring (*24*) and Kittel (*26*) for free volume but has the advantages that (v_o/v) is calculated directly and it does not require the assignment of any arbitrary geometry to the free volume.

An examination of Equation (6) indicates the possibility of dividing the expression for the diffusion coefficient into two parts, namely

$$\frac{5kTV_o\eta_v}{m} \quad \text{and}$$

$$\frac{1}{24L - 15pV_o - 15RT}$$

The first term can be taken to represent the driving force and net resistance inherent in the diffusion medium which lead to Brownian motion of that medium. In the second term the resistance due to the nature of the diffusing solute and the interactions with the solvent molecules is manifested. At very low concentrations of solute in solvent the diffusion process may be considered as the net motion due to the Brownian motion of the solvent and the resistance to that motion of the molecules of the solute. This qualitative picture offers no complications in the case of self-diffusion, since the solvent and the solute are the same, and the terms are very clearly defined.

In the case of mutual diffusion however the interactions between solute and solvent are of a more complicated nature. The net resistance to the Brownian motion is due to interactions of the molecules of the solute with each other and with the molecules of the solvent. At infinite dilution of solute in solvent it can be assumed that the net Brownian motion of the solvent is not affected by the presence of the molecules of the solute. Therefore the first term which is derived for self-diffusion is also valid for mutual diffusion. It is further assumed that the main resistance to diffusion is due to forces on the solute which are similar to those that hold the solute in a homogeneous liquid phase. The internal energy in the second term therefore is estimated to be equal to the heat of vaporization of the solute. Once this energy is overcome, the solute molecule is under the influence of the Brownian motion of the solvent.

TABLE 1. VALUES OF *A* FOR DIFFERENT SOLVENTS

Solvent	Temp., °C.	A	$B \times 10^3$
C_6H_6	15	11.189	5.925
	25	10.763	5.807
CCl_4	15	11.131	
	25	10.714	4.239
C_6H_5Cl	25	12.115	5.676
C_6H_5Br	25	12.677	5.094
$C_6H_5CH_3$	25	11.575	6.109
CH_3OH	15	10.583	6.745
C_2H_5OH	25	6.285	3.831
H_2O	15	6.252	4.050
	25	6.295	4.151

Accepting this qualitative model for the mutual diffusion process at infinite dilution, one is led to the conclusion that only the second term of the two mentioned above is changed by considering mutual rather than self-diffusion. The only change in this term affects L, where the internal energy of the solute has to be used. The mutual diffusion coefficient at infinite dilution, based on this treatment, takes the form

$$D = 1.2021 \left[\left(\frac{RT}{\pi M}\right)^{1/2} \frac{V_o^{1/3}}{(v_o/v)^{2/3}} \times 10^{-8} \left\{ 1.6 \frac{v_o}{v} + 2.56 \frac{v_o^2}{v} N g^{(2)}(\sigma) \right\} \right]_{\text{solvent}} \times \left[\frac{RT}{24L - 15pv - 15RT} \right]_{\text{solute}} \quad (12)$$

The approximation, $L = \Delta H_{\text{vap}} - RT$ can be employed in the calculations, since for a liquid pv is much smaller that RT at ordinary pressures.

It is to be noted that this extension of the theory to mutual diffusion coefficients is strictly qualitative, and that the choice of L is intuitional. It is felt however that the value proposed for L should give a good approximation of the true value.

In order to determine the variation of the diffusion coefficient with concentration it is recommended that the equation derived by Darken (*9*) be employed:

$$D = (N_1D_2^* + N_2D_1^*) \left[1 + N_2 \left(\frac{\partial \ln \gamma_2}{\partial N_2} \right) \right] \quad (13)$$

The values of D_1^* and D_2^* can be determined by calculating the diffusion coefficient of the tracer isotope of the corresponding component at infinite dilution into a solution of the same composition as the solution under consideration. It is suggested that the solution properties employed in Equation (12) be the weighted averages based on mole fractions. Otherwise, the calculations are the same. In deriving Equation (13) it is assumed that no change of volume occurs during the diffusion process, and that the properties of isotopes of the same component are essentially the same.

RESULTS AND DISCUSSION

It is to be noted, before the results predicted by the proposed method of approach are presented, that the available data on liquid diffusion coefficients are meager and not quite accurate. Most of the experimental data available are old, and very few attempts have been made to establish their accuracy. Even data obtained recently are contradictory with each other to a high degree. Reference is made here to the measurements made by Hammond and Stokes (*16*) and Smith and Storrow (*38*) on the system ethanol-water. Among other systems, where different results were reported in the literature, are oxygen-water (*10*) and *n*-butyl alcohol-water (*6, 34*). The self-diffusion coefficient of water also suffers from the same complication. This point is brought up here not to decrease the value of experimental values reported in the literature for diffusion coefficients. It is only intended to show the magnitude of experimental uncertainty that may exist for some systems. In general however one can accept most of the experimental data as correct to within 5 or 10% unless certain evidence indicates the contrary. Most of the data presented and employed in this paper are of such a nature and are reported by one or more of the standard references on physical properties.

For the calculation of diffusion coefficients the values of the physical properties were generally obtained from references *21, 27, 30,* and *33*. Another valuable source of data was the collection of properties of gases and liquids by Reid and Sherwood (*34*).

LIQUID-LIQUID DIFFUSION COEFFICIENTS AT INFINITE DILUTION

Equation (12) was employed for the calculation of the diffusion coefficient at infinite dilution in binary liquid-liquid systems. Equation (12) can be rewritten as

$$D = B\,f(\Delta H)$$

where

$$B = 1.2021 \times 10^{-8} \left(\frac{RT}{\pi M}\right)^{1/2} V_o^{1/3} A \quad (14)$$

$$A = [1.6\,(v_o/v) + 2.56\,(v_o/v)^2\, Ng^{(2)}(\sigma)]\,(v_o/v)^{-2/3} \qquad (15)$$

$$f(\Delta H) = \frac{RT}{24\Delta H_{\text{vap}} - 39RT} \qquad (16)$$

Calculations were made for fifty-six different solute-solvent systems and compared with the values obtained by applying the empirical equation of Wilke (*39*). In the calculation the value (v_o/v) for the solvents benzene, carbon tetrachloride, toluene, bromobenzene, and chlorobenzene is reported by Collins and Navidi (*8*). In the case of methanol, ethanol, and water no satisfactory data on the velocity of sound were available. In order to obtain the value of (v_o/v) for these systems the physical and thermodynamic properties of the solvent were used to determine B and $f(\Delta H)$, and the self-diffusion coefficient was employed for the determination of the quantity A. The values obtained for this quantity for methanol and ethanol at different temperatures are shown in Table 1. Self-diffusion data were taken from the measurements of Partington, Hudson, and Bengall for methanol (*32*), and Graupner and Winter (*15*) and Partington, Hudson, and Bangall for ethanol (*32*). In the case of water conflicting values are reported in the literature for the self-diffusion coefficient (*15, 23, 32*). Employing the lower of these values for the determination of the diffusion coefficient in binary systems, one finds that the results are high by a factor of about 2.0. Employing data on the velocity of sound in water reported by Wood (*40*) one gets values for binary diffusivities low by about 20%. Therefore the value employed for the quantity A was 1.2 times that obtained from velocity of sound data at 3×10^5 sec.$^{-1}$ frequency with a quartz oscillator in the tube. Table 1 shows the values of A calculated for the different solvents in the systems under consideration. The value B is also reported in Table 1. The heat of vaporization of the solute at the temperature under consideration was determined from a monograph reported by Reid and Sherwood (*34*) based on the assumption that

$$\frac{(\Delta H)_{T_2}}{(\Delta H)_{T_1}} = \left(\frac{1 - Tr_2}{1 - Tr_1}\right)^{0.38}$$

Data on the critical properties were obtained from Lynn and Kobe (*28*) and the other standard references mentioned above.

The values obtained for the diffusion coefficient at infinite dilution for fifty-six different solute-solvent systems with eight different solvents were compared with those determined experimentally. The average absolute deviation defined by

$$\%\ \text{Average deviation} = \frac{|\text{Calculated value} - \text{Experimental value}|}{\text{Experimental value}} \times 100 \qquad (17)$$

is about 13% when calculated by Equation (12) and about 10% when calculated by Wilke's equation.

It is possible to reduce the error in the results based on (12) by noting that systems with acetic acid as a solute show high negative deviation. This may be explained by the fact that in the calculation of $f(\Delta H)$ for acetic acid the molecular weight was assumed to be 100. The formula molecular weight of acetic acid is 60.07, but usually a molecular weight of 100 is assumed in the calculation of the molar heat of vaporization due to association on boiling. The amount of error may be reduced more than 1% by basing the calculation on a molecular weight of 80 rather than 100. Similar arguments can be made to improve the results on formic acid and other associating compounds.

In comparing the results obtained by the proposed equation and Wilke's equation, it should be noted that the latter is basically empirical. The present equation claims more theoretical justification and is dimensionally correct.

It was not possible to obtain any correlation between the heat of solution at infinite dilution and the deviation from the experimental values.

An analysis of the variation of diffusion coefficient with temperature was made. Although not complete, owing to the lack of sufficient data, it was apparent that for the system acetic

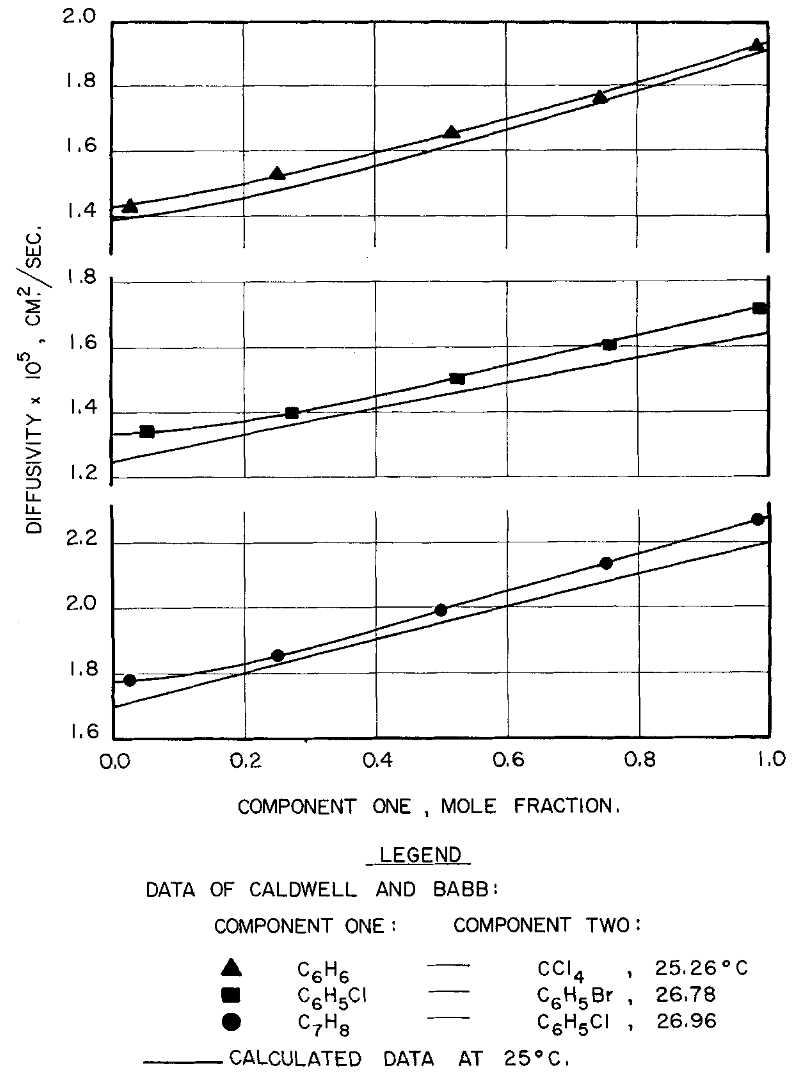

Fig. 1. Effect of concentration on diffusivity.

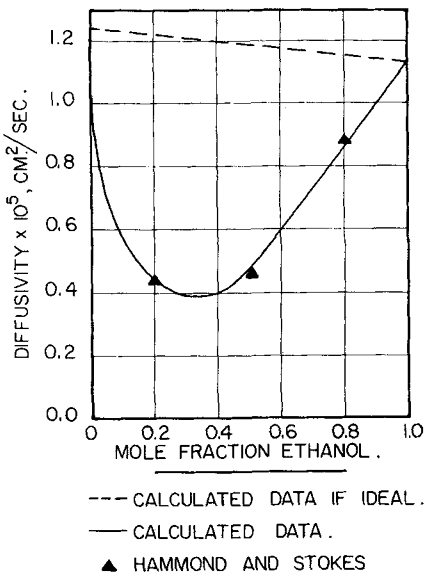

Fig. 2. Effect of concentration on diffusivity in ethanol-water system.

acid-carbon tetrachloride the temperature coefficient of the diffusivity obtained from the proposed equation was lower than the experimental temperature coefficient. Wilke's temperature coefficient on the other hand was higher than the experimental temperature coefficient. Among the controlling variables which are affected by temperature in accordance with Equation (12) are $T^{1/2}$, $V_o^{1/3}$, A, and ΔH. As temperature increases, all these variables except A tend to increase the diffusion coefficient. Generally, except for water, A decreases slowly with temperature. In the case of water A increases with temperature according to velocity of sound measurements between 15° and 35°C. This explains the high-temperature coefficient of the diffusivity of systems where the solvent is water.

In the absence of data such as the velocity of sound or self-diffusion for the solvent and heat of vaporization for the solute, any mutual diffusion data may be used to estimate these values. For example if the solvent properties are known, $f(\Delta H)$ can be calculated for any solute from a known value of diffusivity for that solute in the known solvent. In a like manner if $f(\Delta H)$ is known for any solute, then the unknown solvent properties A and B can be determined from a known value of diffusivity for that solvent-solute system. Once the values of A and B are known for a given solvent, they remain fixed for all solutes. Also once $f(\Delta H)$ is known for a solute, it remains unchanged for all solvents except for temperature adjustments.

EXTENSION TO SOLID-LIQUID AND GAS-LIQUID SYSTEMS

In the case of diffusion of gases and solids in liquid the problem arises as to what is the correct value to be substituted for L in Equation (12). The first obvious substitution that may occur is the heat of sublimation in the case of solids. This however is not correct, since the solid will assume a liquidlike structure when it diffuses in the liquid. The true L to be employed is probably the heat of vaporization of an imaginary liquid that exists at the temperature and pressure of the system. Such a property is hard to evaluate. In fact very few heat of sublimation data are available for solids.

An estimation of the diffusivity of benzoic acid in benzene, carbon tetrachloride, and toluene was made. The value of L used in the calculation was based on the heat of vaporization of benzoic acid determined from vapor-pressure data. The results obtained were compared with the experimental values determined by Wilke and Chang (*34, 39*). The calculated diffusion coefficient showed a negative deviation between 25 and 35%. When one uses an imaginary ΔH_{vap} of 11,220 cal./g.mole rather than the true 16,600 cal./g.mole value, the average deviation is changed to 4%.

Owing to the lack of data on heats of sublimation, and because of the lack of an exact method for the determination of the true value of L, an empirical approach was followed to calculate $f(\Delta H)$ as defined in Equation (16) for several solid solutes. These calculations were based on the experimentally determined diffusion coefficients of the solids in methanol at 15°C. The results obtained for diffusion of seventeen solutes in benzene show an average deviation of 13% compared with 11% if Wilke's equation is employed in the calculation. It is suggested that further study of the nature of $f(\Delta H)$ may relate the true nature of L to the heats of vaporization and fusion of the solid. The same procedure can be applied to gas-liquid systems.

The Variation of Diffusion Coefficients with Concentration

Ideal Solutions. For ideal solutions the term $\left(1 + N_2 \frac{\partial \ln \partial_2}{\partial N_2}\right)$ is equal to unity, and Equation (13) reduces to

$$D = N_1 D_2^* + N_2 D_1^* \qquad (18)$$

Three such systems were considered by Caldwell and Babb (*6*) who studied the variation with concentration of the diffusivity of the following systems: chlorobenzene-bromobenzene, benzene-carbon tetrachloride, and toluene-chlorobenzene. Their results are shown in Figure 1. It is noted that the diffusivity varies linearly, or almost linearly, with the mole fraction. This behavior was confirmed for two of the above three systems by Burchard (*4*).

Calculations were made for the above three systems with Equation (18). The values of D_1^* and D_2^* were obtained by calculating the diffusion coefficient of components 1 and 2 respectively in a solvent having the same properties as the solution under consideration. The values of $M^{1/2}$ and $V_o^{1/3}$ substituted in Equation (12) were those obtained from a weighted average based on mole fractions. The variable A defined in (14) was also a weighted average. In order to make the comparison easier between the experimental and calculated results, the values of A were adjusted at infinite dilution so that the calculated results were identical with those of Caldwell and Babb at 25°C. The calculations were made at 25°C. owing to the availability of physical properties at that temperature.

It is seen from Figure 1 that the calculated results agree closely with those of Caldwell and Babb. They also show a similar behavior regarding the variation of diffusion coefficient with concentration. The calculated results indicate that it is not necessary that D be linear with concentration for ideal systems. This is shown in Figure 1 for the benzene-carbon tetrachloride system.

Nonideal Solutions. In the case of nonideal solutions the term $\left(1 + N_2 \frac{\partial \ln \gamma_2}{\partial N_2}\right)$ is not equal to unity and has to be used in the calculation of

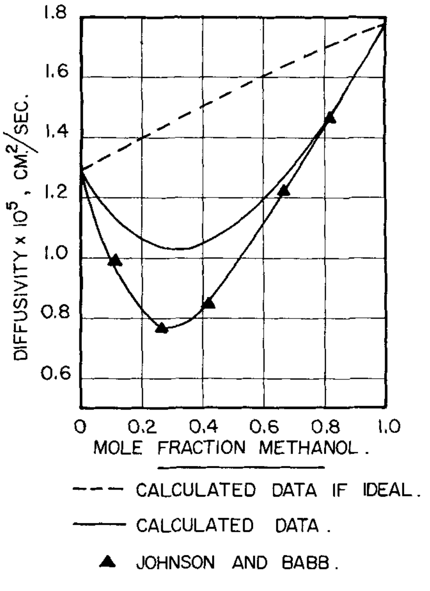

Fig. 3. Effect of concentration on diffusivity in methanol-water systems.

the diffusion coefficient. It is equal to unity however at infinite dilution.

Two highly nonideal solutions on which diffusion measurements were made are ethanol-water and methanol-water. Activity data are also available for these two systems. Figures 2 and 3 show a comparison between the calculated and experimental results for these two systems. The same procedure of calculation was employed as described for ideal solutions.

The experimental values for the diffusion coefficient of the ethanol-water system are those reported by Hammond and Stokes *(16)* at 25°C. In the calculation their reported values for $\left(1 + N_2 \frac{\partial \ln \gamma_2}{\partial N_2}\right)$ were also used. It is seen from Figure 2 that the values calculated for the diffusion coefficient by Equation (13) agree very well with the experimental results.

For the system methanol-water the experimental results are those reported by Johnson and Babb *(23)*. Data on activity coefficients were calculated based on constants recommended by Perry *(33)* obtained from the data reported by Butler, Thomson, and McLeanan *(5)*. The activity data were modified to obtain values at 15°C.

CONCLUSIONS

1. An equation is recommended for the calculation of binary liquid diffusion coefficients at infinite dilution based on the statistical mechanical theory of transport in dense media. Values calculated from the proposed equation for fifty-six different liquid-liquid systems give an average absolute deviation of about 13% from the experimental values.
2. The approach can be extended to apply to solid-liquid and gas-liquid systems. Results for the diffusion coefficients of nine solid solutes in benzene show an average absolute deviation of 13%.
3. The temperature coefficient of the diffusivity predicted by the proposed equation seems to be lower than the true temperature coefficient. On the other hand Wilke's temperature coefficient seems to be higher than the true coefficient.
4. The variation of the diffusion coefficient with concentration is determined for ideal and nonideal solutions with Darken's analysis in conjunction with the equation recommended at the limit of infinite dilutions. Ideal solutions show linear, or near linear, variation of the diffusion coefficient with concentration. In nonideal systems the effect of activity is included, and results obtained for the system ethanol-water are in good agreement with experimental results. Values predicted for the methanol-water system are higher than those determined experimentally.

ACKNOWLEDGMENT

Grateful acknowledgment is hereby made to the Stauffer Chemical Company which supported this research.

NOTATION

A = factor in diffusion equation defined by Equation (15)
B = factor in diffusion equation defined by Equation (14)
Cp = heat capacity at constant pressure
D = diffusion coefficient
D_i^* = diffusivity of an isotope tracer of i in the solution
$g^{(2)}(R_{12})$ = pair correlation function
k = Boltzmann's constant
L = internal energy of vaporization
m = mass of molecule
M = molecular weight
N = Avogadro's number
N_i = mole fraction of component i
p = pressure
T = absolute temperature
T_r = reduced temperature
u_s = velocity of sound
v = total volume per molecule
v_0 = occupied volume per molecule
V_0 = molar volume

Greek Letters

η_v = interaction energy contribution to shear viscosity
γ_i = activity coefficient of component i
σ = diameter of molecule
ξ = frictional resistance to diffusion
ΔH_{vap} = heat of vaporization

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Manuscript received August 29, 1961; revision received October 27, 1961; paper accepted October 30, 1961. Paper presented at A.I.Ch.E. Los Angeles meeting.