MOLECULAR DIFFUSION IN LIQUIDS

- For gases, $D_{AB} \neq f(c)$
- For liquid, $D_{AB} = f(c)$

1. Equimolar Counter Diffusion in Liquids

For this case,

$$N_A = -N_B$$

Therefore, the following equation,

$$N_A = -cD_{AB}\frac{d(x_A)}{dz} + \frac{c_A}{c}(N_A + N_B)$$

leads to,

$$N_A = -cD_{AB}\frac{d(x_A)}{dz} + 0$$

$$N_A = \frac{D_{AB}c_{av}(x_{A1} - x_{A2})}{(z_2 - z_1)} = \frac{D_{AB}(c_{A1} - c_{A2})}{(z_2 - z_1)}$$

where,

$$c_{av} = \left(\frac{\rho}{M}\right)_{av} = \left(\frac{\rho_1}{M_1} + \frac{\rho_2}{M_2}\right)/2$$

2. Diffusion of A through non-diffusing B in liquid phase

$$N_A = \frac{D_{AB}}{(z_2 - z_1)}\frac{P}{RT}\frac{p_{A1} - p_{A2}}{p_{BM}}$$

can be rewritten as,

$$N_A = \frac{D_{AB}}{(z_2 - z_1)} c_{av} \frac{x_{A1} - x_{A2}}{x_{BM}}$$

$$x_{BM} = \frac{x_{B2} - x_{B1}}{\ln \frac{x_{B2}}{x_{B1}}}$$

For dilute solutions (small concentration of A), $x_{BM} \cong 1$. Therefore,

$$N_A = \frac{D_{AB}}{(z_2 - z_1)} (c_{A1} - c_{A2})$$

EXAMPLE 6.3-1. Diffusion of Ethanol (A) Through Water (B)

An ethanol (A)–water (B) solution in the form of a stagnant film 2.0 mm thick at 293 K is in contact at one surface with an organic solvent in which ethanol is soluble and water is insoluble. Hence, $N_B = 0$. At point 1 the concentration of ethanol is 16.8 wt % and the solution density is $\rho_1 = 972.8$ kg/m^3. At point 2 the concentration of ethanol is 6.8 wt % and $\rho_2 = 988.1$ kg/m^3 (P1). The diffusivity of ethanol is 0.740×10^{-9} m^2/s (T2). Calculate the steady-state flux N_A.

Solution: The diffusivity is $D_{AB} = 0.740 \times 10^{-9}$ m^2/s. The molecular weights of A and B are $M_A = 46.05$ and $M_B = 18.02$. For a wt % of 6.8, the mole fraction of ethanol (A) is as follows when using 100 kg of solution.

$$x_{A2} = \frac{6.8/46.05}{6.8/46.05 + 93.2/18.02} = \frac{0.1477}{0.1477 + 5.17} = 0.0277$$

Then $x_{B2} = 1 - 0.0277 = 0.9723$. Calculating x_{A1} in a similar manner, $x_{A1} = 0.0732$ and $x_{B1} = 1 - 0.0732 = 0.9268$. To calculate the molecular weight M_2 at point 2.

$$M_2 = \frac{100 \text{ kg}}{(0.1477 + 5.17) \text{ kg mol}} = 18.75 \text{ kg/kg mol}$$

Similarly, $M_1 = 20.07$. From Eq. (6.3-2),

$$c_{av} = \frac{\rho_1/M_1 + \rho_2/M_2}{2} = \frac{972.8/20.07 + 988.1/18.75}{2} = 50.6 \text{ kg mol/m}^3$$

To calculate x_{BM} from Eq. (6.3-4), we can use the linear mean since x_{B1} and x_{B2} are close to each other.

$$x_{BM} = \frac{x_{B1} + x_{B2}}{2} = \frac{0.9268 + 0.9723}{2} = 0.949$$

Substituting into Eq. (6.3-3) and solving,

$$N_A = \frac{D_{AB} c_{av}}{(z_2 - z_1) x_{BM}} (x_{A1} - x_{A2}) = \frac{(0.740 \times 10^{-9})(50.6)(0.0732 - 0.0277)}{(2/1000)0.949}$$
$$= 8.99 \times 10^{-7} \text{ kg mol/s} \cdot \text{m}^2$$

Diffusion Coefficients for Liquids

1. Experimental determination of liquid diffusivities

- ✓ $D_{AB} = f(c)$
- ✓ $D_{AB} \neq D_{BA}$

Dilute solution and relatively concentrated solution are placed in chambers on opposite sides of a porous membrane of sintered glass.

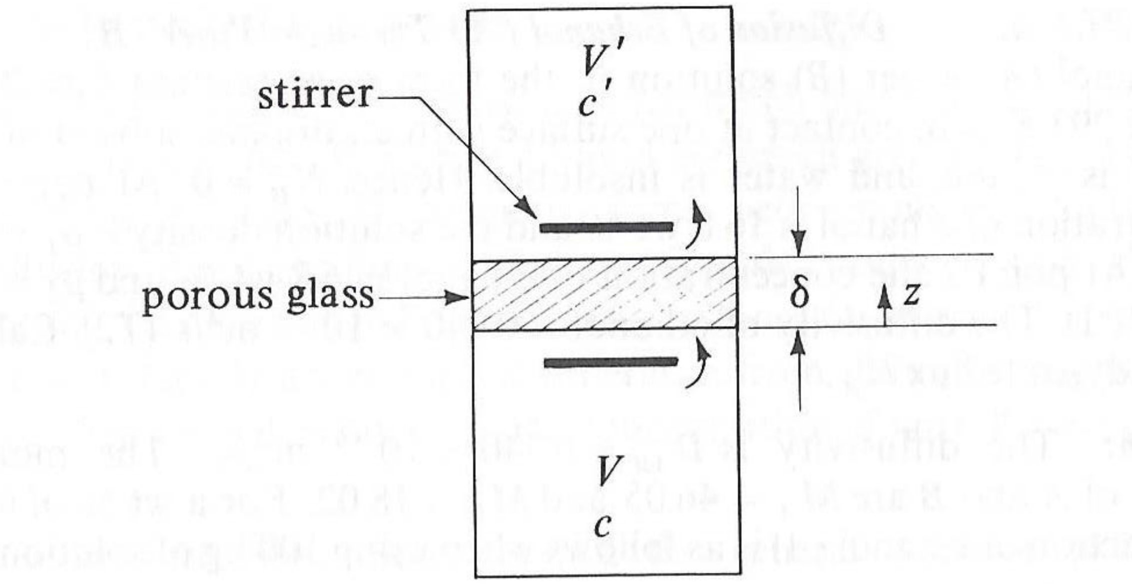

FIGURE 6.3-1. *Diffusion cell for determination of diffusivity in a liquid.*

Diffusion length = $K_1\delta, K_1 > 1$

Another solute with known diffusivity is used to determine the diffusion length. Then,

$$N_A = \frac{\varepsilon D_{AB}}{K_1 \delta}(c - c')$$

ε is the fraction of the open area for diffusion across the membrane. For *V*=*V'*,

$$\ln \frac{(c_0 - c_0')}{(c - c')} = \left(\frac{2\varepsilon A}{K_1 \delta V}\right) D_{AB} t$$

where, c_0 is the initial concentration. Another solute (e.g. KCl) with known diffusivity is used to determine the cell constant $\left(\frac{2\varepsilon A}{K_1 \delta V}\right)$

2. Experimental liquid diffusivity data

$$\text{Range } 0.5 \times 10^{-9} - 5 \times 10^{-9}\ \frac{m^2}{s}$$

TABLE 6.3-1. *Diffusion Coefficients for Dilute Liquid Solutions*

Solute	Solvent	Temperature °C	Temperature K	Diffusivity $[(m^2/s)10^9$ or $(cm^2/s)10^5]$	Ref.
NH_3	Water	12	285	1.64	(N2)
		15	288	1.77	
O_2	Water	18	291	1.98	(N2)
		25	298	2.41	(V1)
CO_2	Water	25	298	2.00	(V1)
H_2	Water	25	298	4.8	(V1)
Methyl alcohol	Water	15	288	1.26	(J1)
Ethyl alcohol	Water	10	283	0.84	(J1)
		25	298	1.24	(J1)
n-Propyl alcohol	Water	15	288	0.87	(J1)
Formic acid	Water	25	298	1.52	(B4)
Acetic acid	Water	9.7	282.7	0.769	(B4)
		25	298	1.26	(B4)
Propionic acid	Water	25	298	1.01	(B4)
HCl (9 g mol/liter)	Water	10	283	3.3	(N2)
(2.5 g mol/liter)		10	283	2.5	(N2)
Benzoic acid	Water	25	298	1.21	(C4)
Acetone	Water	25	298	1.28	(A2)
Acetic acid	Benzene	25	298	2.09	(C5)
Urea	Ethanol	12	285	0.54	(N2)
Water	Ethanol	25	298	1.13	(H4)
KCl	Water	25	298	1.870	(P2)
KCl	Ethylene glycol	25	298	0.119	(P2)

3. Prediction of Diffusivities in Liquids

For dilute solutes in liquids (Eq. 6.3-8 in C. J. Geankoplis):

$$D_{AB} = \frac{9.96 \times 10^{-16}}{V_A^{1/3}}(T)\left(\frac{1}{\mu}\right)$$

where, A is solute molecule present in low concentration in solvent B, D_{AB} is the diffusivity (m^2/s), T is the absolute temperature (K), μ is the viscosity (Pa·s or kg/(m·s)) and V_A is the solute molar volume at its normal boiling point ($m^3/kg\ mol$). This equation give good predictions for very large un-hydrated and spherical-like solute molecules of molecular weight more than 1000 or where $V_A \geq 0.5\ m^3/kg\ mol$ in aqueous solution.

For smaller solute molar volume, the Wilke-Chang correlation can be used (Eq. 6.3-9 in C. J. Geankoplis):

$$D_{AB} = 1.173 \times 10^{-16}(\varphi M_B)^{1/2}\left(\frac{T}{\mu_B V_A^{0.6}}\right)$$

where, A is solute molecule present in low concentration in solvent B, D_{AB} is the diffusivity (m^2/s), T is the absolute temperature (K), μ is the viscosity (Pa·s or kg/(m·s)) and V_A (see Table 6.3-2) is the solute molar volume at its normal boiling point ($m^3/kg\ mol$). φ is an association parameter of the solvent.

Solvent	φ
Water	2.6
Methanol	1.9
Ethanol	1.5
Benzene	1.0
Ether	1.0
Heptane	1.0
Unassociated	1.0

TABLE 6.3-2. *Atomic and Molar Volumes at the Normal Boiling Point*

Material	*Atomic Volume* $(m^3/kg\ mol)\ 10^3$	*Material*	*Atomic Volume* $(m^3/kg\ mol)\ 10^3$
C	14.8	Ring, 3-membered as in ethylene oxide	−6
H	3.7	4-membered	−8.5
O (except as below)	7.4	5-membered	−11.5
Doubly bound as carbonyl	7.4	6-membered	−15
Coupled to two other elements		Naphthalene ring	−30
In aldehydes, ketones	7.4	Anthracene ring	−47.5
In methyl esters	9.1		
In methyl ethers	9.9		
In ethyl esters	9.9		*Molecular Volume* $(m^3/kg\ mol)\ 10^3$
In ethyl ethers	9.9		
In higher esters	11.0		
In higher ethers	11.0	Air	29.9
In acids (—OH)	12.0	O_2	25.6
Joined to S, P, N	8.3	N_2	31.2
N		Br_2	53.2
Doubly bonded	15.6	Cl_2	48.4
In primary amines	10.5	CO	30.7
In secondary amines	12.0	CO_2	34.0
Br	27.0	H_2	14.3
Cl in RCHClR′	24.6	H_2O	18.8
Cl in RCl (terminal)	21.6	H_2S	32.9
F	8.7	NH_3	25.8
I	37.0	NO	23.6
S	25.6	N_2O	36.4
P	27.0	SO_2	44.8

Source: G. Le Bas, *The Molecular Volumes of Liquid Chemical Compounds.* New York: David McKay Co., Inc., 1915.

EXAMPLE 6.3-2. Prediction of Liquid Diffusivity

Predict the diffusion coefficient of acetone (CH_3COCH_3) in water at 25° and 50°C using the Wilke–Chang equation. The experimental value is 1.28×10^{-9} m^2/s at 25°C (298 K).

Solution: From Appendix A.2 the viscosity of water at 25.0°C is $\mu_B = 0.8937 \times 10^{-3}$ Pa·s and at 50°C, 0.5494×10^{-3}. From Table 6.3-2 for

CH_3COCH_3 with 3 carbons + 6 hydrogens + 1 oxygen,

$$V_A = 3(0.0148) + 6(0.0037) + 1(0.0074) = 0.0740 \text{ m}^3/\text{kg mol}$$

For water the association parameter $\varphi = 2.6$ and $M_B = 18.02$ kg mass/kg mol. For 25°C, $T = 298$ K. Substituting into Eq. (6.3-9),

$$D_{AB} = (1.173 \times 10^{-16})(\varphi M_B)^{1/2} \frac{T}{\mu_B V_A^{0.6}}$$

$$= \frac{(1.173 \times 10^{-16})(2.6 \times 18.02)^{1/2}(298)}{(0.8937 \times 10^{-3})(0.0740)^{0.6}}$$

$$= 1.277 \times 10^{-9} \text{ m}^2/\text{s}$$

For 50°C or $T = 323$ K,

$$D_{AB} = \frac{(1.173 \times 10^{-16})(2.6 \times 18.02)^{1/2}(323)}{(0.5494 \times 10^{-3})(0.0740)^{0.6}}$$

$$= 2.251 \times 10^{-9} \text{ m}^2/\text{s}$$

Liquid Diffusivity Using Wilke-Chang Eq.			
Acetone ((CH3)2CO)-Water		Ethanol (C2H5OH)-Water	
Pressure	1	Pressure	1
T	298	T	298
M_B	18.02	M_B	18.02
φ	2.6	φ	2.6
μ	8.94E-04	μ	8.94E-04
Carbon	0.0148	Carbon	0.0148
Hydrogen	0.0037	Hydrogen	0.0037
Oxygen	0.0074	Oxygen	0.0074
V_A	0.074	V_A	0.0592
D_{AB} (Model)	1.277E-09	D_{AB} (Model)	1.4598E-09
D_{AB} (Exptl.)	1.28E-09	D_{AB} (Exptl.)	1.24E-09
Error(%)	0.24	Error(%)	17.73