LECTURE 4
MASS TRANSFER FOR BIOLOGICAL SYSTEMS

INTRODUCTION TO MASS TRANSFER CONT'D

Diffusivity

Fick's law proportionality, D_{AB}, is known as mass diffusivity (simply as diffusivity) or as the diffusion coefficient. D_{AB} has the dimension of L^2 / t, identical to the fundamental dimensions of the other transport properties: Kinematic viscosity, $\nu\eta = (\mu / \rho)$ in momentum transfer, and thermal diffusivity, $\alpha\ (= k / \rho C_\rho)$ in heat transfer.

Diffusivity is normally reported in cm^2 / sec; the SI unit being m^2 / sec.

Diffusivity depends on pressure, temperature, and composition of the system.

In table, some values of D_{AB} are given for a few gas, liquid, and solid systems.

Diffusivities of gases at low density are almost composition independent, incease with the temperature and vary inversely with pressure. Liquid and solid diffusivities are strongly concentration dependent and increase with temperature.

General range of values of diffusivity:

Gases : 5×10^{-6} ------------- 1×10^{-5} m^2 / sec.
Liquids : 10^{-6} ------------- 10^{-9} m^2 / sec.

Solids : 5×10^{-14} ------------- 1×10^{-10} m^2 / sec.

In the absence of experimental data, semitheoretical expressions have been developed which give approximation, sometimes as valid as experimental values, due to the difficulties encountered in experimental measurements.

Diffusivity in Gases:

Pressure dependence of diffusivity is given by

$$D_{AB} \propto \frac{1}{p} \quad \text{(for moderate ranges of pressures, upto 25 atm).}$$

And temperature dependency is according to

$$D_{AB} \propto T^{3/2}$$

Diffusivity of a component in a mixture of components can be calculated using the diffusivities for the various binary pairs involved in the mixture. The relation given by Wilke is

$$D_{1-mixture} = \frac{1}{\dfrac{y'_2}{D_{1-2}} + \dfrac{y'_3}{D_{1-3}} + \ldots\ldots\ldots + \dfrac{y'_n}{D_{1-n}}}$$

Where $D_{1\text{-mixture}}$ is the diffusivity for component 1 in the gas mixture; $D_{1\text{-n}}$ is the diffusivity for the binary pair, component 1 diffusing through component n; and y'_n is the mole fraction of component n in the gas mixture evaluated on a component –1 – free basis, that is

$$y'_2 = \frac{y_2}{y_2 + y_3 + \ldots\ldots y_n}$$

9. Determine the diffusivity of Co_2 (1), O_2 (2) and N_2 (3) in a gas mixture having the composition:

Co_2 : 28.5 %, O_2 : 15%, N_2 : 56.5%,

The gas mixture is at 273 k and $1.2 * 10^5$ Pa. The binary diffusivity values are given as: (at 273 K)

$D_{12}\,P = 1.874\ m^2$ Pa/sec
$D_{13}\,P = 1.945\ m^2$ Pa/sec
$D_{23}\,P = 1.834\ m^2$ Pa/sec

Calculations:

Diffusivity of Co_2 in mixture

$$D_{1m} = \frac{1}{\dfrac{y_2'}{D_{12}} + \dfrac{y_3'}{D_{13}}}$$

where $y_2' = \dfrac{y_2}{y_2 + y_3} = \dfrac{0.15}{0.15 + 0.565} = 0.21$

$$y_3' = \frac{y_3}{y_2 + y_3} = \frac{0.565}{0.15 + 0.565} = 0.79$$

Therefore $D_{1m}\,P = \dfrac{1}{\dfrac{0.21}{1.874} + \dfrac{0.79}{1.945}}$

$= 1.93\ m^2$.Pa/sec

Since P = 1.2 * 10 ^{5} Pa,

$$D_{1m} = \frac{1.93}{1.2 * 10^5} = 1.61 * 10^{-5}\ m^2/\sec$$

Diffusivity of O $_2$ in the mixture,

$$D_{2m} = \frac{1}{\frac{y_1'}{D_{21}} + \frac{y_3'}{D_{23}}}$$

Where $y_1' = \frac{y_1}{y_1 + y_3} = \frac{0.285}{0.285 + 0.565} = 0.335$

(mole fraction on-2 free bans).

and

$$y_3' = \frac{y_3}{y_1 + y_3} = \frac{0.565}{0.285 + 0.565} = 0.665$$

and

$D_{21} P = D_{12} P = 1.874\ m^2.Pa/sec$

Therefore

$$D_{2m} P = \frac{1}{\frac{0.335}{1.874} + \frac{0.665}{1.834}}$$

$= 1.847\ m^2.Pa/sec$

$$D_2 m = \frac{1.847}{1.2 * 10^5} = 1.539 * 10^{-5}\ m^2/\sec$$

By Similar calculations Diffusivity of N $_2$ in the mixture can be calculated, and is found to be, $D_{3m} = 1.588 * 10^{-5}\ m^2/sec$.

Diffusivity in liquids:

Diffusivity in liquid are exemplified by the values given in table … Most of these values are nearer to 10^{-5} cm^2 / sec, and about ten thousand times shower than those in dilute gases. This characteristic of liquid diffusion often limits the overall rate of processes accruing in liquids (such as reaction between two components in liquids).

In chemistry, diffusivity limits the rate of acid-base reactions; in the chemical industry, diffusion is responsible for the rates of liquid-liquid extraction. Diffusion in liquids is important because it is slow.

Certain molecules diffuse as molecules, while others which are designated as electrolytes ionize in solutions and diffuse as ions. For example, sodium chloride (NaCl), diffuses in water as ions Na^+ and Cl^-. Though each ions has a different mobility, the electrical neutrality of the solution indicates the ions must diffuse at the same rate; accordingly it is possible to speak of a diffusion coefficient for molecular electrolytes such as NaCl. However, if several ions are present, the diffusion rates of the individual cations and anions must be considered, and molecular diffusion coefficients have no meaning.

Diffusivity varies inversely with viscosity when the ratio of solute to solvent ratio exceeds five. In extremely high viscosity materials, diffusion becomes independent of viscosity.

Diffusivity in solids:

Typical values for diffusivity in solids are shown in table. One outstanding characteristic of these values is their small size, usually thousands of time less than those in a liquid, which are inturn 10,000 times less than those in a gas.

Diffusion plays a major role in catalysis and is important to the chemical engineer. For metallurgists, diffusion of atoms within the solids is of more importance.

Steady State Diffusion

In this section, steady-state molecular mass transfer through simple systems in which the concentration and molar flux are functions of a single space coordinate will be considered.

In a binary system, containing A and B, this molar flux in the direction of z, as given by Eqn (5) is [section 3.3.1]

$$N_A = -CD_{AB}\frac{dy_A}{dz} + y_A(N_A + N_B) \text{ --- } (1)$$

:

12. Oxygen is diffusing in a mixture of oxygen-nitrogen at 1 std atm, 25°C. Concentration of oxygen at planes 2 mm apart are 10 and 20 volume % respectively. Nitrogen is non-diffusing.

(a) Derive the appropriate expression to calculate the flux oxygen. Define units of each term clearly.
(b) Calculate the flux of oxygen. Diffusivity of oxygen in nitrogen = $1.89 * 10^{-5}$ m^2/sec.

Solution:

Let us denote oxygen as A and nitrogen as B. Flux of A (i.e.) N_A is made up of two components, namely that resulting from the bulk motion of A (i.e.), Nx_A and that resulting from molecular diffusion J_A:

$$N_A = Nx_A + J_A \text{ ---------------------------------- } (1)$$

From Fick's law of diffusion,

$$J_A = -D_{AB}\frac{dC_A}{dz} \text{ --- } (2)$$

Substituting this equation (1)

$$N_A = Nx_A - D_{AB}\frac{dC_A}{dz} \text{ ---------------------------- } (3)$$

Since $N = N_A + N_B$ and $x_A = C_A / C$ equation (3) becomes

$$N_A = (N_A + N_B)\frac{C_A}{C} - D_{AB}\frac{dC_A}{dz}$$

Rearranging the terms and integrating between the planes between 1 and 2,

$$\int \frac{dz}{cD_{AB}} = -\int_{C_{A1}}^{C_{A2}} \frac{dC_A}{N_A C - C_A(N_A + N_B)} \text{ -------------- (4)}$$

Since B is non diffusing $N_B = 0$. Also, the total concentration C remains constant. Therefore, equation (4) becomes

$$\frac{z}{CD_{AB}} = -\int_{C_{A1}}^{C_{A2}} \frac{dC_A}{N_A C - N_A C_A}$$

$$= \frac{1}{N_A} \ln \frac{C - C_{A2}}{C - C_{A1}}$$

Therefore,

$$N_A = \frac{CD_{AB}}{z} \ln \frac{C - C_{A2}}{C - C_{A1}} \text{ ---------------------------- (5)}$$

Replacing concentration in terms of pressures using Ideal gas law, equation (5) becomes

$$N_A = \frac{D_{AB} P_t}{RTz} \ln \frac{P_t - P_{A2}}{P_t - P_{A1}} \text{ --------------------------- (6)}$$

where

D_{AB} = molecular diffusivity of A in B
P_T = total pressure of system
R = universal gas constant
T = temperature of system in absolute scale
z = distance between two planes across the direction of diffusion
P_{A1} = partial pressure of A at plane 1, and
P_{A2} = partial pressure of A at plane 2

Given:

$D_{AB} = 1.89 * 10^{-5}$ m^2/sec
$P_t = 1$ atm $= 1.01325 * 10^5$ N/m^2
T = 25°C = 273 + 25 = 298 K

z = 2 mm = 0.002 m
$P_{A1} = 0.2 * 1 = 0.2$ atm (From Ideal gas law and additive pressure rule)
$P_{A2} = 0.1 * 1 = 0.1$ atm

Substituting these in equation (6)

$$N_A = \frac{(1.89 * 10^{-5})(1.01325 * 10^5)}{(8314)(298)(0.002)} \ln\left(\frac{1-0.1}{1-0.2}\right)$$

$$= 4.55 * 10^{-5} \text{ kmol/m}^2\text{.sec}$$

Psuedo steady state diffusion through a stagnant film:

In many mass transfer operations, one of the boundaries may move with time. If the length of the diffusion path changes a small amount over a long period of time, a pseudo steady state diffusion model may be used. When this condition exists, the equation of steady state diffusion through stagnant gas' can be used to find the flux.

If the difference in the level of liquid A over the time interval considered is only a small fraction of the total diffusion path, and $t_0 - t$ is relatively long period of time, at any given instant in that period, the molar flux in the gas phase may be evaluated by

$$N_A = \frac{C D_{AB} (y_{A1} - y_{A2})}{z y_{B,lm}} \quad \text{------------------ (1)}$$

where z equals $z_2 - z_1$, the length of the diffusion path at time t.

The molar flux N_A is related to the amount of A leaving the liquid by

$$N_A = \frac{\rho_{A,L}}{M_A} \frac{dz}{dt} \quad \text{-------------------------- (2)}$$

where $\frac{\rho_{A,L}}{M_A}$ is the molar density of A in the liquid phase

under Psuedo steady state conditions, equations (1) & (2) can be equated to give

$$\frac{\rho_{A,L}}{M_A} \frac{dz}{dt} = \frac{C D_{AB} (y_{A1} - y_{A2})}{z y_{B,lm}} \quad \text{--------------- (3)}$$

Equation. (3) may be integrated from t = 0 to t and from $z = z_{t0}$ to $z = z_t$ as:

$$\int_{t=0}^{t} dt = \frac{\rho_{A,L}\, y_{B,lm} / M_A}{C\, D_{AB}\,(y_{A1} - y_{A2})} \int_{Z_{t0}}^{Z_t} z\, dz$$

yielding

$$t = \frac{\rho_{A,L}\, y_{B,lm} / M_A}{C\, D_{AB}\,(y_{A1} - y_{A2})} \left(\frac{z_t^2 - z_{t0}^2}{2} \right) \quad \text{-------- (4)}$$

This shall be rearranged to evaluate diffusivity D_{AB} as,

$$D_{AB} = \frac{\rho_{A,L}\, y_{B,lm}}{M_A\, C\,(y_{A1} - y_{A2})\, t} \left(\frac{z_t^2 - z_{t0}^2}{2} \right)$$

1. A vertical glass tube 3 mm in diameter is filled with liquid toluene to a depth of 20mm from the top openend. After 275 hrs at 39.4 °C and a total pressure of 760 mm Hg the level has dropped to 80 mm from the top. Calculate the value of diffusivity.

Data:

vapor pressure of toluene at 39.4°C = 7.64 kN / m^2,
density of liquid toluene = 850 kg/m^3
Molecular weight of toluene = 92
($C_6H_6CH_3$)

$$D_{AB} = \frac{\rho_{A,L}\, y_{Blm}}{M_A\, C\left(y_{A1} - y_{A2}\right) t} \left(\frac{Z_t^2 - Z_{t0}^2}{2} \right)$$

where $y_{B,lm} = \dfrac{y_{B2} - y_{B1}}{\ln\left(\dfrac{y_{B2}}{y_{B1}}\right)}$

$y_{B2} = 1 - y_{A2}$ $\qquad$ $y_{B1} = 1 - y_{A1}$

$y_{A1} = \dfrac{p_{A1}}{P} = \dfrac{7.64}{101.3}$ $\qquad$ (760 mm Hg = 101.3 kN/m^2)

$= 0.0754$ $\qquad$ $y_{B1} = 1 - 0.0754 = 0.9246$

$y_{A2} = 0$ $\qquad$ $y_B = 1 - y_{A2} = 1$

Therefore $y_{B,lm} = \dfrac{1 - 0.9246}{\ln\left(\dfrac{1}{0.9246}\right)} = 0.9618$

$$C = \frac{P}{RT} = \frac{1.01325 * 10^{5}}{8314 * (273 + 39.4)}$$

$$= 0.039 \text{ k mol /m}^3$$

Therefore

$$D_{AB} = \frac{850 * 0.9618}{92 * 0.039 * (0.0754 - 0) * 275 * 3600}\left(\frac{0.08^{2} - 0.02^{2}}{2}\right)$$

$$= 1.5262 * 10^{-3} (0.08^{2} - 0.02^{2})$$

$$= 9.1572 * 10^{-6} \text{ m}^2/\text{sec.}$$