

Assignment 1

Section 1

(Based on Lecture Notes)

Q 1. Define

- 1) Mass Average velocity (2) Molar average velocity
- 3) m, i and j (4) N, I and J

Ans =

- 1) Mass average velocity is the average velocity where each component's velocity is weighted against the mass fraction.

$$v_{\text{avg}} = \frac{\sum_{i=1}^n e_i v_i}{\sum_{i=1}^n e_i}$$

- 2) Molar average velocity is the average velocity where each component is weighted against its mole fraction (/ fraction of concentration from total concentration)

$$v_{\text{avg}} = \frac{\sum_{i=1}^n c_i v_i}{\sum_{i=1}^n c_i}$$

- 3) m, i and j

$n \rightarrow$ total mass flux (when reference velocity is 0) i.e.

$$n_i = e_i (v_i - 0)$$

$i \rightarrow$ mass flux when reference velocity is mass average velocity

$$i = e_i (v_i - \bar{v})$$

$j \rightarrow$ mass flux when reference velocity is molar average velocity (also called diffusional mass flux)

$$j = e_i (v_i - \bar{v})$$

4) N, T and J

N \rightarrow Total molar flux; reference velocity taken as 0

$$N_i = c_i (v_i - 0)$$

T \rightarrow Molar flux when reference velocity is mass average velocity

$$T_i = c_i (v_i - \bar{v})$$

J \rightarrow Molar flux when reference velocity is molar average velocity (also called diffusion molar flux)

$$J_i = c_i (v_i - V)$$

Q2. Write the statement of Fick's Law and express it in mathematical terms. Express Fick's Law in terms of other fluxes.

Ans: Fick's law states:

Molar flux of a species moving with molar avg velocity relative to an observer is proportional to the concentration gradient of the species

$$J_A \propto \frac{dC_A}{dn} \quad (\text{in 1 dimension})$$

$$J_A = - (D_{AB}) \frac{dC_A}{dn}$$

where C_A is concentration, and D_{AB} is diffusivity of A in mixture of A and B. J_A is diffusional flux.

Fick's Law in terms of other fluxes:

$$N_A = - D_{AB} \frac{dC_A}{dn} + \frac{c_A (N_A + N_B)}{(C_A + C_B)}$$

↳ total flux

Derivation: $J_A = C_A (C_{A,B} - U)$, $N_A = e A u F$

$$\therefore N_A = J_A + C_A \left(\frac{N_A + N_B}{C_A + C_B} \right) (= J_A + U C_A) = J_A + \frac{(C_A + C_B)}{C_A + C_B}$$

$$\therefore N_A = -D_{AB} \frac{d C_A}{d n} + C_A \left(\frac{N_A + N_B}{C_A + C_B} \right) = J_A - \frac{(C_A + C_B)}{C_A + C_B}$$

Q3. What is diffusivity? What are the factors which affect the diffusivity? What is the unit of diffusivity?

Ans: Diffusivity D_{ij} is the proportionality constant between diffusional flux and concentration gradient of i in mixture of i and j .

$$J_A = -D_A \frac{d C_A}{d n}$$

↗ Diffusion coefficient / Diffusivity

Factors affecting:

(i) In gaseous phase: Temperature, Pressure, Molecular weight of components, intermolecular attraction and associated factors such as chemical nature.

(ii) In liquid phase: Temperature, Viscosity, Concentration, Molecular weight of components, solvent-solute interaction parameters (chemical nature).

Unit of diffusivity $\rightarrow m^2/s$.

Q4. Prove $D_{AB} = D_{BA}$ (for ideal gas).

Ans: Let us assume that $C = C_A + C_B$ remains constant or all times.

By Fick's Law,

$$J_A = -D_{AB} \frac{dc_A}{dn}$$

$$J_B = -D_{BA} \frac{dc_B}{dn}$$

{(i)}

Also, $N_A = J_A + c_A (\underline{N_A + N_B})$
 $(c_A + c_B)$

$$N_B = J_B + c_B (\underline{N_A + N_B})$$

 $(c_A + c_B)$

$$\therefore N_A + N_B = (J_A + J_B) + (c_A + c_B) (\underline{N_A + N_B})$$

 $(c_A + c_B)$

$$= J_A + J_B + (N_A + N_B)$$

$$\therefore J_A + J_B = 0$$

Also, But $J_A + J_B = -D_{AB} \frac{dc_A}{dn} - D_{BA} \frac{dc_B}{dn}$ (from (i))

$$\therefore -D_{AB} \frac{dc_A}{dn} - D_{BA} \frac{dc_B}{dn} = 0$$

Now, $\frac{dc_A}{dn} = \frac{d(c - c_B)}{dn} = \frac{dc}{dn} - \frac{dc_B}{dn}$
 \Rightarrow const (assumption)
 $= 0 - \frac{dc_B}{dn}$
 $= -\frac{dc_B}{dn}$

$$\therefore -D_{AB} \left(-\frac{dc_B}{dn} \right) - D_{BA} \frac{dc_B}{dn} = 0$$

$$\Rightarrow (+D_{AB} - D_{BA}) \frac{dc_B}{dn} = 0$$

$$\therefore \boxed{D_{AB} = D_{BA}}$$

Hence, the statement is proved.

Ques. State Next Equation.

Ans =

$$D_{AB} = \frac{\mu}{\rho k T} \frac{\text{charge mobility}}{\text{temperature}}$$

↑ charge

Q6. Write the equations for the following correlations to estimate gas phase diffusivity:

- (i) Chapman - Enskog Correlation based on kT .
- (ii) Fuller correlation.

Ans = (i) Chapman - Enskog Correlation based on kT :

$$D_{AB} = 0.001858 T^{\frac{3}{2}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}} \quad (\text{cm}^2/\text{s})$$

$\rho \sigma_{AB}^2 \sigma_D$

$M_A, M_B \rightarrow$ molar mass

$T, \rho \rightarrow$ Temperature, Pressure

$\sigma_{AB}, \sigma_D \rightarrow$ Lennard Jones parameters

(ii) Fuller correlation

$$D_{AB} = 10^{-3} T^{1.75} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}} \quad (\text{cm}^2/\text{s})$$

$\rho \left[\left(\sum v \right)_A^{\frac{1}{3}} + \left(\sum v \right)_B^{\frac{1}{3}} \right]^2$

Q7. Write the equation for following correlation to estimate liquid phase diffusivity

(i) Stokes Einstein Equation

(ii) Wilke Chang Equation

Ans = (i) Stokes Einstein Equation

$$D_{AB} = \frac{kT}{6\pi\eta\mu_B}$$

(ii) Wilke Chang Equation

$$D_{AB} \mu_B = \frac{7.1 \times 10^{-8} (\mu_B M_B)^{\frac{1}{2}}}{V_A^{0.6}}$$

association factor

$V_A = 0.285 V_c^{2.048}$ solution

Q8. Provide the relationship to estimate gas mixture diffusing from binary diffusivity.

Ans:

If binary diffusivity of i component in mixture of i & j is N_{ij} , and y_i is the gas phase mol fraction of i ,

then

$$D_{im} = N_i - y_i \frac{\sum_{j=1}^n N_{ij}}{\sum_{j=1}^n \frac{1}{N_{ij}}} (y_j N_i - y_i N_j)$$

Q9. Describe (1) Knudsen (pore) diffusing

(2) Knudsen number

(3) Values of Knudsen number for Knudsen diffusing to occur.

Ans: (1) Knudsen diffusion is the phenomenon of diffusion transport solely by its collision with walls of porous medium. The Knudsen diffusing is the diffusivity / diffusional coefficient used to describe this in terms of being proportional to concentration gradient, analogous to Fick's law.

$$J_A = D_{KA} \frac{dc_A}{dz} \rightarrow \text{cylindrical channel}$$

(2) Knudsen number

$$k_n = \frac{L}{\lambda} \rightarrow \text{mean free path} \\ \rightarrow \text{characteristic length}$$

(3) For Knudsen diffusion, $k_n > 1$.

Q10. What is surface diffusivity?

Ans: Surface diffusion is the diffusional transfer of components on the surface due to concentration gradients. The surface diffusivity (D_s) is analogous proportionality constant used to relate surface diffusional flux to concentration gradient.

$$J_s = -D_s \frac{dc_s}{dz}$$

Section 2

1. From foot : Principles of mass transfer by B.K. Datta
Ex. 2.1 page No. 10.

Q. (Calculation of average velocity) A gas mixture ($N_2 = 5\%$, $H_2 = 15\%$, $NH_3 = 76\%$ and $Ar = 4\%$) flows through a pipe, 25.4 mm in diameter, at 1.05 bar total pressure. If the velocities of the respective components are 0.03 m/s, 0.035 m/s, 0.03 m/s and 0.02 m/s, calculate the mass average, molar average and volume average velocities of the mixture.

Ans = Let N_2 be 1, H_2 be 2, NH_3 be 3 and Ar be 4.

The volume average velocity (= molar average velocity) is given by

$$V = \frac{1}{c} \sum_{i=1}^4 c_i v_i = \gamma_1 v_1 + \gamma_2 v_2 + \gamma_3 v_3 + \gamma_4 v_4$$

$$= 0.05(0.03) + 0.15(0.035) + 0.76(0.03) + 0.04(0.02)$$

$$= 0.0303 \text{ m/s}$$

Mass average velocity

$$v = \frac{1}{c} \sum_{i=1}^4 e_i v_i$$

$$\text{Now, } P_i M_i = e_i P T \Rightarrow e_i = \frac{P_i M_i}{P T} \quad (e = \frac{P M}{P_T} \text{ avg. molar mass})$$

$$\therefore \frac{e_i}{e} = \frac{P_i}{P} \frac{M_i}{M} = \gamma_i \frac{M_i}{M}$$

$$\therefore \bar{M} = \sum_{i=1}^4 M_i \gamma_i = 0.05(28) + 0.15(2) + 0.76(17) + 0.04(40) = 16.22$$

$$\therefore v = \frac{1}{c} \sum_{i=1}^4 \frac{e_i}{e} v_i = \frac{1}{c} \sum_{i=1}^4 \gamma_i \frac{M_i}{M} v_i = \frac{1}{16.22} (0.05(28)(0.03) + 0.15(2)(0.035) + 0.76(17)(0.03) + 0.04(40)(0.02)) = 0.029 \text{ m/s}$$

Ans = 0.0303 m/s, 0.029 m/s.

Section 3

(Unsolved Problems)

- Q1. Liquified natural gas, LNG, is to be shipped from the Alaskan Kenai Peninsula by an ocean carrier to the processing plant in Yaquina Bay, Oregon. The molar composition of the commercial LNG is

Methane, CH_4 93.5 mole %

Ethane, C_2H_6 4.6 mole %

Propane, C_3H_8 1.2 mole %

Carbon dioxide, CO_2 0.7 mole %

Determine

- the weight fraction of ethane
- the average molecular weight of the LNG mixture
- the density of the gas mixture when heated to 20°F and $1.4 \times 10^5 \text{ Pa}$.
- the partial pressure of methane when the total pressure is $1.4 \times 10^5 \text{ Pa}$.
- the mass fraction of carbon dioxide in parts per million by weight.

Ans = (a) w_i . Weight fraction,

$$w_i = \frac{n_i M_i}{\sum n_i M_i} = \frac{\gamma_i M_i}{M}$$

$$\begin{aligned} M &= 16 \times 0.935 + 30 \times 0.046 + 44 \times 0.012 \\ &\quad + 44 \times 0.007 \\ &= 17.17 \end{aligned}$$

$$\therefore w_i = \frac{0.046 \times 30}{17.17} = 0.0803 \approx 0.08$$

$$\begin{aligned}
 (b) \quad \bar{M} &= \frac{\sum y_i m_i}{\sum \bar{m}_i} = \sum y_i m_i / \\
 &= 16 \times 0.935 + 30 \times 0.046 + 44 \times 0.012 + 44 \times 0.007 \\
 &= 17.176 \text{ g/mol}
 \end{aligned}$$

(c) $T \ll 10^0 \text{ bar}$

Thus, we apply ideal gas behavior

$$\begin{aligned}
 \rho \bar{M} &= \bar{e} RT \\
 \therefore \bar{e} &= \frac{\rho \bar{M}}{RT} = \frac{1.1 \times 10^5 \times 17.176 \times 10^{-3}}{8.314 \times 207} \\
 &= 1.397 \text{ kg/m}^3
 \end{aligned}$$

$$(d) \quad P_{\text{methane}} = Y_{\text{methane}} P_{\text{total}} = 0.935 \times 1.1 \times 10^5 = 1.039 \times 10^5 \text{ Pa}$$

$$\begin{aligned}
 (e) \quad \text{CO}_2 \rightarrow \text{ppm by weight} &= w_{\text{CO}_2} \times 10^6 \\
 &= y_{\text{CO}_2} \frac{M_{\text{CO}_2}}{\bar{M}} \times 10^6 \\
 &= \frac{0.007 \times 44}{17.176} \times 10^6 \\
 &= 1.793 \times 10^4
 \end{aligned}$$

Q2. Evaluate the diffusion coefficient of carbon disulphide in air at 20°C and atmospheric pressure by Chapman and Enskog relation.

Ans: Chapman - Enskog relation

$$D_{AB} = 0.001858 T^{\frac{3}{2}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}$$

$$\begin{aligned}
 M_A &= M_{\text{CS}_2} = 76, \quad M_B = M_{\text{air}} = 28.84 \\
 &= 1 \text{ (arm)}
 \end{aligned}$$

$$\sigma_{AB} \rightarrow \sigma_{\text{CS}_2} = 1.183 \text{ Å}, \quad \sigma_{\text{air}} = 3.712 \text{ Å}$$

$$\therefore \sigma_{AB} = \frac{\sigma_{\text{CS}_2} + \sigma_{\text{air}}}{2} = 1.097$$

$\text{L}_D \rightarrow \text{At } 20^\circ\text{C},$

$$\frac{\epsilon/k}{\epsilon_{\text{air}}} |_{\text{CS}_2} = 467.0 \text{ K}$$

$$\frac{\epsilon/k}{\epsilon_{\text{air}}} |_{\text{air}} = 78.6 \text{ K}$$

$$(\frac{\epsilon/k}{\epsilon})_{\text{avg}} = \sqrt{(\frac{\epsilon/k}{\epsilon})_{\text{CS}_2} (\frac{\epsilon/k}{\epsilon})_{\text{air}}} = 191.59 \text{ K}$$

$$\frac{kT}{\epsilon} = 1 \times (20 + 273) \text{ K} = 1.529$$

$$\Omega_D |_{1.529} \approx \frac{(1.529 - 1.50) \times 1.167 + (1.529 + 1.60) 1.189}{1.60 - 1.50}$$

(by interpolation
between 1.5 and
1.6)

$$= 1.189$$

$$\therefore D_{AB} = 0.001858 (293)^{\frac{3}{2}} \left(\frac{1}{76} + \frac{1}{28.89} \right)^{\frac{1}{2}}$$
$$1 \times 1.097^2 \times 1.189$$

$$= 0.102 \text{ m/s}$$

$$= 0.102 \text{ cm}^2/\text{s}$$

$$= 1.02 \times 10^{-5} \text{ m}^2/\text{s}$$

$$\text{Ans} = 1.02 \times 10^{-5} \text{ m}^2/\text{s}.$$

- Q3. Re-evaluate the diffusion coefficient of carbon disulfide in the air at 20°C and atmospheric pressure using the Fuller, Schettler and Giddings equation and compare the new value with the one reported in Q82 question 2. Explain intuitively the reason behind difference in results from these relations.

$$\text{Ans: } D_{AB} = 10^{-3} T^{2.75} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}$$
$$1 \left[\left(\sum v_A \right)^{\frac{1}{3}} + \left(\sum v_B \right)^{\frac{1}{3}} \right]^2$$

$$\sum v_A = v_C + 2v_{S_2} = 26.5 + 2 \times 17 = 40.5$$

$$\sum v_B = \eta_{\text{air}} v_{\text{air}} = 22.4$$

$$M_A = 76, M_B = 28.89$$

$$D_{AB} = 10^{-3} (28 + 273)^{1.75} \left(\frac{1}{76} + \frac{1}{28.84} \right)^{0.5} \\ 2 \times (40.5^{\frac{1}{3}} + 22 \cdot 2^{\frac{1}{3}})^2$$

$$= 0.056 \text{ cm}^2/\text{s}$$

The difference in results from these relations is primarily because of the change in temperature, as well as assumption that D_{AB} is equivalent to $\sqrt{v_A v_B} \left(\frac{v_A}{2} + \frac{v_B}{2} \right)^2$ (i.e. spherical molecule).

Q.1. In the manufacture of conductive contacts of photovoltaic materials, a thin film of solid tungsten is used as a conductive layer due to good conductivity for electronics electrical materials. The tungsten is uniformly deposited (WF_6) in presence of hydrogen gas. If the gas composition is maintained at 10 mol% WF_6 and 10 mol% H_2 and 50 mol% N_2 , determine:

- Calculate the diffusivity of WF_6 in hydrogen (cm^2/s) through Hinchfelder Spate relation of tungsten hexafluoride through the gas mixture at 400°C , and a system pressure of 20 bar and the effective diffusivity through the gas mixture if WF_6 has a diffusivity of $0.0157 \text{ cm}^2/\text{s}$ in nitrogen.
- Calculate the same at 190°C and 17 bar.
- What is the significance of the Leonard - Jones parameters and are empirical correlations always valid for calculations of diffusivity, if not why not and what assumptions are made?

(Assume required Constants and use atmospheric conditions if not specified)

	σ	ϵ/k (400°C)	ϵ/k 400°C
WF_6	4.028	200 K	180 K
Carrier gas (H_2)	3.28	206.1 K	195 K

Ans: Hirschfelder spot relation

$$D_{AB} = 1.558 \times 10^{-3} T^{\frac{3}{2}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}$$

$\times \frac{R}{\rho \Omega_D} \bar{\Omega}_D$

$M_A = 29.5$, $M_B = 2$, $\epsilon_{AB} = \frac{\epsilon_A + \epsilon_B}{2} = 3.5 \pm 5$,
This value is taken from graph
of ϵ/k vs T .

$$\therefore D_{AB} = \frac{1.558 \times 10^{-3}}{2 \times 3.55^2} \left(\frac{1}{29.5} + \frac{1}{2} \right)^{\frac{1}{2}} \left(\frac{T^{\frac{3}{2}}}{\Omega_D} \right)^{\frac{1}{2}}$$
$$= 1.04 \times 10^{-4} \times \left(\frac{T^{\frac{3}{2}}}{\Omega_D} \right)$$

(a) $T = 100 + 273 = 373 \text{ K}$, $\rho = 20 \text{ atm} = 29.50 \text{ atm}$

$$\epsilon/k|_{WF_6} = 200 \text{ K}$$

$$\therefore \epsilon/k|_{H_2} = 205.1 \text{ K}$$

$$\therefore (\epsilon/k)_{\text{eq}} = \sqrt{200 \text{ K} \times 205.1 \text{ K}} = 203.03 \text{ K}$$

$$\therefore \frac{kT}{\epsilon} = \frac{4 \times 373}{203.03} = 3.315$$

$$\therefore \frac{R}{\rho \Omega_D} = f(3.315) \approx \begin{aligned} & \frac{f(3.315) - f(3.5)}{(3.5 - 3.315)} \\ & + \frac{f(3.5) - f(3.315)}{(3.5 - 3.315)} \frac{1}{0.5} \\ & = 0.925 \end{aligned}$$

$$\therefore D_{AB} = 1.04 \times 10^{-4} \times \frac{373^{\frac{3}{2}}}{29.50 \times 0.925}$$
$$= 0.099 \text{ cm}^2/\text{s}$$

(b) $T = 490^\circ\text{C} = 490 + 273 = 763 \text{ K}$, $\rho = 17 \text{ atm} = 16.33 \text{ atm}$

$$\epsilon/k|_{WF_6} = 180 \text{ K}, \quad \epsilon/k|_{H_2} = 195 \text{ K}$$

$$\therefore (\epsilon/k)_{\text{eq}} = \sqrt{180 \times 195} = 187.35 \text{ K}$$

$$\therefore \frac{kT}{\epsilon} = \frac{763}{187.35} = 3.806$$

$$\therefore \Omega_D = f(3.806) = \frac{f(3.806) - f(3.5)}{(3.806 - 3.5)} (0.8935) + (3.8 - 3.806) (0.9122)$$

≈ 0.895

Interpolation
between 3.5 and 4.0

$$\therefore D_{AB} = 2 \cdot 04 \times 10^{-4} \times \frac{723^2}{26.83 \times 0.895} \\ = 0.131 \text{ cm}^2/\text{s} \quad \text{intermolecular}$$

(c) The Lennard Jones parameter characterises the interaction between medium components, which has an effect on the overall diffusivity of the system.

Empirical relations are not always correct. This is because many gross assumptions such as are taken such as : f) i, spherical molecule, (ii) no effect of temperature on σ_A

Q5. Calculate the diffusivity of ethyl benzene (EB) into water at 293 K. The viscosity of water at this temperature is 1 cP and the density of ethyl benzene at normal boiling temperature is 0.761 gm/cc by Wilke Chang correlation. Solute molar volume for EB is 139.5 cm³/mol (Assume required constants and atmospheric conditions if not specified).

(a) Compare with the experimental value of $D_{AB} = 0.81 \times 10^{-5}$ cm²/s and find the deviation.

(b) Estimate the diffusivity of EB at an elevated temperature of 393 K and viscosity of 0.5 cP using the temperature-diffusivity relations.

(c) Which factors predominantly affects the diffusivity in liquids and which operations in everyday life show its significance? Comment on the diffusion of NaCl crystals in water and does ionic mobility play a role in diffusion?

Ans = Wilke Chang Relation

$$D_{AB} \frac{\rho_B}{T} = 1.172 \times 10^{-16} (\frac{\rho_B M_B}{V_A})^{\frac{1}{2}} \quad C_A^{0.6} \rightarrow \text{in S.I. Unit}$$

$$D_{AB} \frac{\rho_B}{T} = 7.1 \times 10^{-8} (\frac{\rho_B M_B}{V_A})^{\frac{1}{2}} \quad V_A^{0.5} \quad \rightarrow \text{not in S.I. Unit)$$

For water,

$$P_B = \frac{1 \text{ atm}}{0.762 \text{ gm/cc}} = 1.31 \times 10^{-6}$$

$$T = 293 \text{ K}$$

μ \rightarrow c_{water}

$$\rho_B = 0.6$$

Also, $v_A = 1.395 \times 10^{-4} \text{ m}^3/\text{mol} = 139.5 \text{ cm}^3/\text{mol}$

$$\therefore v_{EB}$$

$$M_B = 1.8 \times 10^{-2} \text{ kg/mol}$$

$$\therefore D_{AB} \frac{(1.31 \times 10^{-6})}{293} = 1.173 \times 10^{-6} \left(\frac{2.6 \times 1.8 \times 10^{-2}}{(1.395 \times 10^{-4})^{0.6}} \right)^{\frac{1}{2}}$$

$$\therefore D_{AB} = \frac{293}{1.31 \times 10^{-6}} \times 1.173 \times 10^{-6} \left(\frac{2.6 \times 1.8 \times 10^{-2}}{(1.395 \times 10^{-4})^{0.6}} \right)^{\frac{1}{2}}$$

$$= 1.168 \times 10^{-6} \text{ m}^2/\text{s}$$

$$= 1.168 \times 10^{-2} \text{ cm}^2/\text{s}$$

(b)

$$D_{AB} \propto T$$

$$\mu_B$$

$$\therefore D_{AB} = \frac{1.168 \times 10^{-2}}{\left(\frac{393}{293} \right)^{\frac{1}{2}} \times \frac{0.5}{0.5}} = \frac{393}{293} \times \frac{1}{0.5}$$

$$= 2.68$$

$$\therefore D_{AB} = 1.168 \times 10^{-2} \times 2.68$$

$$= 0.031 \text{ cm}^2/\text{s}$$

$$= 3.1 \times 10^{-2} \text{ cm}^2/\text{s}$$

(c) Factor predominantly affecting is T , and its strong function such as μ . Its significance is shown on a daily basis, as sugar dissolves faster in hot rather than cold tea, and dirt gets removed faster when washed with hot water, etc.

~~NaCl~~ has ionic mobility such as NaCl diffuses faster in water than sugar due to its ionic mobility, owing to which is essentially a representation of the diffusive speed in a hindered medium. Thus, ionic mobility does have a significant effect in diffusion.

Q6. Diffusion of CO_2 is to be carried out through a porous membrane. The porous membrane has been characterized by scattered pore diameter sizes ranging from 0.5 nm to 9 nm in an inert nitrogen atmosphere. The conditions for the entire system are maintained at 300 K and twice the atmospheric pressure. (Assume required constants and use atmospheric conditions if not necessary) (Specified).

- (a) Calculate the diffusivity of CO_2 with following data:
 Leonard Jones constant of $\text{CO}_2 - \text{N}_2$ mixture are
 $\sigma_{\text{CO}_2 - \text{N}_2} = 0.3636$, $\epsilon/k = 101.48 \text{ K}$.
- (b) Estimate the pore diffusivity in the two extreme pore ranges and the effective diffusivity of the system.
- (c) Comment about the porous media diffusion parameters and whether they are dependent on pressure why, why not.

Ans: (a) Using Enskog-Chapman correlation

$$D_A = 0.602858 \times T^{\frac{3}{2}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}} \frac{P \sigma_{AB}^2}{R}$$

$$\sigma_{AB} = 0.3636, T = 300 \text{ K},$$

$$f\left(\frac{kT}{2}\right) = f\left(\frac{300}{101.48}\right) = f(2.96) = 0.95$$

$$P = 3 \text{ atm}$$

$$M_A = 1 \text{ g/mol}, M_B = 9 \text{ g/mol}$$

$$\therefore D_{AB} = 0.001858 \times 300^{\frac{3}{2}} \left(\frac{1}{14} + \frac{1}{28} \right)^{\frac{3}{2}}$$

$$= \frac{3 \times 0.95 \times 0.3636^{\frac{3}{2}}}{0.95 \times 0.3636^{\frac{3}{2}}} \text{ cm}^2/\text{s}$$

$$= 6.19 \text{ cm}^2/\text{s}$$

(b) deposit pore diffusivity,

$$D_{KA} = 1850 d_{\text{pore}} \sqrt{\frac{T}{M_A}} \text{ cm}^2/\text{s}$$

$$P_{PT} = 1850 \sqrt{\frac{300}{14}} d_{\text{pore}} \text{ cm}^2/\text{s}$$

$$= 1266 + d_{\text{pore}} \text{ cm}^2/\text{s}$$

$$(i) d_{\text{pore}} = 0.5 \times 10^{-7} \text{ cm}$$

$$\therefore D_{KA} = 1266 \times (0.5 \times 10^{-7}) \text{ cm}^2/\text{s}$$

$$= 1.21 \times 10^{-9} \text{ cm}^2/\text{s}$$

$$(ii) d_{\text{pore}} = 9 \times 10^{-7} \text{ cm}$$

$$\therefore D_{KA} d_{\text{pore}} = 1266 \times (9 \times 10^{-7}) \text{ cm}^2/\text{s}$$

$$= 1.11 \times 10^{-2} \text{ cm}^2/\text{s}$$

$$(iii) D_{eff} = \frac{1}{\frac{1}{D_{KA}} + \frac{1}{d_{\text{pore}}}}$$

$$\frac{1}{D_{KA}} + \frac{1}{d_{\text{pore}}}$$

$$= \frac{1}{6.33 \times 10^{-9}} + \frac{1}{1.11 \times 10^{-2}} \text{ cm}^2/\text{s}$$

$$= 5.997 \times 10^{-4} \text{ cm}^2/\text{s}$$

(C) Porous medium diffusion parameter

$$D_{PA} \propto d_{\text{pore}} \sqrt{P_T} = d_{\text{pore}} \sqrt{P}$$

Thus, diffusivity depends on pressure.

It is expected as pressure is an essential decisive factor in a molecule's mean velocity; more the pressure, faster it moves on an average, thus enhancing the diffusion.

Q7. For the hydrogenation of α -mylene, Nickel catalyst has a mean pore diameter of $200\text{ }\text{\AA}$.

- (a) Calculate the diffusivity of hydrogen by Chapman - Enskog relation for this catalyst in hydrogen-ethane mixture at 100°C , pressure 10 atm.
- (b) Calculate the diffusivity of hydrogen by Chapman - Enskog relation in the bulk medium over the catalyst surface with the following compositions 40% hydrogen, 40% ethylene and 20% ethane.

Ans = (a) Enskog - Chapman relation

$$D_{AB} = \frac{0.001858 T^{\frac{3}{2}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}}{P \cdot \epsilon_{AB}^2 \Omega_D}$$

$$P = 10 \text{ atm}, \quad T = 373 \text{ K}, \quad M_A = 2, \quad M_B = 28$$

$$\epsilon_{AB} = \frac{1}{2} (\epsilon_A + \epsilon_B) = \frac{1}{2} (2.827 + 4.163) = 3.495 \text{ A}_{H_2}^{0.7} \quad \text{C}_2\text{H}_4$$

$$(\epsilon/k)_{\text{req}} = \sqrt{(\epsilon/k)_{H_2} (\epsilon/k)_{\text{ethylene}}} = \sqrt{(24.7 \times 50.7)} \\ = 125.82 \text{ K}$$

$$\therefore \frac{kT}{\epsilon} = \frac{373}{125.82} \approx 2.97 \quad \text{Interpolation between } 3 \text{ & } 3.5$$

$$\therefore D_{AB} \Omega_D = f(3.22) = \approx 0.933 \quad 0.5$$

$$\therefore D_{AB} = \frac{0.001858 \times 373^{\frac{3}{2}} \times \left(\frac{1}{2} + \frac{1}{28} \right)^{\frac{1}{2}}}{20 \times 3.495^2 \times 0.933} = 0.08596 \text{ cm}^2/\text{s}$$

$$(b) \text{ Given, } y_{H_2} = 0.9,$$

$$y_{C_2H_6} = 0.1,$$

$$y_{C_2H_6} = 0.2$$

$$D_{H_2-C_2H_6} = 0.08596 \text{ cm}^2/\text{s} \text{ (calculated)}$$

For $H_2 - C_2H_6$ diffusivity,

$$(E/E)_{H_2} = 59.7 \text{ K}$$

$$(E/E)_{C_2H_6} = 215.7 \text{ K}$$

$$\therefore (E/E)_{\text{avg}} = \sqrt{215.7 \times 59.7} = 113.48 \text{ K}$$

$$\therefore \frac{T_E}{E} = \frac{373}{113.48} = 3.287$$

$$\therefore D = (3.287 - 1)(0.912 + 0.5 \cdot 3.287)(0.919)$$

(Interpolation between 3 and 3.5) $= 0.928$

$$D_{H_2-C_2H_6} = \frac{1}{2}(E_{H_2} + E_{C_2H_6}) = \frac{1}{2}(2.87 + 4.413) \\ = 3.635$$

$$M_B = 30, M_A = 2$$

$$\therefore D_{AB} \Big|_{\substack{A=H_2, \\ B=C_2H_6}} = \frac{0.001856 \times 373^{\frac{3}{2}} \left(\frac{1}{30} + \frac{1}{2} \right)^{\frac{1}{2}}}{20 \times 3.635^2 \times 0.928}$$

$$= 0.0797 \text{ cm}^2/\text{s}$$

$$\therefore D_{H_2, m} = \frac{y_{C_2H_6}}{D_{H_2-C_2H_6}} + \frac{y_{C_2H_6}}{D_{H_2-C_2H_6}} = \frac{1}{0.08596 + 0.0797} \text{ cm}^2/\text{s}$$

$$= 0.1398 \text{ cm}^2/\text{s}$$

Q8. For the mixture of carbon monoxide and hydrogen, predict the diffusing using the Fuller Empirical relation for the following condition

a) 1 atm pressure, 100°C temperature

b) 2 atm pressure, 100°C temperature

c) 1 atm pressure, 200°C temperature

Ans: ~~to~~ Fuller empirical relation

$$D_{AB} = 10^{-3} T^{1.75} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}}$$

$$P \left((\sum v_A)^{\frac{2}{3}} + (\sum v_B)^{\frac{2}{3}} \right)^2$$

$$M_A = 28, M_B = 2; P = ?$$

$$\sum v_A = (16.5 + 5.48) = 21.98$$

$$\sum v_B = 2 \times 2.31 = 4.62$$

(a)

$$\therefore D_{AB} = \frac{10^{-3} \left(\frac{1}{28} + \frac{1}{2} \right)^{\frac{1}{2}}}{\left(21.98^{\frac{2}{3}} + 4.62^{\frac{2}{3}} \right)^2} T^{1.75}$$

$$= 3.66 \times 10^{-5} \cdot \frac{T^{1.75}}{P} \text{ cm}^2/\text{s}$$

a) $P = 1, T = 373$

$$\therefore D_{AB} = 3.66 \times 10^{-5} \times \frac{373^{1.75}}{1}$$

$$= 1.1587 \text{ cm}^2/\text{s}$$

b) $P = 2, T = 373$

$$\therefore D_{AB} = 3.66 \times 10^{-5} \times \frac{373^{1.75}}{2}$$

$$= 0.579 \text{ cm}^2/\text{s}$$

c) $P = 1, T = 473$

$$\therefore D_{AB} = 3.66 \times 10^{-5} \times \frac{473^{1.75}}{1}$$

$$= 1.7559 \text{ cm}^2/\text{s}$$

9. Estimate the diffusivity of acetone in water at 30°C and 60°C by Wilke Chang relation.

	Molar vol
Carbon	0.0118
Hydrogen	0.0037
Oxygen	0.0074

Molar volume at Normal Boiling point (v_c)
 Viscosity of water are 0.8007×10^{-3} Pas and
 0.4688×10^{-3} Pas at 30°C and 60°C respectively.
 Ans = Wilke Chang relation

$$D_{AB} \frac{\mu_B}{T} = 1.74 \times 10^{-16} \sqrt{\alpha_B M_B} \frac{v_A^{0.6}}{v_A^{0.6}}$$

$$\alpha_B = 2.26$$

$$v_A = 0.285 v_c^{1.048}$$

$$\begin{array}{ccc} \text{CH}_3 & \text{CH}_3 & \\ \text{C} & \text{C} & \\ \text{H}_3 & \text{H}_3 & \\ & & = 3v_c + v_o + 6v_H \\ & & = 0.074 \end{array}$$

$$\therefore v_A = 0.074^{1.048} \times 0.285 \\ = 0.019$$

$$M_B = 18$$

$$\mu_B = \frac{v}{e} = \frac{v}{10^3} = 10^{-3} e$$

$$\therefore D_{AB} = 1.74 \times 10^{-16} \sqrt{2.26 \times 18} \times 10^{-3} (e^T) \frac{0.019^{0.6}}{0.019^{0.6}}$$

$$= 8.07 \times 10^{-18} e^T$$

$$(i) 30^\circ C \rightarrow 0.8007 \times 10^{-3} \times (273+30) \times 8.07 \times 10^{-18} \\ = 6.46 \times 10^{-21} \text{ m}^2/\text{s} \quad 1.96 \times 10^{-18} \text{ m}^2/\text{s}$$

$$(ii) 60^\circ C \rightarrow 0.4688 \times 10^{-3} \times (273+60) \times 8.07 \times 10^{-18} \\ = 1.26 \times 10^{-18} \text{ m}^2/\text{s}$$

10. An absorption tower has been proposed to remove selectively two pollutants, hydrogen sulphide (H_2S) and sulphur dioxide (CO_2) from an exhaust gas stream containing

H_2S 3 vol %

SO_2 5 vol %

N_2 92 vol %

Estimate the diffusivity of hydrogen sulphide in the gas mixture at 350 K and 1.013×10^5 Pa.

Ans = For this case, we use the diffusivity formula for multi diffusion

$$D_{A,m} = \frac{1}{\frac{y_2}{D_{A,2}} + \frac{y_3}{D_{A,3}}}$$

Now, since y is mole fraction, it is also volume %, as equal numbers of moles occupy equal volume at same T and P (one of the gas laws) (from ideal gas equation),
($P = 1 \text{ atm}$)

Let SO_2 be 2, N_2 be 3 and H_2 be 1 or A.

Then, for $D_{A,2}$, $M_A = 2$, $M_B = 64$

$$\sigma_{A,2} = \frac{1}{2} (\sigma_{H_2} + \sigma_{SO_2}) = \frac{1}{2} (2.827 + 4.112) \\ = 3.4695$$

$$(E/k)_A = 59.7 \text{ K}, (E/k)_B = 335.4 \text{ K}$$

$$\therefore (E/k)_{req} = \sqrt{59.7(335.4)} = 141.504 \text{ K}$$

$$\therefore \frac{T_k}{E} = \frac{350}{141.504} = 2.473$$

$$\therefore \sigma_D = f(2.473) \approx \frac{(2.473 - 2)(2.473 - 2.5)}{0.5} = 0.075$$

Interpolation between σ_2 and σ_3

$$= (2.473 - 2)(0.9998) + (2.5 - 2.473)(1.075) \\ = 1.0037$$

Using Chapman-Enskog relation, we get

$$\begin{aligned} D_{AB} &= 0.001858 \times 7^{\frac{3}{2}} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{\frac{1}{2}} \\ &= 0.001858 \times \frac{350^{\frac{3}{2}}}{2 \times 1.0037 \times 3.4695^2} \left(\frac{1}{2} + \frac{1}{28} \right)^{\frac{1}{2}} \\ &= 0.7231 \text{ cm}^2/\text{s} \end{aligned}$$

For D_{A_3} , $M_B = 28$

$$\epsilon_{AB} = \frac{1}{2} (2.827 + 3.798) = 3.3125$$

$$(\epsilon/k)_3 = 71.4k, (\epsilon/k)_1 = 59.7k$$

$$\begin{aligned} \therefore (\epsilon/k)_{\text{req}} &\approx \cancel{65.2884} \quad (\cancel{71.4 \times 59.7}) \\ &= \sqrt{71.4 \times 59.7} \text{ k} \\ &= 65.2884 \text{ k} \end{aligned}$$

$$\therefore \frac{k_T}{\Sigma} = \frac{350}{65.2884} = 5.3608$$

$$\begin{aligned} \therefore \Omega_D &= f(5.3608) = \frac{(5.3608 - 5) \times 0.7896 + (7 - 5.3608) \times 0.84}{2} \\ &= 0.8327 \quad \text{Interpolation between 5 and 7} \end{aligned}$$

$$\begin{aligned} \therefore D_{AB} &= 0.001858 \times 350^{\frac{3}{2}} \left(\frac{1}{2} + \frac{1}{28} \right)^{\frac{1}{2}} \\ &= \frac{2 \times 0.8327 \times 3.3125^2}{0.9746 \text{ cm}^2/\text{s}} \end{aligned}$$

$$\therefore D_{H_2 \text{ (mix)}} = \frac{1}{y_{H_2} + y_{N_2}} \frac{D_{H_2} D_{N_2}}{D_{H_2} + D_{N_2}}$$

= $\frac{1}{y_{H_2} + y_{N_2}}$ cm^2/s

$\frac{0.05}{0.7232} + \frac{0.92}{0.9746} \rightarrow \text{vol \%}$
 given,
 and shown
 to be equal
 to y_i by
 ideal gas
 law

= $0.9870 \text{ cm}^2/\text{s}$

$$\text{Ans} = 0.9870 \text{ cm}^2/\text{s}$$

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