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CHAPTER 2: MOLECULAR DIFFUSION

Short and MCQ's

(2.1)

1. Diffusion of the reactants and products within the pores of a solid catalyst; diffusion of moisture in a wet solid during drying; diffusion through a membrane; diffusion of a solute within a 'rigid' drop in liquid extraction; diffusion of an ionic species in an ion-exchange resin.
2. If the molecular weights of all the species in a mixture are equal.
3. (i) Concentration, (ii) length of the diffusion path, (vi) partial pressure are scalar quantities; others are vectors.
4. (i) ft^2/s ; (ii) $\text{lbmol}/\text{ft}^2 \cdot \text{s}$; (iii) $\text{lbmol}/(\text{ft}^3) \cdot (\text{ft})$
5. (i) If the bulk ^{flow} term is small, or (ii) for transport in a dilute solution.
6. Ideal gas mixture.
7. (a) Absorption of a solute from an inert (insoluble) carrier; (b) distillation, if the components have equal molar heats of vaporization.
8. Since $N_B = 0$, $N_A = N_A \cdot \frac{p_A}{P} - \frac{D_{AB}}{RT} \frac{dp_A}{dz} = \text{constant}$ (A → ethanol, B → air)
 p_A is maximum at the liquid surface \Rightarrow contribution of the bulk flow term is the maximum at the liquid surface.
9. From Eq(2.19), $-\frac{dp_A}{dz} = N_A \cdot \frac{P - p_A}{P} \cdot \frac{RT}{D_{AB}}$. At $z = z_2$, $p_A = p_{A2}$ is the minimum and the magnitude of $\frac{dp_A}{dz}$ is maximum.
10. If the other two components are non-diffusing and these are present in the same volume ratios along the diffusion path.
11. Yes, by virtue of the Cauchy's Mean Value Theorem.
12. Compare the fluxes given by Eq(2.27) and (2.30).

2.2

12 contd... $\frac{(N_A)_{\text{nondiffusing B}}}{(N_A)_{\text{equimolar counterdiffusion}}} = \frac{P}{P_{B,M}} > 1$. Reason: molecules

of B in counterdiffusion offer more 'resistance' to diffusion of A compared to the case when these are non-diffusing.

13. D_{AB} depends inversely with total pressure, P , since at a higher pressure there are more molecular collisions (less mean free path) offering more 'resistance' to diffusion.

D_{AB} increases as $T^{3/2}$ to $T^{1.75}$, since higher temperature means higher velocity or mobility of the molecules.

14. The flux will be very high and pseudo steady state assumption will not be applicable.

15. The diffusivity increases with T and decreases with μ .

16. (a) \rightarrow (ii) zero; (b) \rightarrow (i) $u > U$; (c) \rightarrow (iii) multicomponent...;
 (d) \rightarrow (i) -2; (e) \rightarrow (i) $-78/94 = -0.83$; (f) \rightarrow Diffusion vel. $v_{A,d}$

$$= u_A - U = J_A / C_A = -\frac{D_{AB}}{C_A} \cdot \frac{dC_A}{dz} = -\frac{D_{AB}}{P_A} \cdot \frac{dp_A}{dz}$$

Equimolar counterdiffusion for $p_{A1} = 0.3 \text{ atm}$, $p_{A2} = 0.1 \text{ atm}$ midway in the film, $p_A = 0.2 \text{ atm}$; $\frac{dp_A}{dz} = \frac{0.1 - 0.3}{1} \frac{\text{atm}}{\text{cm}} = -0.2 \frac{\text{atm}}{\text{cm}}$

$$v_{A,d} = -\frac{0.2 \text{ cm}^2/\text{s}}{0.2 \text{ atm}} \cdot (-0.2 \frac{\text{atm}}{\text{cm}}) = 0.2 \text{ cm/s} = \underline{2 \text{ mm/s}} \quad (\text{i})$$

$$(g) \quad N_A \left(\frac{P - p_A}{P} \right) = -\frac{D_{AB}}{RT} \cdot \frac{dp_A}{dz} \Rightarrow \frac{(dp_A/dz)_1}{(dp_A/dz)_2} = \frac{(P - p_A)_1}{(P - p_A)_2}$$

$$= \frac{2 - (2)(0.1)}{2 - (2)(0)} = \frac{1.8}{2} = 0.9, \quad (\text{iii})$$

$$(h) \quad (dp_B/dz) = -(dp_A/dz) = \text{constant everywhere (since } p_A + p_B = P)$$

$$= -(-7 \text{ atm/m}) = \underline{7 \text{ atm/m}} \quad (\text{iii})$$

(i) After 10 hr, partial pressures of A and B in bulb 1 are:
 $p_{A1} = 0.5 \text{ atm}$; $p_{B1} = 0.5 \text{ atm}$ (since half of A diffuses out).

(2.3)

16 (i) contd... Material balance of A: $V_1 \cdot \frac{1 \text{ atm}}{RT} = V_1 \cdot \frac{0.5 \text{ atm}}{RT} + V_2 \cdot \frac{p_{A2}}{RT}$

$$\Rightarrow p_{A2} = \frac{(V_1)(0.5)}{V_2} = \left(\frac{5}{10}\right)(0.5) = 0.25 \text{ atm.} \quad \left[\begin{array}{l} \text{I} \rightarrow \text{initial} \\ \text{II} \rightarrow \text{after 10 hours} \end{array} \right]$$

$$\frac{(N_A)_I}{(N_A)_II} = \frac{(D_{AB}/RTL)(p_{A1} - p_{A2})_I}{(D_{AB}/RTL)(p_{A1} - p_{A2})_{II}} = \frac{1 - 0.0}{0.5 - 0.25} = \frac{1}{0.25} = \underline{4}$$

(j) Equimolar counterdiffusion of A and B occurs. Since the area of diffusion is variable,

$$\pi r_1^2 (N_A)_I = \pi r_2^2 (N_B)_{II} \Rightarrow (N_B)_{II} = -\left(\frac{r_1^2}{r_2^2}\right) \cdot (N_A)_I = -\left(\frac{1}{2}\right)^2 (10^{-6} \text{ kmol/m}^2 \text{ s})$$

$$= \underline{2.5 \times 10^{-7} \text{ kmol/m}^2 \text{ s}} \text{ towards vessel 1}$$

(k) \rightarrow (ii). It is the geometric mean dia = $(1 \times 4)^{1/2} = \underline{2 \text{ cm}}$

(l) \rightarrow (ii). Since $\pi r^2 N_A = \text{constant}$, N_A is the highest where the radius is the smallest.

(m) For equimolar counterdiffusion through a spherical film,

$$4\pi r^2 N_A = \text{constant}, \quad N_A = -\frac{D_{AB}}{RT} \cdot \frac{dp_A}{dr} \Rightarrow 4\pi r^2 \left(-\frac{D_{AB}}{RT} \frac{dp_A}{dr}\right) = W$$

$$\Rightarrow -\int_{p_{A1}}^{p_{A2}} dp_A = \frac{W \cdot RT}{D_{AB} \cdot 4\pi} \int_{r_i}^{r_i + \delta} \frac{dr}{r^2} \Rightarrow p_{A1} - p_{A2} = \Delta p = \frac{W RT}{D_{AB} \cdot 4\pi} \left(\frac{1}{r_i} - \frac{1}{r_i + \delta}\right)$$

$$\Rightarrow \text{Flux at } r = r_i \text{ is } (N_A)_I = \frac{W}{4\pi r_i^2} = \frac{D_{AB}}{RT} \cdot \frac{r_i + \delta}{r_i \cdot \delta} \cdot \Delta p_A$$

For diffusion through a flat film of this thickness, $(N_A)_{II} = \frac{D_{AB}}{RT \cdot \delta} \cdot \Delta p_A$

$$\frac{(N_A)_I}{(N_A)_{II}} = 1.05 \text{ (given)} \Rightarrow \frac{r_i + \delta}{r_i} = 1.05 \Rightarrow \frac{\delta}{r_i} = 0.05 \Rightarrow \underline{\delta = 0.05 r_i}$$

(n) \rightarrow (i), because of spherical symmetry; (o) \rightarrow (i);

(p) \rightarrow (iii), other values are out of range; (q) \rightarrow (iii), other values are out of range; (r) \rightarrow (ii) methanol, since it has the smallest molecular size among the three; (s) \rightarrow (ii) largest molecular size/weight; (t) \rightarrow (iii), since $D_{AB} \cdot P$ is constant for gas-phase diffusion; (u) \rightarrow (i); use the relation $\frac{D_1 \mu_1}{T_1} = \frac{D_2 \mu_2}{T_2}$

- 16 (v) \rightarrow (ii), $0.09 \text{ cm}^2/\text{s}$, use the relation $D_{AB} \propto T^{1.5}/P$;
 (w) \rightarrow (ii), velocity of the interface, $\frac{dz}{dt} \propto \frac{1}{z}$, see Eq (2.51a);
 (x) \rightarrow (i), surface diffusion; (y) \rightarrow (ii); (z) \rightarrow (ii).

Problems

2.1 Water vapor (A) diffuses through a stagnant film of air (B). Use Eq (2.26) to calculate the flux.

Water temp. = $23^\circ\text{C} = 296\text{K}$, vapor pressure $p_{A0} = 13.8573 - \frac{5160.2}{296}$

Ambient air temp. = 27°C ; $p_{AL}^v = 0.0353 \text{ bar} = 0.0280 \text{ bar}$

R. Humidity of air = 65% \Rightarrow partial pressure of moisture in bulk air, $p_{AL} = (0.0353)(0.65) = 0.023 \text{ bar}$.

Mean value of diffusivity of water vapor in the film = $(0.257 + 0.262)/2 = 0.2595 \text{ cm}^2/\text{s}$; mean film temperature = $(296 + 300)/2 = 298\text{K}$.

Film thickness, $l = 3 \text{ mm} = 3 \times 10^{-3} \text{ m}$; $P = 1 \text{ atm} = 1.013 \text{ bar}$

Flux of water vapor at steady state, $N_A = \frac{D_{AB} P}{RTl} \ln \frac{P - p_{AL}}{P - p_{A0}}$
 $\Rightarrow N_A = \frac{(2.595 \times 10^{-5})(1.013)}{(0.08317)(298)(3 \times 10^{-3})} \ln \frac{1.013 - 0.023}{1.013 - 0.028} = 1.79 \times 10^{-6} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s}}$
 $= 0.116 \text{ kg/m}^2 \cdot \text{h} = \text{rate of evaporating water per m}^2$

2.2 Use Eq (2.26). The flux of moisture is given, calculate film thickness.

Amount water evaporated per m^2 of surface in 10 days
 $= (20 \text{ mm})(1 \text{ m}^2) = 0.02 \text{ m}^3 = 20 \text{ kg} = 20/18$, or 1.111 kmol

Flux = $\frac{1.111 \text{ kmol}}{(1 \text{ m}^2)(10 \times 24 \times 3600 \text{ s})} = 1.286 \times 10^{-6} \text{ kmol/m}^2 \cdot \text{s} = N_A$

Given: $D_{AB} = 1 \text{ ft}^2/\text{h} = (30.48)^2/3600 \rightarrow 0.258 \text{ cm}^2/\text{s} = 2.58 \times 10^{-5} \text{ m}^2/\text{s}$

$P = 1.013 \text{ bar}$; $R = 0.08317 \text{ m}^3 \cdot \text{bar}/\text{kmol} \cdot \text{K}$; $T = 23^\circ\text{C} = 296\text{K}$.

Humidity of bulk air = $0.0135 \text{ kg moisture/kg dry air}$.

2.2) Cond... $y_{AL} = \frac{0.0135/18}{(0.0135/18) + (1/28.9)} = 0.0212$ [mol wt of air = 28.9]

$p_{AL} = P \cdot y_{AL} = (1.013)(0.0212) = 0.0215$ bar.

Vapor pressure of water at 296 K = 0.028 bar = p_{A0} ; $l = ?$
 (from Antoine eq)

Substitute in Eq (2.26) $\rightarrow 1.286 \times 10^{-6} = \frac{(2.58 \times 10^{-5})(1.013)}{(0.08317)(296)(l)} \ln \frac{1.013 - 0.0215}{1.013 - 0.028}$

$\Rightarrow l = 5.4 \times 10^{-3} \text{ m} = 5.4 \text{ mm} = \text{thickness of the air film}$

2.3) Temperature, $T = 35^\circ\text{C} = 308^\circ\text{C}$; vapor press. of water, $p_A^v = 0.0552$ bar

Relative humidity of bulk air = 30% $\Rightarrow p_{A0} = (0.0552)(0.3) = 0.01656$ bar

Partial pressure of moisture at the acid surface, $p_{AL} \approx 0$

Thickness of air film, $l = 1.2 \times 10^{-3} \text{ m}$ (since the acid has a high affinity for water)

Moisture flux: $P = 1.013$ bar
 $D_{AB} = 0.257 \text{ cm}^2/\text{s}$ at 23°C ;

from Eq (2.26), at 308 K, $D_{AB} = (0.257)(308/296)^{1.5} = 0.2728 \text{ cm}^2/\text{s}$

$N_A = \frac{(2.728 \times 10^{-5})(1.013)}{(0.08317)(308)(1.2 \times 10^{-3})} \ln \frac{1.013 - 0.01656}{1.013} = 1.482 \times 10^{-6} \text{ kmol/m}^2\cdot\text{s} = 9.602 \times 10^{-2} \text{ kg/m}^2\cdot\text{h}$

2.4) Temperature, $T = 300 \text{ K}$; total pressure = 400 mm Hg; partial pressure of ammonia in the bulk (40% by volume) = $(400)(0.4) = 160 \text{ mmHg}$

Diffusivity of NH_3 at 1 atm and 333 K = $2.53 \times 10^{-5} \text{ m}^2/\text{s}$ [Table 2.1].

Diffusivity at 400 mm pressure and 300 K = $(2.53 \times 10^{-5}) \left(\frac{760}{400}\right) \left(\frac{300}{333}\right)^{1.5}$

$p_{AL} = 0$ at the acid surface; $l = 0.01 \text{ m}$ $\Rightarrow 4.11 \times 10^{-5} \text{ m}^2/\text{s}$; $P = 0.533$ bar
 $p_{A0} = 160 \text{ mmHg} = 0.2133$ bar

Flux of ammonia, $N_A = \frac{(4.11 \times 10^{-5})(0.533)}{(0.08317)(300)(0.01)} \ln \frac{0.533 - 0}{0.533 - 0.2133} = 4.488 \times 10^{-5} \text{ kmol/m}^2\cdot\text{s}$

(i) Rate of absorption of ammonia through an area, $a = 0.1 \text{ m}^2$
 $= (4.488 \times 10^{-5})(0.1) = 4.488 \times 10^{-6} \text{ kmol/s}$

(ii) In order to calculate the partial pressure gradient at

(2.6)

2.4) contd... a point in the film, calculate the partial pressure of the species at the particular point using Eq. (2.28), and then calculate the gradient, $(\frac{dp_A}{dz})$, using the Fick's law, Eq. (2.24).

The given point is 4 mm from the acid surface $\Rightarrow z = 10 - 4 = 6 \text{ mm} = 6 \times 10^{-3} \text{ m}$.

Put the values in Eq. (2.28) $\rightarrow 4.488 \times 10^{-5} = \frac{(4.11 \times 10^{-5})(0.533)}{(0.08317)(300)(0.006)} \ln \frac{0.533 - p_A}{0.533 - 0.2133}$

From Eq. (2.24),
 $4.488 \times 10^{-5} \left(1 - \frac{0.0985}{0.533}\right) = - \frac{(4.11 \times 10^{-5})}{(0.08317)(300)} \cdot \frac{dp_A}{dz} \Rightarrow p_A = 0.0985 \text{ bar}$

$\Rightarrow \frac{dp_A}{dz} = -22.2 \text{ bar/m}$

(iii) Acid-side end of the film $\rightarrow z = 0.01 \text{ m}; p_A = 0$

Contribution of 'bulk flow' to the flux [see Eq. (2.15)] $\boxed{N_B = 0}$

$= (N_A + N_B) \frac{C_A}{C} = N_A \cdot \frac{p_A}{P} = (4.488 \times 10^{-5}) \left(\frac{0}{0.533}\right) = 0$

Contribution of the diffusion term $= N_A - N_A \cdot \frac{p_A}{P} = 4.488 \times 10^{-5} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s}}$

[i.e. there is no contribution of the bulk flow term at $z = 0.01 \text{ m}$]

Gas-side end of the film $\rightarrow z = 0; p_A = 0.2133 \text{ bar}$

Contribution of the bulk flow term $= N_A \cdot \frac{p_A}{P} = (4.488 \times 10^{-5}) \left(\frac{0.2133}{0.533}\right) = 1.796 \times 10^{-5} \text{ kmol/m}^2 \cdot \text{s}$

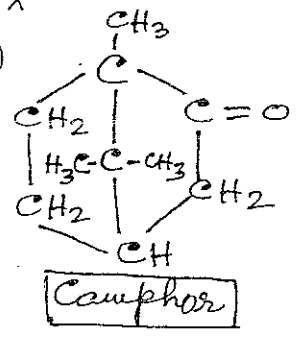
Contribution of the diffusion term to the flux $= 4.488 \times 10^{-5} - 1.796 \times 10^{-5} = 2.692 \times 10^{-5} \text{ kmol/m}^2 \cdot \text{s}$

2.5) Estimation of diffusivity of Camphor, $C_{10}H_{16}O$ (A)

'Diffusion volume', see Table 7.4

- 10 Carbons $\rightarrow (10)(16.5) = 165$
- 16 Hydrogen atoms $\rightarrow (16)(1.98) = 31.68$
- 1 oxygen atom $\rightarrow 5.48$

Total, $(\sum V)_A = 165 + 31.68 + 5.48 = 202.16$



For air, $(\sum V)_B = 20.1; M_A = 152.13; M_B = 28.9; T = 293 \text{ K}; P = 1.013 \text{ bar}$

Eq. (2.57) $\rightarrow D_{AB} = \frac{(1.0133 \times 10^{-7})(293)^{1.75}}{(1.013) [(202.16)^{1/3} + (20.1)^{1/3}]} \cdot \left[\frac{1}{152.13} + \frac{1}{28.9} \right]^{1/2} = 5.644 \times 10^{-6} \frac{\text{m}^2}{\text{s}}$

(2.5)

2.5 contd... Eq. (2.26), Flux = $\frac{(5.644 \times 10^{-6})(1.013)}{(0.08317)(293)(0.12)} \ln \frac{1.013-0}{1.013-0.13} = 2.685 \times 10^{-7} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s}}$

$l = 0.12 \text{ m}; P_{A0} = 97.5 \text{ mm Hg} = 0.13 \text{ bar}, P_{A2} = 0$

q of camphor in the tube = 0.4 gm
 $= \frac{0.4}{(1000)(152.13)} = 2.63 \times 10^{-6} \frac{\text{kmol}}{\text{s}} = m_A$

Area of the tube = $\frac{\pi}{4} (0.015)^2 = 1.767 \times 10^{-4} \text{ m}^2 = a$

$N_A \cdot a \cdot t = m_A = 2.63 \times 10^{-6} \Rightarrow t = \frac{2.63 \times 10^{-6}}{(2.685 \times 10^{-7})(1.767 \times 10^{-4})} \text{ s} = 15.4 \text{ hr}$

2.6 For diffusion of A through non-diffusing B at steady state in the spherical geometry, we write the following equation [see Eq. (2.73)].

$-\frac{dP_A}{P-P_A} = \frac{WRT}{4\pi D_{AB} P} \cdot \frac{dr}{r^2}$; $W = 4\pi r^2 N_A = \text{constant rate of transport at steady state.}$

Integrate from $r=r_i, P_A=P_{Ai}$ to $r=r_o=r_i+\delta, P_A=P_{Ao}$ and simplify.

$W = \frac{4\pi D_{AB} P}{RT \delta} \cdot r_i(r_i+\delta) \cdot \ln \frac{P-P_{Ao}}{P-P_{Ai}} \dots (i)$

$T = 40^\circ\text{C} = 313\text{K}; P_{Ao} = 0.3 \text{ atm}$
 $D_{AB} \text{ at } 313\text{K}, 1 \text{ atm} = (1.62 \times 10^{-5}) \left(\frac{313}{298}\right)^{1.5} = 1.744 \times 10^{-5} \frac{\text{m}^2}{\text{s}}$
 $P_{Ai} = 0; \delta = 0.0035 \text{ m}; r_i = 7/2 \text{ mm} = 0.0035 \text{ m}$

$= \frac{(4\pi)(1.744 \times 10^{-5})(1.013)(0.0035)(0.0035+0.0035)}{(0.0821)(313)(0.0035)} \times \ln \frac{1-0.3}{1-0} = 2.13 \times 10^{-8} \frac{\text{kmol}}{\text{s}}$

Flux of CO₂ midway in the film:

Midway in the film, $r_m = r_i + \delta/2 = 0.0035 + 0.0035/2 = 0.00525 \text{ m}$

$4\pi r_m^2 N_A = W = 2.13 \times 10^{-8} \text{ kmol/s}$ (constant). Put $r = 0.00525 \text{ m}$ to get

N_A (midway in the film) = $\frac{-2.13 \times 10^{-8}}{4\pi (0.00525)^2} = -6.15 \times 10^{-5} \text{ kmol/m}^2 \cdot \text{s}$

'Diffusion velocity' at $r_m = 0.00525 \text{ m}$: This means that diffusion occurs towards decreasing r , i.e. towards the pellet.

Eq. (2.18) is to be used. (i) Calculate P_A from Eq. (i) above written for $r=r_m$, (ii) calculate dP_A/dz from the expression for Fick's law, Eq. (2.19).

Eq. (i) above written for $r=r_m$ and $P=P_A$ is

$W = \frac{4\pi D_{AB} P}{RT (\delta/2)} \cdot (r_i)(r_m) \cdot \ln \frac{P-P_A}{P-P_{Ai}} \dots (ii)$. Equate (i) and (ii) to get

$2r_m \ln \frac{P-P_A}{P-P_{Ai}} = (r_i+\delta) \ln \frac{P-P_{Ao}}{P-P_{Ai}}$

$\Rightarrow (2)(0.00525) \ln \frac{1-P_A}{1-0} = (0.007) \ln \frac{1-0.3}{1-0} \Rightarrow P_A = 0.2116 \text{ atm, midway in the film.}$

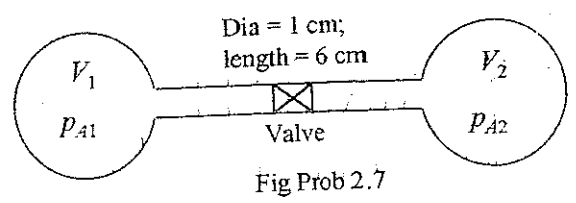
(2.6) contd... Eq(2.19) $\rightarrow N_A = (N_A + N_B) \cdot \frac{p_A}{p} - \frac{D_{AB}}{RT} \frac{dp_A}{dr}$
 $\Rightarrow (-6.15 \times 10^{-5}) \left(1 - \frac{0.2}{1.0}\right) = -\frac{D_{AB}}{RT} \frac{dp_A}{dr} = -4.848 \times 10^{-5} \text{ kmol/m}^2\text{s}$

Diffusion velocity [Eq(2.18)] $\rightarrow v_{A,d} = -\frac{D_{AB}}{C_A} \cdot \frac{dC_A}{dr}$
 $\Rightarrow v_{A,d} = -\frac{D_{AB}}{p_A} \cdot \frac{dp_A}{dr} = (-4.848 \times 10^{-5}) \left(\frac{0.0821 \times 313}{0.2116}\right) = -5.9 \times 10^{-3} \text{ m/s}$

\Rightarrow The diffusion velocity (5.9 mm/s) is directed towards the pellet, i.e. in the direction of decreasing r .

(2.7) $N_2 \rightarrow A$; $CO_2 \rightarrow B$; $P = 1.013 \text{ bar}$

$p_{A1} = 10^4 p_A = 0.1 \text{ bar}$; $p_{A2} = 0.8 \text{ bar}$;
 $p_{B1} = 0.913 \text{ bar}$; $p_{B2} = 0.213 \text{ bar}$; $l = 0.06 \text{ m}$
 Equimolar counterdiffusion occurs at steady state.



(i) Use Eq(2.30) to calculate the flux. Since the vessels are 'large', the partial pressures remain virtually unchanged.

Flux of N_2 (A) $= \frac{D_{AB}}{RTL} (p_{A1} - p_{A2})$; $D_{AB} = 1.69 \times 10^{-5} \text{ m}^2/\text{s}$, calculated from the value at 298 K, Table 2.1.
 $\Rightarrow N_A = \frac{(1.69 \times 10^{-5})}{(0.08317)(303)(0.06)} \cdot (0.1 - 0.8) = -7.824 \times 10^{-6} \text{ kmol/m}^2\text{s}$

(The flux is negative, diffusion occurs from vessel 2 to 1)

Velocity of the molecules of species A w.r.t. a stationary observer is

$u_A = N_A / C_A$. At vessel 1 end of the tube, $C_{A1} = p_{A1} / RT = \frac{0.1}{(0.08317)(303)}$
 $u_{A1} = \frac{-7.824 \times 10^{-6}}{(0.1)/(0.08317)(303)} = -0.00197 \text{ m/s}$.

Similarly, $u_{A2} = \frac{-7.824 \times 10^{-6}}{(0.8)/(0.08317)(303)} = -2.46 \times 10^{-4} \text{ m/s}$

Average velocity of the nitrogen molecules $= \frac{1.97 \times 10^{-3} + 2.46 \times 10^{-4}}{2} = 1.108 \times 10^{-3} \text{ m/s}$

\Rightarrow velocity of the observer, $u_0 = -1.108 \times 10^{-3} \text{ m/s}$

Molar flux of N_2 w.r.t. the observer moving with the above velocity,

$= (u_A - u_0) C_A = u_A C_A - u_0 C_A = N_A - (-1.108 \times 10^{-3}) (p_A / RT)$

Since the partial pressure is linear in distance for equimolar counterdiffusion,

(2.7) contd... $P_A = (P_{A1} + P_{A2})/2 = (0.1 + 0.8)/2 = 0.45 \text{ bar}$, midway in the tube.

Required flux $= -7.824 \times 10^{-6} + (1.108 \times 10^{-3}) \left[\frac{0.45}{(0.08317)(303)} \right] = 1.19 \times 10^{-5} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s}}$

This flux occurs in the direction of vessel 1 \rightarrow vessel 2.

(ii) To calculate the rate of transport through a tapered tube, use Eq. (2.79), $(\pi r^2 N_A) = W = \frac{\pi D_{AB}}{RT} \cdot \frac{r_1 r_2}{L} (P_{A1} - P_{A2})$ (compare, Fig 2.9)

Given: $r_1 = 0.005 \text{ m}$, $r_2 = 0.01 \text{ m}$. $W = \frac{(\pi)(1.69 \times 10^{-5})}{(0.08317)(303)} \cdot \frac{(0.005)(0.01)}{0.06} \cdot (0.1 - 0.8)$
 $= -1.229 \times 10^{-9} \text{ kmol/s}$

(from vessel 2 to 1, in reality)

(iii) From the above equation it appears that the rate of transport does not change if the tube is reversely fitted.

(iv) The theoretical approach of Section 2.5.1 applies. Start with Eq. (2.49) and integrate from $t=0$, $P_{A10} - P_{A20}$ to $t=t$, $P'_{A1} - P'_{A2} \Rightarrow \ln \frac{P_{A10} - P_{A20}}{P'_{A1} - P'_{A2}} = \frac{a \cdot D_{AB}}{L} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \cdot t \dots (i)$

$P_{A0} = 0.1 \text{ bar}$; $P_{A20} = 0.8 \text{ bar}$; $a = \frac{\pi}{4} (0.01)^2 = 7.853 \times 10^{-5} \text{ m}^2$;

$P'_{A1} = 2 P_{A0}$ (given) $\Rightarrow P'_{A1} = 0.2 \text{ bar}$; $V_1 = 0.005 \text{ m}^3$; $V_2 = 0.003 \text{ m}^3$.

Obtain P'_{A2} by material balance.

$V_1 C_{A10} + V_2 C_{A20} = V_1 C'_{A1} + V_2 C'_{A2} \Rightarrow V_1 P_{A10} + V_2 P_{A20} = V_1 P'_{A1} + V_2 P'_{A2}$

$\Rightarrow (0.005)(0.1) + (0.003)(0.8) = (0.005)(0.2) + (0.003)(P'_{A2}) \Rightarrow P'_{A2} = 0.633 \text{ bar}$

$\Rightarrow \ln \frac{0.1 - 0.8}{0.2 - 0.633} = \frac{(7.853 \times 10^{-5})(1.69 \times 10^{-5})}{0.06} \cdot \left(\frac{1}{0.005} + \frac{1}{0.003} \right) \cdot t$

$\Rightarrow t = 11.3 \text{ hr}$

Partial pressure of N_2 midway in the connecting tube after 20 hr

Put the values in the above equation (i) to get

$\ln \frac{0.1 - 0.8}{P_{A1f} - P_{A2f}} = \frac{(7.853 \times 10^{-5})(1.69 \times 10^{-5})}{0.06} \cdot \left(\frac{1}{0.005} + \frac{1}{0.003} \right) \cdot (20 \times 3600)$

$\Rightarrow \ln \frac{-0.7}{P_{A1f} - P_{A2f}} = 0.85 \Rightarrow (P_{A1f} - P_{A2f}) = -0.3 \text{ bar} \dots (ii)$

P_{A1f} and P_{A2f} are also related by material balance.

(2.7) contd... $(0.005)(0.1) + (0.003)(0.8) = (0.005)(P_{A1f}) + (0.003)(P_{A2f})$
 $\Rightarrow 5P_{A1f} + 3P_{A2f} = 2.9 \dots (iii)$

Solve eqs. (ii) and (iii) to get $P_{A1f} = 0.2502 \text{ bar}$, $P_{A2f} = 0.5496 \text{ bar}$

Partial pressure of N_2 midway in the tube at $t = 20 \text{ hr}$,

$(P_A)_{av} = (0.2502 + 0.5496) / 2 = 0.4 \text{ bar}$

(2.8) Partial pressures of A and B in the bulk $\rightarrow P_{A0}, P_{B0}$; those at the catalyst surface $(z = \delta) \rightarrow P_{As}, P_{Bs}$; $P_{As} = 0$. Also $P = P_{A0} + P_{B0}$

(a) Reaction: $A \rightarrow B$. $N_A = -N_B$ at steady state. Use Eq (2.19).

$$N_A = (N_A + N_B) \frac{P_A}{P} - \frac{D_{AB}}{RT} \frac{dP_A}{dz} \Rightarrow N_A \int_0^\delta dz = - \frac{D_{AB}}{RT} \int_{P_{A0}}^{P_{As}=0} dP_A$$

$$\Rightarrow N_A = \frac{D_{AB}}{RT\delta} \cdot P_{A0} \Rightarrow \text{Reaction rate per unit area} = N_A = \frac{D_{AB}}{RT\delta} \cdot (P - P_{B0})$$

(b) Reaction: $2A \rightarrow B \Rightarrow N_A = -2N_B$ at steady state. From Eq (2.19),

$$N_A = (N_A - N_A/2) \frac{P_A}{P} - \frac{D_{AB}}{RT} \frac{dP_A}{dz} \Rightarrow N_A \int_0^\delta dz = - \frac{2D_{AB}P}{RT} \int_{P_{A0}}^0 \frac{dP_A}{2P - P_A}$$

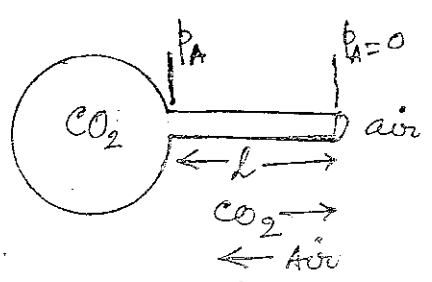
$$\Rightarrow N_A = \frac{2D_{AB}P}{RT\delta} \ln \frac{2P}{2P - P_{A0}} \Rightarrow \text{Rate of reaction, } N_A = \frac{2D_{AB}P}{RT\delta} \ln \frac{2P}{P + P_{B0}}$$

(c) Reaction: $2A \rightarrow 3B \Rightarrow 3N_A = 2N_B$ (at steady state) $\Rightarrow N_B = -\frac{3}{2}N_A$

$$N_A = (N_A - \frac{3}{2}N_A) \frac{P_A}{P} - \frac{D_{AB}}{RT} \frac{dP_A}{dz} \Rightarrow N_A \int_0^\delta dz = - \frac{2D_{AB}P}{RT} \int_{P_{A0}}^0 \frac{dP_A}{2P + P_A}$$

$$\Rightarrow N_A = \frac{2D_{AB}P}{RT\delta} \ln \frac{2P + P_{A0}}{2P} \Rightarrow \text{Rate of reaction, } N_A = \frac{2D_{AB}P}{RT\delta} \ln \frac{3P - P_{B0}}{2P}$$

(2.9) Equimolar counterdiffusion of CO_2 and air occurs through the tube. Assume Pseudo-steady state. Refer to the theoretical analysis in Section 2.5.1.



2.9) Contd... The time rate of change of the partial pressure of CO_2 in the bulb is given by:

$$-\frac{V}{RT} \frac{dp_A}{dt} = \text{Rate of diffusion of } \text{CO}_2 \text{ through the tube} = a \cdot N_A$$

$$\Rightarrow -\frac{V}{RT} \frac{dp_A}{dt} = a \cdot \frac{D_{AB}}{RTl} (p_A - 0); \quad p_A = \text{CO}_2 \text{ partial pressure at any time, } t, \\ a = \text{area of cross-section of the tube.}$$

The partial pressure of CO_2 at the air-side end of the tube is zero.

Integrate to get $-\int_{p_{Ai}}^{p_{Af}} \frac{dp_A}{p_A} = \frac{a \cdot D_{AB}}{V \cdot l} \int_0^{t_f} dt \Rightarrow \ln \frac{p_{Af}}{p_{Ai}} = \frac{a D_{AB} \cdot t_f}{V \cdot l} \dots (i)$

Given: p_{Ai} = initial partial pressure of CO_2 in the bulb = 1 atm.

p_{Af} = final partial pressure = 0.5 atm; $V = 2 \text{ liters} = 2 \times 10^{-3} \text{ m}^3$;

$l = 3 \text{ cm} = 3 \times 10^{-2} \text{ m}$; $a = \frac{\pi}{4} (0.005)^2 = 1.96 \times 10^{-5} \text{ m}^2$; $D_{AB} = 1.62 \times 10^{-5} \frac{\text{m}^2}{\text{s}}$

Substituting in Eq. (i) above,

$$\text{Time of diffusion, } t_f = \frac{(0.002)(0.03)}{(1.96 \times 10^{-5})(1.62 \times 10^{-5})} \ln \frac{1.0}{0.5} = \frac{1.31 \times 10^5 \text{ s}}{*} = \underline{\underline{36.38 \text{ hr.}}}$$

2.10) Reaction: $2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2$; $\text{CO} \rightarrow \text{Component 1}$, $\text{O}_2 \rightarrow 2$, $\text{CO}_2 \rightarrow 3$

Flux relation: $N_1 = 2N_2 = -N_3$; $y \rightarrow$ mole fraction, $C =$ total conc.

Use Eq. (2.37) for concentration distribution of component 1 (CO) in the film.

$$-C \frac{dy_1}{dz} = N_1 \left(\frac{y_2}{D_{12}} + \frac{y_3}{D_{13}} \right) - y_1 \left(\frac{N_2}{D_{12}} + \frac{N_3}{D_{13}} \right)$$

$$\Rightarrow -C \frac{dy_1}{dz} = N_1 \left(\frac{y_2}{D_{12}} + \frac{y_3}{D_{13}} \right) - y_1 \cdot N_1 \left(\frac{1}{2D_{12}} - \frac{1}{D_{13}} \right) \quad (i)$$

Similarly, putting the flux relations in Eq. (2.38),

$$-C \frac{dy_2}{dz} = \frac{N_1}{2} \left(\frac{y_1}{D_{21}} + \frac{y_3}{D_{23}} \right) - y_2 \cdot N_1 \left(\frac{1}{D_{21}} - \frac{1}{D_{23}} \right) \quad (ii)$$

Put the diffusivity values in Eq. (i) and (ii) above,

take $D_{ij} = D_{ji}$ for an ideal mixture

and use the relation $y_1 + y_2 + y_3 = 1$ to get

$$-\frac{C}{N_1} \cdot \frac{dy_1}{dz} = 2.755 - 1.02 y_1 - 0.714 y_2 \quad (iii)$$

$$\text{and } -\frac{C}{N_1} \frac{dy_2}{dz} = 1.359 - 0.338 y_1 - 0.682 y_2 \quad (iv)$$

For the $\text{CO}-\text{O}_2$ pair
 $D_{12} = 0.185 \text{ cm}^2/\text{s}$, at 1 atm
 and at 273 K

At 250 = 523 K,

$$D_{12} = (0.185) \left(\frac{523}{273} \right)^{1.5} = 0.363 \text{ cm}^2/\text{s}$$

Similarly,

$$D_{23} = 0.368; \quad D_{12} = 0.49 \frac{\text{cm}^2}{\text{s}}$$

Since the given mixture has three components, two simultaneous ordinary differential equations are to be solved