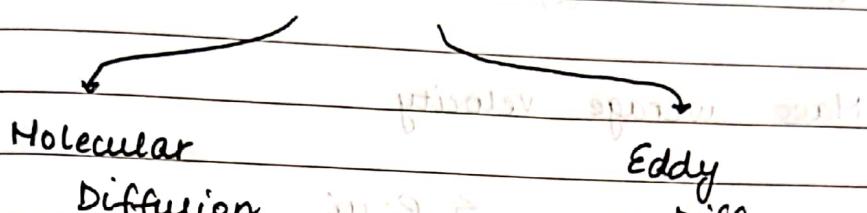


Mass Transfer

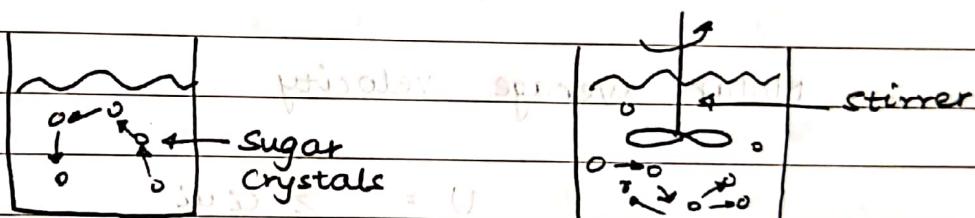
The driving force for mass transfer is the chemical potential.

ΔG_A is for molecular diffusion.

Diffusion



- Occurs in entire domain
- Kinetic energy of molecules
- convective Mass Transfer
- Diffusion occurs in small areas

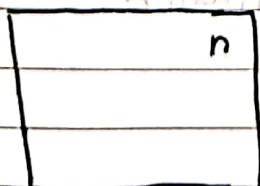


NO external stirrer
diffusion occurring
only due to kinetic
energy of molecules
Thus, $\Delta G_A = \gamma_A$

Path in b/w consec.
collisions is shorter
Movement is going
on the medium

Terms: Apparent adsorb. rates & molar

mass diff. to equilibrium with medium



$n \rightarrow$ Mass
 $n \rightarrow$ Moles
 $n \rightarrow$ Molar mass
 $n \rightarrow$ Molar volume
 $n \rightarrow$ Molar density
 $n \rightarrow$ Molar concentration
 $n \rightarrow$ Molar fraction
 $n \rightarrow$ Molar activity

$\rho_i \rightarrow$ mass concentration (density)

of i^{th} comp

$$\rho_i = \frac{\text{Mass}}{\text{Vol}}$$

$c_i = \frac{\text{mole}}{\text{Vol}} \rightarrow$ mole concentration of i^{th} comp.

$$w_i = \frac{P_i}{\sum P_i} \rightarrow \text{weight fraction of } i^{\text{th}} \text{ comp}$$

$$x_i, y_i = \frac{c_i}{\sum c_i} \rightarrow \text{mole fraction}$$

$$\sum w_i = 1, \sum x_i = 1, \sum y_i = 1, \sum P_i = P$$

If we know y_i, c_i we can find P, P_i

Mass average velocity

$$u = \frac{\sum P_i u_i}{P}$$

$u_i \rightarrow$ linear velocity of i^{th} species

↳ (statistical mean of velocities of molecules of comp i)

Molar average velocity

$$U = \sum c_i u_i$$

$$[\text{Solute}] \ll [\text{Solution}] \Rightarrow U_{\text{solute}} \ll U_{\text{solvent}}$$

$$\text{Thus, } U_{\text{solution}} = U_{\text{solvent}}$$

- Flux means net rate at which a species in a soln. passes through an area, normal to direction of diffusion

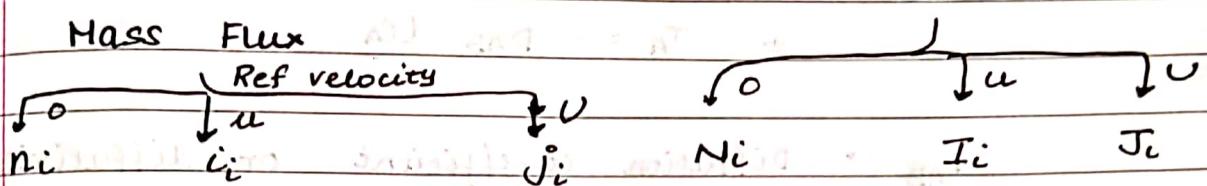
Flux \rightarrow Molar Flux

Mass Flux

Frame of References

- References → stationary object
 → Moving with mass avg velocity u
 → Moving with molar avg velocity v

Flux



↳ Total flux of i -th comp

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

$$n_i = P_i (u_i - 0)$$

$$J_i = c_i (u_i - v)$$

$$j_i = P_i (u_i - v)$$

$$I_{it} = c_i (u_i - u)$$

$$i_i = P_i (u_i - u)$$

$$\therefore J_i = N_i - \sum_{i=1}^c \frac{c_i}{c} N_i \quad \text{Total flux of all comp.}$$

↳ convective flux

$J_i \rightarrow$ diffusive flux

Consider a binary soln: (A+B)

$$v = \frac{C_A u_A + C_B u_B}{C_A + C_B}$$

$$u = \frac{P_A u_A + P_B u_B}{P_A + P_B}$$

$$N_A = C_A u_A$$

$$N_B = C_B u_B$$

$$J_A = N_A - \frac{C_A}{C} (N_A + N_B)$$

Fick's Law

Molar flux of a species relative to an observer moving with the molar average velocity is proportional to conc. gradient of the species

$$J_A \propto \frac{dC_A}{dx}$$

$$\Rightarrow J_A = - D_{AB} \frac{dC_A}{dx}$$

D_{AB} → Diffusion co-efficient or diffusivity of A in a mixture of A and B.

The diffusion occurs spontaneously in the direction of decreasing concentration, the -ve sign is incorporated

J_A is w.r.t an observer moving with molar average velocity.

$$D_{AB} = \frac{J_A}{(dC_A/dx)} = \frac{\text{mol/m}^2\text{s}}{(\text{mol/m}^3/\text{m})} = \text{m}^2/\text{s}$$

$$U = \frac{1}{c} (N_A + N_B), \quad N_A = C_A U_A, \quad N_B = C_B U_B$$

$$J_A = - D_{AB} \frac{dC_A}{dx} = C_A (U_A - U)$$

$$= C_A U_A - C_A U$$

$$= N_A - \frac{C_A}{c} (C_A U_A + C_B U_B)$$

$$= N_A - \frac{C_A}{c} (N_A + N_B)$$

$$\therefore N_A = - D_{AB} \frac{dc_A}{dx} + \frac{c_A}{c} (N_A + N_B) \quad \text{--- (1)}$$

$$N_B = - D_{BA} \frac{dc_B}{dx} + \frac{c_B}{c} (N_A + N_B) \quad \text{--- (2)}$$

From (1), (2)
 Molecular Diffusion Bulk Flow

$$(N_A + N_B) = - \left(D_{AB} \frac{dc_A}{dx} + D_{BA} \frac{dc_B}{dx} \right) + \left(\frac{c_A + c_B}{c} \right) (N_A + N_B)$$

Considering Binary closed soln,
 $\therefore D_{AB} = D_{BA}$

Fick's law in terms of Chemical Potential,

$$\begin{aligned} \mu_A &= \mu_A^\circ + RT \ln a_A \\ &= \mu_A^\circ + RT \ln (r_A c_A) \end{aligned}$$

$$\frac{d\mu_A}{dx} = \frac{RT}{c_A} \frac{dc_A}{dx}$$

$$J_A = - D_{AB} \frac{c_A}{RT} \frac{dc_A}{dx}$$

Analogy with Fourier's law and Newton's law

$$\tau_{zz} = - \mu \frac{du}{dz}$$

The shear stress in a viscous fluid in laminar motion can be shown to be equivalent to the flux of momentum from a faster-moving layer to an adjacent slower moving one.

$$q_z = -k \frac{dT}{dz}$$

In heat conduction ("diffusion of heat") the flux of thermal energy is prop. to temp. gradient

Diffusion velocity

$$V_{A,d} = u_A - U = \frac{J_A}{c_A} = - \frac{D_{AB}}{c_A} \frac{dc_A}{dx}$$

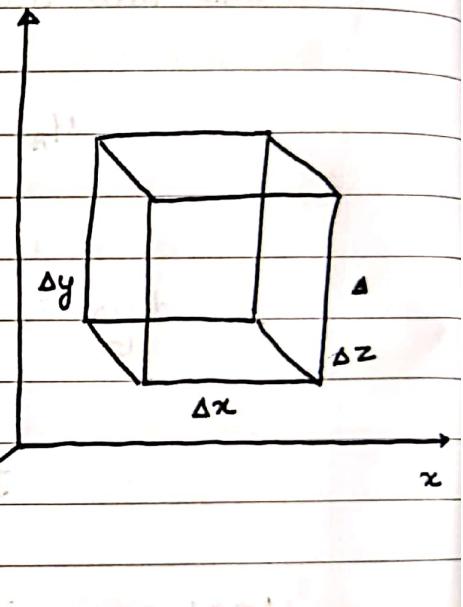
Mass Balance

For x-direction,

$$\text{In Mass in} = \rho v_x \Delta y \Delta z |_{x,z} \quad \text{at } T_B$$

$$\text{Mass out} = \rho v_x \Delta y \Delta z |_{x+\Delta x} \quad \text{at } T_A$$

$$\text{Accumulation} = (\rho v_x)_x - \rho v_x|_{x+\Delta x} \quad \frac{\Delta y \Delta z}{\Delta t}$$



Similarly for y-direction and z-direction

$$\text{Accumulation} = \frac{dm}{dt} = \frac{\partial \rho}{\partial t} \Delta x \Delta y \Delta z$$

$$\Delta m = \Delta x \Delta y \Delta z \frac{\partial \rho}{\partial t}$$

$$(\rho v_x)_x - \rho v_x|_{x+\Delta x} \Delta y \Delta z + (\rho v_y)_y - \rho v_y|_{y+\Delta y} \Delta x \Delta z \\ + (\rho v_z)_z - \rho v_z|_{z+\Delta z} \Delta y \Delta x = \Delta x \Delta y \Delta z \frac{\partial \rho}{\partial t}$$

$$\frac{1}{\Delta x} (PV_x|_x - PV_x|_{x+\Delta x}) + \frac{1}{\Delta y} (PV_y|_y - PV_y|_{y+\Delta y}) + \frac{1}{\Delta z} (PV_z|_z - PV_z|_{z+\Delta z}) = \frac{\partial P}{\partial t}$$

Taking $\Delta x, \Delta y, \Delta z \rightarrow 0$

$$-\frac{\partial PV_x}{\partial x} - \frac{\partial PV_y}{\partial y} - \frac{\partial PV_z}{\partial z} = \frac{\partial P}{\partial t}$$

$$\frac{\partial PV_x}{\partial x} + \frac{\partial PV_y}{\partial y} + \frac{\partial PV_z}{\partial z} + \frac{\partial P}{\partial t} = 0$$

↳ Total continuity equation

$\nabla \cdot \vec{PV} + \frac{\partial P}{\partial t} = 0$ + Eqn: that can be used for all co-ordinate

systems

Fick's second law of diffusion

In rectangular co-ordinates,

$$\frac{\partial C_A}{\partial t} = D_{AB} \left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2} \right)$$

However, we approach to this eqn: considering no fluid motion, no consumption or generation and const. diffusivity and density

$$\frac{\partial C_A}{\partial t} = D_{AB} \nabla^2 C_A$$

If only density & diffusivity are const.

$$-D_{AB} \nabla^2 C_A + V \nabla \cdot C_A + \frac{\partial C_A}{\partial t} - R_A = 0$$

If no consumption/generation along with const. P, D

$$-D_{AB} \nabla^2 C_A + V \nabla \cdot C_A + \frac{\partial C_A}{\partial t} = 0$$

Steady State Molecular Diffusion through a const. area

For gaseous mixture at const. P, T, (C, D_{AB} are const., independent of position & comp.)

$$N_A = -CD_{AB} \frac{dy_A}{dx} + y_A N$$

$$\Rightarrow - \frac{dy_A}{N_A - y_A N} = \frac{dx}{CD_{AB}}$$

$$\text{At } x = x_1, \quad y_A = y_{A1}$$

$$\text{At } x = x_2, \quad y_A = y_{A2}$$

$$\text{Let } z = N_A - y_A N$$

$$\Rightarrow - \frac{dy_A}{N_A - y_A N} = \frac{dz}{N}$$

$$\int_{z_1}^{z_2} \frac{dz}{N} = \int_{x_1}^{x_2} \frac{dx}{CD_{AB}}$$

$$\ln \left[\frac{N \left(\frac{N_A}{N} - y_{A2} \right)}{N \left(\frac{N_A}{N} - y_{A1} \right)} \right] = \frac{N}{CD_{AB}} (x_2 - x_1)$$

$$N_A = \frac{N}{N} \frac{CDAB}{x_2 - x_1} \ln \left(\frac{\frac{N_A}{N} - y_{A_2}}{\frac{N_A}{N} - y_{A_1}} \right)$$

Steady state diffusion through non-diffusing B

$$N_A = N$$

$$\rightarrow N_A = \frac{CDAB}{x_2 - x_1} \ln \left(\frac{1 - y_{A_2}}{1 - y_{A_1}} \right)$$

For mixture of ideal gases, $y_A = \frac{P_A}{P_t}$

$$N_A = \frac{D_{AB} P_t}{(x_2 - x_1) RT} \ln \left(\frac{P_t - P_{A_2}}{P_t - P_{A_1}} \right)$$

For a binary mixture, $P_t = P_A + P_B$

$$P_{A_1} - P_{A_2} = P_{B_2} - P_{B_1}$$

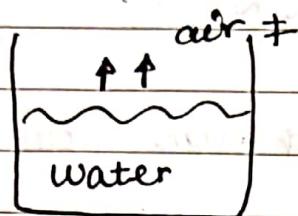
$$N_A = \frac{D_{AB} P_t}{RT (x_2 - x_1)} (P_{A_1} - P_{A_2})$$

$$P_{BLM} = \frac{P_{B_2} - P_{B_1}}{\ln \left(\frac{P_{B_2}}{P_{B_1}} \right)}$$

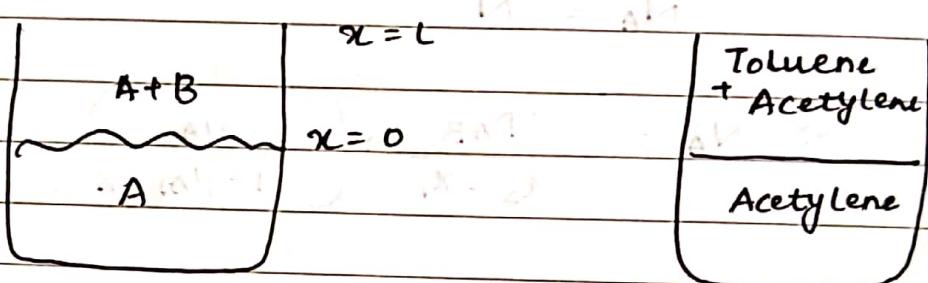
\rightarrow Comp. A diffused by conc. gradient $\frac{\partial y_A}{\partial x}$

\rightarrow Flux $\propto 1/P_{BLM}$

Consider steady state, binary, homogeneous single phase, non-reactive system



$A \rightarrow$ diffusing
 $B \rightarrow$ non-diffusing



$$N_A = - D_{AB} \frac{dc_A}{dx} + \frac{C_A}{C} (C_{NA} + N_B)$$

$$\text{At } x=0, C_A = C_{A_1}, \quad N_B = 0 \\ x=L, \quad C_A = C_{A_2}$$

$$N_A = - D_{AB} \frac{dc_A}{dx} + \frac{C_A N_A}{C}$$

$$N_A \int dx = - D_{AB} \cdot C \int \frac{dc_A}{C - C_{A_2}}$$

$$\therefore N_A = \frac{D_{AB} \cdot C}{L} \ln \left(\frac{C - C_{A_2}}{C - C_{A_1}} \right)$$

$$N_A = \frac{D_{AB} \bar{C}}{L C_{Bm}} (C_{A_1} - C_{A_2})$$

$$C_{Bm} = \frac{C_{B_2} - C_{B_1}}{\ln \left(\frac{C_{B_2}}{C_{B_1}} \right)}$$

← Mass transfer co-efficient

In reality,

$$N_A \rightarrow \text{const.}$$

$$L \rightarrow L \gg \Delta L$$

$$N_A = \frac{D_A c}{c - c_A} \frac{dc_A}{dx} \quad \frac{dN_A}{dx} = 0$$

$$d \left(\frac{D_A c}{c - c_A} \frac{dc_A}{dx} \right) = 0$$

$$\frac{dc_A}{dx(c - c_A)} = \frac{1}{D_A} \Rightarrow \ln(c - c_A) = -\frac{1}{D_A} x + C_2$$

$$\frac{c - c_A}{c - c_{A_1}} = \left(\frac{c - c_{A_2}}{c - c_{A_1}} \right)^{x/L}$$

$$y_A = \frac{c_{A_1}}{c}$$

$$N_A = \frac{D_{AB} c}{L(c_B)_{cm}}$$

$$y_B = \frac{c_{A_2}}{c}$$

For gas

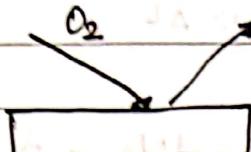
$$N_A = \frac{D_{AB} c}{L} \left[\frac{y_{A_1} - y_{A_2}}{(y_B)_{cm}} \right]$$

$$N_A = \frac{D_{AB} P}{RT L} \left[\frac{P_{A_1} - P_{A_2}}{(P_B)_{cm}} \right]$$

For liquid

$$N_A = \frac{P_{AB} c}{R} \left[\frac{x_{A_1} - x_{A_2}}{(x_B)_{cm}} \right]$$

Case 2: Equimolar Diffusion



$$C + O_2 = CO_2$$

$$N_A = N_B$$

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

$$\therefore N_A = - D_{AB} \frac{(C_{A1} - C_{A2})}{L}$$

$$\frac{dN_A}{dx} = 0$$

$$C_A = - \frac{C_1 - x_L + C_2}{D_{AB}}$$

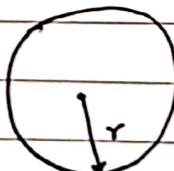
$$\therefore N_A = \frac{D_{AB} C}{L} \left[\frac{x_{A1} - x_{A2}}{x_{B1} - x_{B2}} \right]$$

$$\text{Case 3: } N_A = - s N_B, s \neq 1$$

Variable Area

① A ↑, B ↓

a) spherical geometry

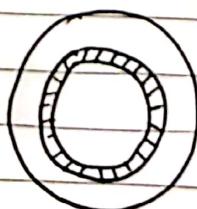


$$At t = t, r = r, C = C_{As}$$

$$t = 0, r = R_{so}$$

$$t = t_f, r = R_{sf}$$

$$t = 0, r = \infty, C_A = C_{A,\infty}$$



From shell balance

$$N_A A = \text{const.}$$

$$N_A (4\pi r^2) = \text{const.} \\ = W$$

$$N_A = - \frac{P_{AB} C}{C - C_A} \frac{dC_A}{dr}$$

$$\int_0^\infty \frac{w dr}{4\pi r^2} = - P_{AB} C \int_{C_{A,S}}^{C_0} \frac{dC_A}{C - C_A}$$

$$\frac{w}{4\pi r} = + P_{AB} C \left[\ln \left(\frac{C}{C - C_A} \right) \right]_{C_{A,S}}^{C_0}$$

$$\text{done so } w = 4\pi P_{AB} r \ln \left(\frac{C}{C - C_{A,S}} \right) \quad C_{A,S} \rightarrow 0$$

$$C - C_{A,S} = \cancel{C} \cdot e^{-4\pi P_{AB} C r}$$

$$C_{A,S} = C \left(1 - e^{-4\pi P_{AB} C r} \right)$$

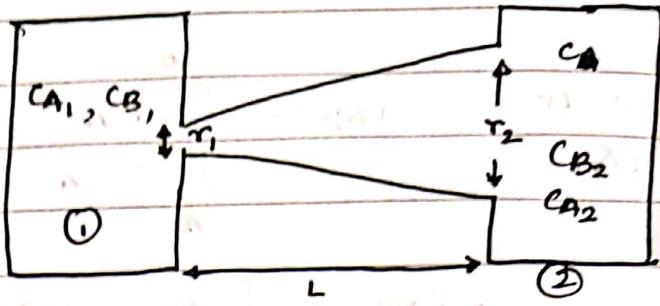
$$\therefore w = 4\pi P_{AB} C \left[\ln \left(\frac{C - C_{A,S}}{C - C_{A,S}} \right) \right] r$$

$$w = - \frac{d}{dt} \left(\frac{4}{3} \pi r^3 \frac{P_A}{M_A} \right)$$

$$-4\pi P_{AB} C r \ln \left(\frac{C - C_{A,S}}{C - C_{A,S}} \right) = 4\pi \left(\frac{P_A}{M_A} \right) r$$

$$\therefore t = \frac{r_0^2}{2} \frac{P_A}{M_A C P_{AB} \ln \left(\frac{C - C_{A,S}}{C - C_{A,S}} \right)}$$

Tapered Tube



$c_{A1} > c_{A2} \rightarrow A$ diffuses from ① to ②
maintained at same temp
and pressure

$$N_A \pi r^2 = W$$

$$N_A = - D_{AB} \frac{dc_A}{dx}$$

$$\frac{W}{\pi} \frac{dx}{r^2} = - D_{AB} dc_A$$

$$r = r_1 + \frac{x}{L} (r_2 - r_1)$$

$$\frac{W}{\pi} \int_0^L \frac{dx}{(r_1 + \frac{x}{L} (r_2 - r_1))^2} = - D_{AB} \int_{c_{A1}}^{c_{A2}} dc_A$$

$$\therefore W = \pi D_{AB} \frac{r_1 r_2}{c} (c_{A1} - c_{A2})$$

Depletion Time (Binary steady state)

Case - 1

Diff. surface area is large
compared to depth

Case - 2

Diff. surface area is small
compared to depth

Amt. present $t = \frac{A d \rho_A / M_A}{N_A}$

Flux



$$N_A = \frac{D_{AB} C}{L c_{Bm}} (c_{A1} - c_{A2})$$

$$N_A \cdot A = \frac{D_{AB}}{L} (c_{A1} - c_{A2})$$

Gas Phase Diffusivity

Kinetic Theory of Gases

$$\text{D}_{\text{AA}^+} = \frac{1}{3} \frac{\lambda_{\text{AA}}}{\lambda_{\text{A}}} \cdot \frac{\text{Mean free path}}{\text{Mean speed}}$$

self-diffusivity

$$\lambda_{\text{A}} = \frac{kT}{\sqrt{2} \pi \sigma_{\text{A}}^2 P}$$

Lennard Jones dia

$$\lambda = \sqrt{\frac{8kNT}{\pi M_A}}$$

From ①, ②, ③

$$\text{D}_{\text{AA}^+} = \frac{2}{3} \left(\frac{k}{\pi} \right)^{1/3} N^{1/2} T^{3/2} \left(\frac{(Y_{\text{A}})^{1/2}}{P \sigma_{\text{A}}^2} \right)$$

Lennard Jones diameter

For diffusivity of A in B

$$\text{D}_{\text{AB}} = \frac{2}{3} \left(\frac{k}{\pi} \right)^{1/3} N^{1/2} T^{3/2} \left(\frac{\left(\frac{1}{2M_A} + \frac{1}{2M_B} \right)^{1/2}}{P \left(\sigma_{\text{A}/2}^2 + \sigma_{\text{B}/2}^2 \right)} \right)$$

However, this eqn. is applicable only to ideal gas, since intermolecular forces aren't accounted for, it's a non-polar system.

For real gases,

$$\text{D}_{\text{AB}} = \frac{\left(\frac{2}{3} \right) \left(\frac{k}{\pi} \right)^{3/2}}{\Omega_D} \frac{N^{1/2} T^{3/2}}{P \sigma_{\text{AB}}^2} \left[\frac{1}{2M_A} + \frac{1}{2M_B} \right]^{1/2}$$

↑ Leonard Jones Parameters

Hirshmen

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

const = 0.001858 (CGS units)

in cm^2/s

$$\sigma_{AB} = f \left(\frac{kT}{\epsilon_{AB}} \right)$$

$$\epsilon_{AB} = (\epsilon_A \cdot \epsilon_B)^{1/2}$$

↳ Lennard Jones' parameters

Diffusivity is dependent on temp., P, M_i , nature of the molecules

The eqn. is arrived to, at considering non-polar system (previously). Hirshmen eqn. considers non-polar nature (ω_D)

$$D_{AB} = \frac{1.858 \times 10^{-7} T^{3/2}}{P \sigma_{AB}^2 \omega_D} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2}$$

↳ $\sigma_A/2 + \sigma_B/2$

We get ϵ values from table 2.2.

If the data table isn't available, then we can get the value of ϵ from V_b , T_b , T_c , V_c & P_c data.

$$\sigma = 1.18 V_b^{1/3}$$

$x_c \rightarrow$ critical "x"

$$\sigma = 0.841 V_c^{1/3}$$

$$\sigma = 2.44 \left(\frac{T_c}{P_c} \right)^{1/3}$$

$$\epsilon_A/k = 0.77 T_c$$

Fuller eqn:

$$D_{AB} = \frac{10^{-3} T^{1.75}}{P} \left[\frac{1/M_A + 1/M_B}{(\sum v_A)^{1/3} + (\sum v_B)^{1/3}} \right]^{1/2}$$

If A is CO_2

$$(\sum v_A) = v_c + 2 v_0$$

$v_A \rightarrow$ summation of atomic vol. of all comp.

Factor affecting gas phase diffusivity

- Temperature
- Pressure
- Mol. wt.
- Any other parameters affecting intermolecular force or non-ideality such as chemical nature

$$\frac{D_{AB} I_1}{D_{AB} I_2} = \left(\frac{T_1}{T_2} \right)^{1.5} \left(\frac{P_2}{P_1} \right) \left(\frac{\sigma_{D_2}}{\sigma_{D_1}} \right)$$

σ_D increased with temp. as $\sigma_D = f \left(\frac{kT}{E_{AB}} \right)$

Depletion

Multicomponent Diffusion

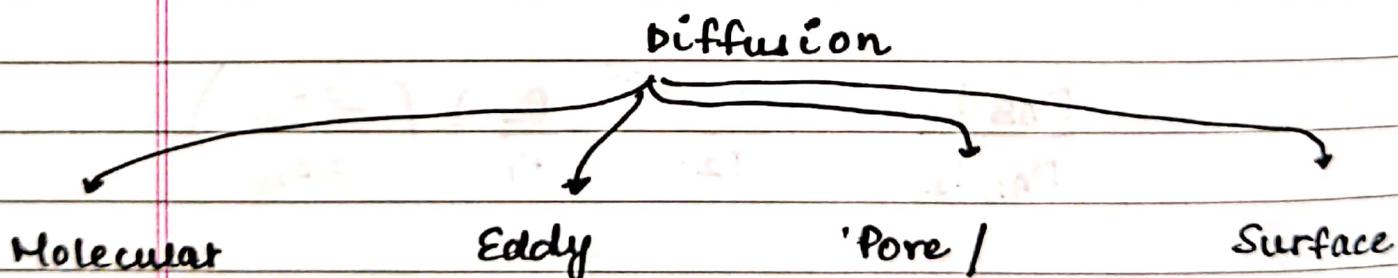
If only A is diffusing and all others aren't,

$$D_{AM} = \frac{1}{\sum_{i=2}^n \frac{y'_i}{D_{Ai}}} = \frac{1}{\frac{y'_B}{D_{AB}} + \frac{y'_C}{D_{AC}} + \dots}$$

$$D_{AN} = \frac{1}{\frac{y_B / (1-y_A)}{D_{AB}} + \frac{y_C / (1-y_A)}{D_{AC}} + \dots}$$

$$y'_B = \frac{y_B}{1-y_A}, \quad y'_C = \frac{y_C}{1-y_A}$$

$$J = -D_{AM} \frac{dc_A}{dx}$$



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

$$N_A = (HTE)(DF)$$

$$J_A = -D_{eff} \frac{dc_A}{dx}$$

$$J_A = -D_{AS} \frac{dc_A}{dx}$$

Knudsen diffusivity based on kinetic theory of gases

$$D_K = \frac{2}{3} r_p v \rightarrow \text{avg. velocity of molecules}$$

\hookrightarrow radius of passage

$$2r_p = d \text{ or } d_{\text{pore}}$$

$$v = \left(\frac{8RT}{\pi M} \right)^{1/2} \quad T \rightarrow \text{Temp.} \\ M \rightarrow \text{Molecular wt.}$$

$$J_K = - P_K \frac{dc_A}{dx} = - \frac{D_K}{RT} \frac{dp_A}{dx}$$

$$P_{AA} = \frac{1}{3} d_{\text{pore}} \sqrt{\frac{8kNT}{\pi M_A}}$$

$$D_{KA} = 4850 d_{\text{pore}} \sqrt{\frac{T}{M_A}}$$

$$\frac{1}{D_{AE}} = \frac{1 - \alpha y_A}{D_{AB}} + \frac{1}{D_{KA}}$$

↓

effective diff.

when both

mol. and Knud.

diff. are present

$$\alpha = 1 + \frac{N_B}{N_A}$$

For Knudsen diffusion, $d_{\text{pore}} < v$

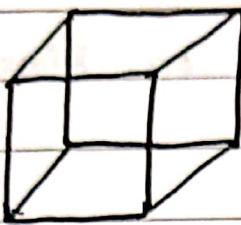
$$k_n = \lambda / d_{\text{pore}}, \quad k_n \rightarrow \text{Knudsen number}$$

$$J_A = - \frac{P_{KA}}{\tau} \frac{dc_A}{dx} \quad \tau \rightarrow \text{tortuosity}$$

~ porosity correction factor $\frac{1}{\tau} = \frac{\text{torus vol}}{\text{actual vol}}$

$$\epsilon = V_{\text{eff}} / V_T, \quad J_A = - \frac{D_{KA} \epsilon}{\tau} \frac{dc_A}{dx} \quad \text{Actual len}$$

Proof of Fick's 2nd law,



Rate of

$$(\text{moles in} - \text{moles out} + \text{moles gen}) = \text{Rate of moles accumulated}$$

$$\begin{aligned}
 & \left(N_A|_x - N_A|_{x+\sigma^z} \right) \sigma^y \sigma^z + \left(N_A|_y - N_A|_{y+\sigma^z} \right) \sigma^x \sigma^y \\
 & + \left(N_A|_z - N_A|_{z+\sigma^z} \right) \sigma^x \sigma^y + R_A \sigma^x \sigma^y \sigma^z \\
 & = \frac{d}{dt} (C_A \sigma^x \sigma^y \sigma^z)
 \end{aligned}$$

For steady state, binary, non-reacting system and const-area

$$-\frac{dN_A}{dx} + R_A = \frac{dC_A}{dt}$$

$$\frac{dN_A}{dx} = 0$$

$J_A = C_A (v_A - v)$, for $v=0$, there is no bulk convective flow

$$\frac{dJ_A}{dx} = 0 \Rightarrow \frac{d^2C_A}{dx^2} = 0$$

Liquid Phase Diffusivity

Eyring's Theory

Ideal liquid is treated as quasi-crystalline lattice interspersed with holes. Diffusion occurs due to jumping of solute molecules into holes within the lattice.

Hydrodynamic Theory relates b/w force and velocity.

$$\frac{D_{AB} \mu_B}{T} = f(v_A)$$

\downarrow v_A Molar vol.

Applicable for conc. soln:

Based on above Wilke Chang proposed,

$$\frac{D_{AB} \mu_B}{T} = 7.4 \times 10^{-8} \left(\frac{\phi_B \mu_B}{v_A} \right)^{1/2} (D_{AB} \text{ in } \text{cm}^2/\text{s})^{2/3}$$

$\phi_B \rightarrow$ Association factor (from graph)

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

$$\frac{D_{AB} \mu_A}{T} = 1.173 \times 10^{-16} \left(\frac{\phi_B \mu_B}{v_A} \right)^{1/2} \text{ all are in SI units}$$

solute viscosity
for conc. soln:

Hayduk and laudi Correlation

$$D_{AB}^\circ = 13.26 \times 10^{-5} \mu_B^{-1.14} v_A^{-0.589} \quad \left. \begin{array}{l} \text{For dil.} \\ \text{soln's} \end{array} \right\}$$

$$D_{BA}^\circ = 13.26 \times 10^{-5} \mu_A^{-1.14} v_B^{-0.589}$$

$$D_{AB} \mu = (D_{AB}^\circ \mu_B)^{x_B} (D_{BA}^\circ \mu_A)^{x_A} \quad \left. \begin{array}{l} \text{For conc.} \\ \text{soln} \end{array} \right\}$$

Stoke's ϵ , Einstein eqn:

→ Based on hydrodynamical theory

→ For colloidal particles ϵ_1 large round molecules

$$D_{AB} = \frac{kT}{6\pi r \bar{M}_B}$$

Established the fact, $\frac{D_{AB} M_B}{r} = \text{const.}$

Factors affecting liquid phase diffusivity

→ Temperature

→ Viscosity

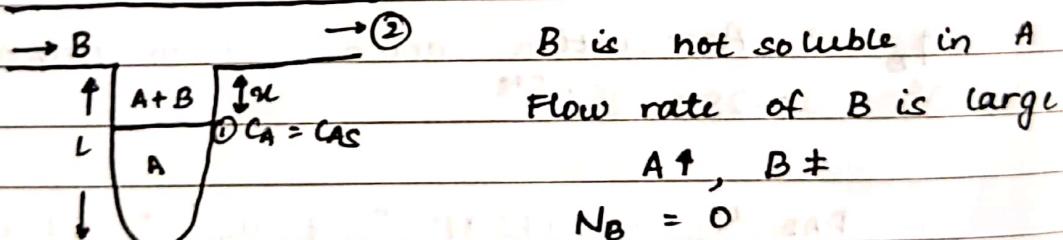
→ Concentration

→ Mol. wt.

→ Solvent - solute interaction parameter

Experimental Measurements

① Stefan Tube / Arnold Cell



A should be in liq. form

$$\text{At } t=0, x=x_1; C_{A1} = C_{AS} = C_A,$$

$$t=t_f, x=x_f; C_{A1} = 0 = C_{A2}$$

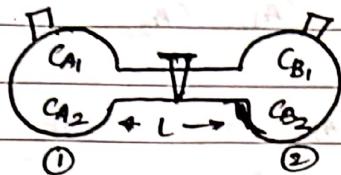
$$N_A = \frac{D_{AB} C}{CBM x} (C_{A1} - C_{A2})$$

$$\frac{d}{dt} \left(a(l-x) \frac{P_A}{M_A} \right) = -N_A a$$

$$\frac{P_A}{M_A} \int_{x_1}^{x_f} x dx = \frac{D_{AB} C}{CBM} (C_{A1} - C_{A2}) \int_0^{t_f} dt$$

$$\therefore \frac{\rho}{2M_A} (x_f^2 - x_i^2) = \frac{D_{AB}}{c_{BLM}} C t_f (C_{A_1} - C_{A_2})$$

② Twin Bulb



equimolar counter diffusion
as both bulbs are
maintained at same
pressure

$$\text{At } t=0, C_{A_1} = C_{A_0}, C_{A_2} = C_{A_20}$$

$$t = t_f, C_{A_1} = C_{A_{f1}}, C_{A_2} = C_{A_{f2}}$$

$$\underline{N_A} = \frac{D_{AB}}{L} (C_{A_1} - C_{A_2}) = - N_B$$

$$\frac{d}{dt} (V_1 C_{A_1}) = - N_A \cdot a$$

$$\frac{d C_{A_1}}{dt} = - \frac{a}{V_1} \frac{D_{AB}}{L} (C_{A_1} - C_{A_2}) \quad \text{--- (1)}$$

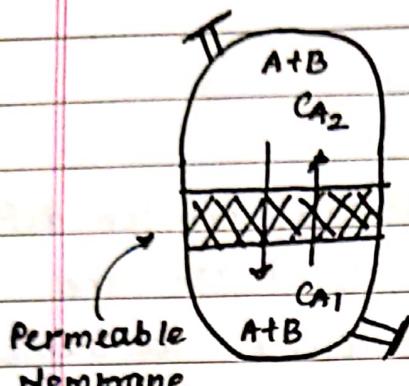
$$\frac{d (V_2 C_{A_2})}{dt} = \frac{a}{V_2} \frac{D_{AB}}{L} (C_{A_1} - C_{A_2}) \quad \text{--- (2)}$$

$$(\because N_A = - N_B)$$

Subtracting and Integrating,

$$\frac{C_{A_1} - C_{A_2}}{C_{A_1,0} - C_{A_2,0}} = \exp \left[- \frac{a D_{AB}}{L} \left[\frac{1}{V_2} + \frac{1}{V_1} \right] t_f \right]$$

③ Diaphragm Cell



$$t=0, \quad CA_1 = CA_{1,0}, \quad CA_2 = CA_{2,0}$$

$A \uparrow, B \downarrow$

$$t=t_f, \quad CA_{1,f}, \quad CA_{2,f}$$

$$\frac{CA_{1,f} - CA_{2,f}}{CA_1 - CA_2} = \frac{d(CA_1 - CA_2)}{l\tau} = -\frac{D_{AB} \alpha \epsilon}{l\tau} \left[\frac{1}{v_1} + \frac{1}{v_2} \right]$$

$$CA_{1,0} - CA_{2,0}$$

$l \rightarrow$ Thickness of diaphragm

$l\tau \rightarrow$ effective length of diffusion

$$-v_1 \frac{dCA_1}{dt} = \alpha \epsilon N_A, \quad v_2 \frac{dCA_2}{dt} = \alpha \epsilon N_A$$

$$\therefore D_{AB} = \frac{l\tau}{\alpha \epsilon t_f} \left(\frac{1}{v_1} + \frac{1}{v_2} \right)^{-1} \ln \left(\frac{CA_{1,0} - CA_{2,0}}{CA_{1,f} - CA_{2,f}} \right)$$

$$\text{Let } \beta = \frac{\alpha \epsilon}{l\tau} \left(\frac{1}{v_1} + \frac{1}{v_2} \right)$$

$$\therefore D_{AB} = \frac{1}{B t_f} \ln \left(\frac{CA_{1,0} - CA_{2,0}}{CA_{1,f} - CA_{2,f}} \right)$$

Surface Diffusion

$$\xrightarrow{000 \quad 0000} \quad J_A = -D_s \frac{dCA}{dx}$$

$D_s \rightarrow$ Diffusivity in surface