2) Prediction of diffusivity

❖ For gases

Theory : $D_v = \frac{1}{3}\bar{u}\lambda$

where, $\bar{u}$ is average molar velocity, λ is mean free path

Note, $\bar{u} \propto \frac{1}{P}, \therefore D_v \propto \frac{1}{P}, D_v \times P \sim$ constant (up to 1 atm)

* $\bar{u} \propto T^{0.5}, \lambda \propto T^{1.5}$

2) Prediction of diffusivity

Chapman-Enskog equation (for binary equation)

$$D_v (= D_{AB}) \left[\frac{cm^2}{s}\right] = \frac{0.001858\, T^{1.5} \left(\frac{M_A + M_B}{M_A M_B}\right)^{0.5}}{P[atm] \cdot \sigma_{AB}[\text{Å}]\Omega_D}$$

$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$: effective collision diameter

$\Omega_D = f(kT / \epsilon_{AB})$: collision integral

$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$

온도상승에 따라 감소하는 값
하지만, 300~1,000K 에서 크게 변화하지 않음
$\therefore D_v$ 전체를 근사하면 → $D_v \propto T^{1.75}$

Fuller equation

$$D_v (= D_{AB}) \left[\frac{cm^2}{s}\right] = \frac{1.0110 \times 10^{-3} \cdot T^{1.5}}{P\left[(\Sigma V_A)^{\frac{1}{3}} + (\Sigma V_B)^{\frac{1}{3}}\right]^2} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{0.5}$$

ΣV_i : Sum of diffusion volume of the component i
from table

2) Prediction of diffusivity

For pore size diffusion

- Knudsen diffusion : Diffusion in **VERY SMALL PORES**
  molecular collision on pore walls, the diffusivity → less than normal volume

pore size $\ll \lambda$, thus pore size determines the diffusivity

$$D_K = 9{,}700r\sqrt{T/M} \text{ (for cylindrical pores)}$$

- For intermediate-sized pores,
  collisions with both pore walls & other molecules

$$\frac{1}{D_{pore}} = \frac{1}{D_{AB}} + \frac{1}{D_K}$$

2) Prediction of diffusivity

❖ For liquids

Avg. travel dst. btw. collision is VERY LOW (→ λ 가 주로 분자크기보다 작음)
therefore, D_v in liquids are much smaller than those in gases.

$$D_v(l) \simeq 10^{-5} \sim 10^{-4} D_v(g)$$

But Densities of : GASES << LIQUIDS (→ @ atmos. pressure),
the fluxes for a given molar fraction gradient in liquid/gas may be nearly the same.

Stokes - Einstein equation : for Large & Spherical molecules in dilute solution

=> 유체의 흐름으로 인한 항력 (drag)' 고려
=> the simplest equation

$$D_v = \frac{kT}{6\pi r_o \mu} \simeq 7.32 \times 10^{-16} \frac{T}{r_o \mu} \qquad D_v \propto \frac{1}{V^{1/3}}$$

2) Prediction of diffusivity

Wilke-Chang equation : for solutes of small to moderate size,
=> the $D_v(l)$ becomes greater as the drag is less than predicted
.

➢ the empirical equation is:

$$D_v = 7.4 \times 10^{-8} \frac{T\sqrt{\psi_B M_B}}{V_A^{0.6}\mu}$$

$$D_v \propto \frac{1}{V^{1/6}}$$

A: solute, B: solvent

ψ_B: association parameter (to be given)

17.2 Turbulent diffusion

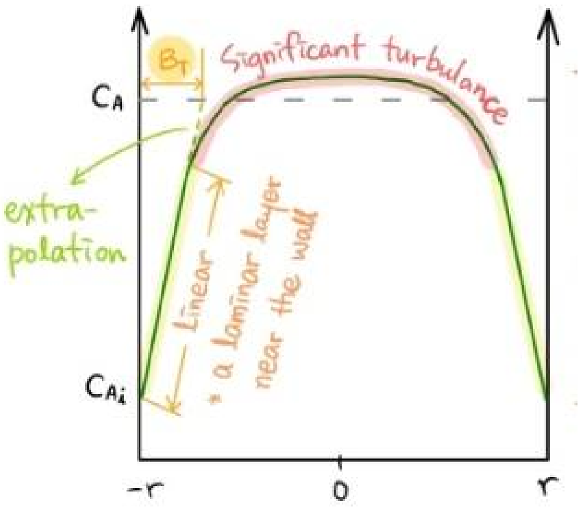
Turbulent → Eddies transport matter ! (transfer momentum & heat energy)

$$J_{A,m} = -D_v \frac{dC_A}{dz}$$

D_v → Diffusivity, physical property

$$J_{A,t} = -\varepsilon_D \frac{dC_A}{dz}$$

ε_D → Eddie Diffusivity of mass
NOT physical property
BUT flow pattern



$$J_A = J_{A,m} + J_{A,t} = -(D_v + \varepsilon_D)\frac{dC_A}{dz}$$

17.3 Mass transfer coefficient

$$N_A \propto \Delta C_A$$

$$N_A = k_c \Delta C_A$$

k_c → Mass transfer coefficient [m/s]

For gases

$$N_A = k_c \Delta C_A = k_y \Delta y_A$$

$$\therefore k_y = k_c C$$

$$N_A = k_G \Delta P_A$$

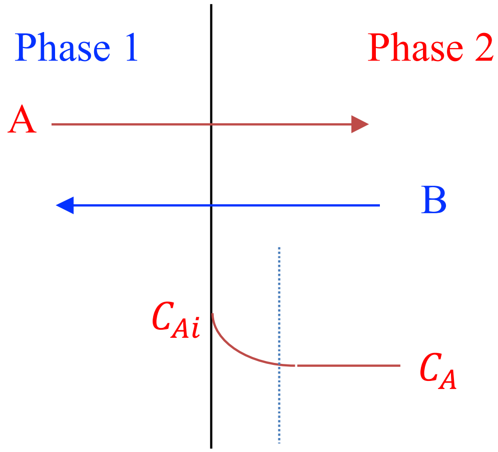
$$k_G = \frac{k_c}{RT} \left[\frac{kmol/m \cdot s}{N/m^2} \right]$$

For liquids

$$N_A = k_c \Delta C_A$$

$$= k_c C \Delta x_A = k_x \Delta x_A$$

$$\therefore k_x = k_c C$$



δ (film thickness)
Film theory

$$N_A = D_v \frac{\Delta C_A}{\delta} \left(= D_v C \frac{\Delta y_A}{\delta} \right)$$

$\frac{D_v}{\delta}$: mass transfer coefficient

17.3 Mass transfer coefficient

① equimolar diffusion

- $N_A = k_c \Delta C_A = k_y \Delta y_A$
- $N_A = D_v \frac{\Delta C_A}{\delta} = D_v C \frac{\Delta y_A}{\delta}$
- $k_c = \frac{D_v}{\delta},\ k_y = \frac{D_v}{\delta} \cdot C (= k_c \cdot C)$

② one-way diffusion

- $N_A = k_c' \Delta C_A = k_y' \Delta y_A$
- $N_A = D_v \frac{C}{\overline{(C - C_A)}_m} \frac{\Delta C_A}{\delta} \Rightarrow D_v \frac{1}{\overline{(1 - y_A)}_m} \frac{\Delta C_A}{\delta}$

  $= D_v C \frac{1}{\overline{(1 - y_A)}_m} \frac{\Delta y_A}{\delta}$
- $k_c' = \frac{D_v}{\delta} \frac{1}{\overline{(1 - y_A)}_m}, \dashrightarrow k_c' = k_c \frac{1}{\overline{(1 - y_A)}_m}$

  $k_y' = \frac{D_v \cdot C}{\delta} \frac{1}{\overline{(1 - y_A)}_m}, \dashrightarrow k_y' = k_y \frac{1}{\overline{(1 - y_A)}_m}$

  $\therefore \frac{k_y'}{k_y} = \frac{k_c'}{k_c} \frac{C}{C} \left(= \frac{1}{\overline{(1 - y_A)}_m} \right)$