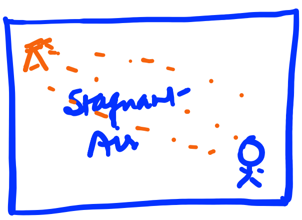
Lecture 3 : Molecular Diffusion

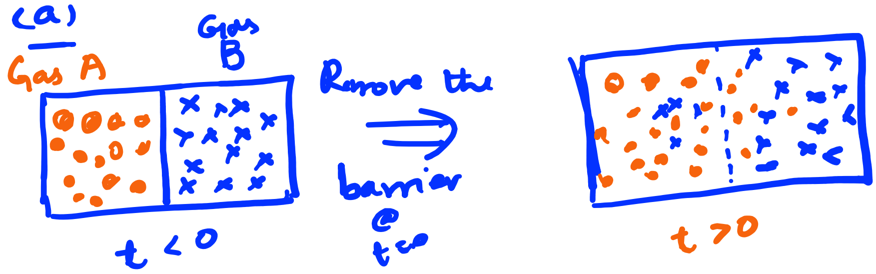


For large t : Homogeneous mixture

- Due to the random thermal motion of molecules, components in a mixture have the tendency to reduce conc. gradients

- Bulk mixing:

← Bulk mixing: Macroscopic movement of fluid elements

- 

Given enough time, a homogeneous mixture will be obtained.

- Gas / Liquids / Solids : In which case do you expect diffusion to be faster? (Given that molecular diffusion is due to random thermal motion).

Few Terminologies

(a) u_{ix} : Statistical mean average velocity of component 'i' in the x-direction w.r.t a stationary frame of reference.

(b) Mass average velocity of fluid mixture in x-dir w.r.t stationary frame :

Fluid mixture has 'n' components : $1, 2 \ldots n$

Mass avg. velocity of fluid mixture in x-dir w.r.t stationary frame.

$$u_x = \frac{1}{\sum_{i=1}^{n} \rho_i} \sum_{i=1}^{n} \rho_i u_{ix} \; ; \quad \rho_i = \text{mass of component } i \text{ per unit volume of solution}$$

$$\left| \; \sum_{i=1}^{n} \rho_i = \rho \text{ (Density of fluid mixture)} \right.$$

(c) Molar average velocity of fluid mixture w.r.t stationary frame

$$U_x = \frac{1}{\sum_{i=1}^{n} c_i} \sum_{i=1}^{n} c_i u_{ix} \; ; \quad c_i = \text{moles of component 'i' per unit volume of solution.}$$

$\sum c_i = c$: Total conc.

(d) Molar flux of component 'i' w.r.t stationary frame in x-dir

Quantity / area / time

$$\boxed{N_{ix} = c_i u_{ix}}$$

c_i : mol/m^3
u_{ix} : m/s

$c_i u_{ix}$: $\frac{mol}{m^3} \cdot \frac{m}{s}$ = mol/m^2.s

(e) Mass flux of component 'i' in x-dir w.r.t stationary frame

$n_{ix} = \rho_i u_{ix}$; Units : ____

(f) Mass flux w.r.t frame moving with mass average velocity

$$i_{ix} = \rho_i (u_{ix} - u_x)$$

mass flux of comp. i in x-dir w.r.t a frame moving with mass avg. velocity

mass avg. velocity in x-dir

f(g) Mass flux w.r.t frame moving with molar average velocity

$$j_{ix} = \rho_i (u_{ix} - U_x)$$

(h) Molar flux: in x-dir

a(i) w.r.t mass avg velocity in x

$$I_{ix} = c_i (u_{ix} - u_x)$$

c_i: molar conc.

(ii) w.r.t molar average velocity in x-dir

$$J_{ix} = c_i (u_{ix} - U_x)$$

$$J_{ix} = c_i(u_{ix} - U_x) = c_i u_{ix} - c_i U_x$$

$$= c_i u_{ix} - c_i \frac{1}{\underbrace{\sum_{i=1}^{n} c_i}_{(c)}} \sum_{i=1}^{n} c_i u_{ix}$$

$$= \underbrace{c_i u_{ix}}_{N_{ix}} - \frac{c_i}{c} \sum_{i=1}^{n} c_i u_{ix} :$$

mole fraction: c_i/c

$$\boxed{J_{ix} = N_{ix} - x_i \sum_{i=1}^{n} N_{ix}}$$

x_i: mole fraction of component i

Gas mixture with two components: A & B

$$J_{Ax} = N_{Ax} - x_A (N_A + N_B) \quad \text{— (i)}$$

$$J_{Bx} = N_{Bx} - x_B (N_A + N_B) \quad \text{— (ii)}$$

(i) & (ii) : $J_{Ax} + J_{Bx} = (N_{Ax} + N_{Bx}) - \underbrace{(x_A + x_B)}_{1} (N_{Ax} + N_{Bx})$

$$\Rightarrow J_{Ax} + J_{Bx} = 0$$

Mass avg. : Two component gas mixture

$$n_{Ax} = \cancel{J_{Ax}} + w_A (n_{Ax} + n_{Bx})$$

i_{Ax}

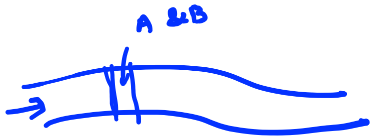
w_A: mass fraction: $w_A = \frac{\rho_A}{(\rho_A + \rho_B)} = \frac{\rho_A}{\rho}$

Correction

$$\boxed{n_{Ax} = i_{Ax} + w_A (n_{Ax} + n_{Bx})}$$

$\rightarrow \cancel{J_{Ax}} + \cancel{J_{Bx}} = 0 \leftarrow$ HW $\Rightarrow i_{Ax} + i_{Bx} = 0$

correction



$$J_{Ax} = N_{Ax} - x_A (N_{Ax} + N_{Bx})$$

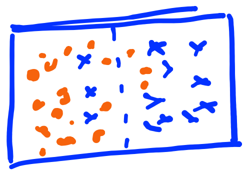
$N_{Ax} + N_{Bx} = N_x = c U_x \times \frac{c_A}{c} = c_A U_x$

$$\Rightarrow N_{Ax} = J_{Ax} + x_A (N_{Ax} + N_{Bx})$$

N_{Ax}: Molar flux of comp. A in x-dir w.r.t stationary frame

J_{Ax}: Flux which is due to molecular diffusion

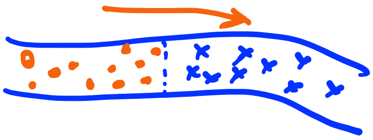
$x_A (N_{Ax} + N_{Bx})$: Molar flux due to the bulk motion of the fluid

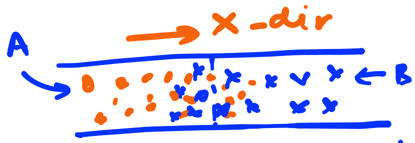


N_{Ax}: is a result of two vectors

(i) The flux caused by the bulk flow

(ii) Flux due to molecular diffusion

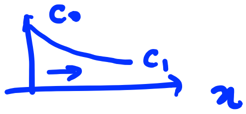




For A: Fluxes / vectors i & ii are in same dir. (x-dir)

For B: vectors (i) & (ii) are in opposite direction

Fick's law of diffusion: Gas mixture of two components (A & B)



$$J_{Ax} = -D_{AB} \frac{dC_A}{dx}$$

Diffusion coefficient / mass diffusivity

$$D_{AB}: \quad J_{Ax} / \left(\frac{dC_A}{dx}\right) \equiv \left(\frac{\text{moles}}{m^2 . s}\right) / \frac{\text{moles}}{m^3 . m} = m^2/s$$

i_{Ax} $\cancel{J_{Ax}} = -D_{AB} \frac{d\rho_A}{dx}$; i.e. $\boxed{i_{Ax} = -D_{AB} \frac{d\rho_A}{dx}}$

correction

$$J_{Ax} = c_A (u_{Ax} - U_x) = -D_{AB} \frac{dc_A}{dx}$$

$$i_{Ax}\ \cancel{j_{Ax}} = \rho_A(u_{Ax}-u_x) = -D_{AB}\frac{d\rho_A}{dx}$$

Correction

Generalized form: $J_{Ax} = -D_{AB}\frac{dC_A}{dx}$

$$= -D_{AB}\, c\, \frac{d(C_A/c)}{dx} = -D_{AB}\, c\, \frac{dx_A}{dx}$$

$$\underline{J_{Az}} = -D_{AB}\, c\, \frac{dx_A}{dz}\ ;\quad x_A = \text{Mole fraction}$$

Similarly, $i_{Az} = -D_{AB}\frac{d\rho_A}{dz} = -D_{AB}\,\rho\,\frac{d(\rho_A/\rho)}{dz}$

$$= -D_{AB}\,\rho\,\frac{d\omega_A}{dz} \quad \& \quad \omega_A: \text{Mass fraction}$$

We have made the following assumptions:

(i) We consider ordinary diffusion which occurs due to conc. gradient. Diffusion can also occur due to temp gradient, external forces, etc.

(ii) ~~j_{Ax}~~ i_{Ax}, J_{Ax} are w.r.t reference frame moving with mass avg & molar avg velocities in x dir. respectively.

Add
$$\left[\begin{array}{l} N_{Az} = x_A(N_{Az}+N_{Bz}) - D_{AB}\dfrac{dC_A}{dz} \\ N_{Bz} = x_B(N_{Az}+N_{Bz}) - D_{BA}\dfrac{dC_B}{dz} \end{array}\right.$$

$x_A + x_B = 1$

$\omega_A + \omega_B = 1$

$\rightarrow \underline{D_{AB} = D_{BA}}$; HW

For ideal gases: $PV = nRT$; $P = CRT$

$C = P/RT$

$C_A = P_A/RT$; $C_B = P_B/RT$

$P_A + P_B = P$ (Total pressure)

partial pressure of comp. A

partial pressure of comp. B

$$N_{Az} = \left(\frac{P_A}{P}\right)(N_{Az} + N_{Bz}) - \frac{D_{AB}}{RT}\frac{dP_A}{dz}$$