CHE 318 L07
Jan-19 2026

Recap

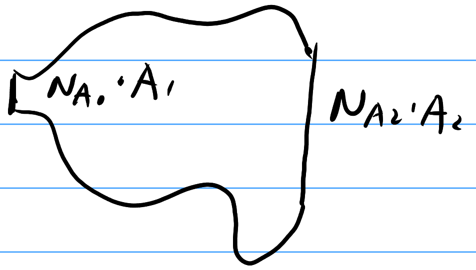
1° Steady State diffusion eq

2° Examples with steady state { gas / liquid / solid

3. Usage of { weight % form / log-mean form / pressure – solubility – permeability

Diffusion through varying cross-section areas

Steady state : In · Area_in − Out · Area_out = 0

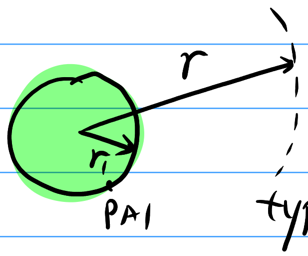


$$N_{A1} \cdot A_1 = N_{A2} \cdot A_2$$

Can be used to solve diffusion through
① sphere
② cylinder
③ tube with varying dia.
④ ······ (Any given $A = A(z)$ system)

$$\text{mole/s} \leftarrow \text{Let } \bar{N_A} = N_A \cdot A \rightarrow \text{area}$$

Case 1: through sphere



Which condition? 1) Steady state
2) Stagnant B

typical case: evaporation of droplet
sublimation of solid organic sphere

Governing equation (see stag B)

Do not use the full solution for 1D! Use the ODE form

$$N_A = -\frac{D_{AB}}{RT}\frac{dP_A}{dr} + \frac{P_A}{P_T}N_A \quad \left(\begin{array}{c}\text{Spherical} \\ \nabla\psi|_r = \frac{\partial\psi}{\partial r}\end{array}\right)$$

$$N_A\left(1 - \frac{P_A}{P_T}\right) = -\frac{D_{AB}}{RT}\frac{dP_A}{dr}$$

$$\begin{cases} N_A(r) \text{ is changing} \longrightarrow \text{Cannot appear in L.H.S} \\ \overline{N_A}(r) = N_A \cdot 4\pi r^2 \text{ is constant} \rightarrow \text{OK. for L.H.S} \end{cases}$$

$$\frac{\overline{N_A}\, dr}{4\pi r^2} = -\frac{D_{AB}}{RT} \frac{1}{1-\frac{p_A}{P_T}}\, dp_A$$

$\Downarrow$

Integrate

$$\int_{r_1}^{r_2} \frac{\overline{N_A}}{4\pi r^2}\, dr = -\int_{p_{A1}}^{p_{A2}} \frac{D_{AB}}{RT} \frac{1}{1-\frac{p_A}{P_T}}\, dp_A$$

$$\frac{\overline{N_A}}{4\pi}\left(-\frac{1}{r}\right)\Bigg|_{r_1}^{r_2} = \cancel{-}\frac{D_{AB}}{RT} \cdot P_T \cdot \cancel{-} \ln(1-p_A)\Bigg|_{p_{A1}}^{p_{A2}}$$

$$\frac{\overline{N_A}}{4\pi}\left(\frac{1}{r_1}-\frac{1}{r_2}\right) = \frac{D_{AB} P_T}{RT} \ln\left(\frac{P_T - p_{A2}}{P_T - p_{A2}}\right)$$

Conditions

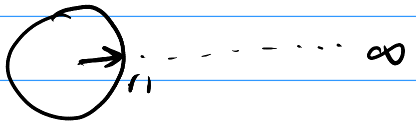
1) p_{A1} : equilibrium pressure / vapor pressure at interface

p_{A2} : $\begin{cases} \text{partial pressure at far end} \\ \text{Could be } 0 \text{ if } r \to \infty \end{cases}$

We can simplify this equ. for some conditions

① $r_2 \gg r_1 \quad (r_2 \to \infty)$

example droplet evaporating / naphthalene sphere sublimatio



Use the P_{Bm} term, we have

$$\frac{\overline{N_A}}{4\pi} \cdot \frac{1}{r_1} = \frac{D_{AB}}{RT} \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2})$$

$$N_{A1} = \frac{\overline{N_A}}{4\pi r_1^2} = \frac{D_{AB}}{RT} \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2}) \cdot \frac{1}{r_1}$$

(Do we have the correct unit ?)

(looks like diffusion through sphere of radius r_1 has the same flux as through stagnant film with thickness $= r_1$)

If $P_{A1} \ll P_T \Rightarrow P_{Bm} \simeq P_T$

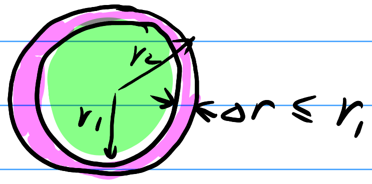
Use C_A form ($P_A = C_A RT$)

$$N_{A1} = \frac{D_{AB}}{r} \cdot (C_{A1} - C_{A2})$$

↳ more used in liquid

② If $\Delta r = r_2 - r_1 \ll r_1$ (thin membrane through sphere)

$$\frac{1}{r_1} - \frac{1}{r_2} = \frac{r_2 - r_1}{r_1 r^2} \simeq \frac{\Delta r}{r_1^2}$$



$4\pi r_1^2 \cdot N_A$

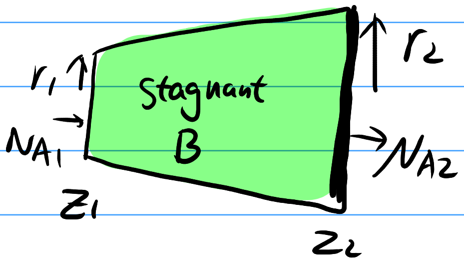
$$\frac{N_A}{4\pi}\underbrace{\left(\frac{1}{r_1} - \frac{1}{r_2}\right)}_{\Delta r / r_1^2} = \frac{D_{AB} P_T}{RT} \ln\left(\frac{P_T - P_{A2}}{P_T - P_{A2}}\right)$$

$$\frac{\cancel{4\pi} \cancel{r_1^2} \cdot N_A}{\cancel{4\pi}} \cdot \frac{\Delta r}{\cancel{r_1^2}} = \frac{D_{AB}}{RT} \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2})$$

$$N_A = \frac{D_{AB}}{RT} \cdot \underbrace{\frac{1}{\Delta r}}_{\text{membrane thickness}} \cdot \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2})$$

membrane thickness ! just like 1D stagnant B solution

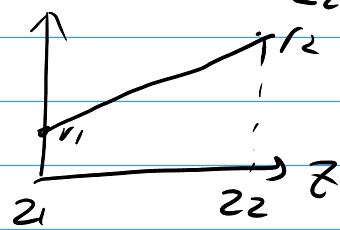
Case 2 Diffusion through non-uniform area conduit



Again, use the ODE form of N_A

$r(z)$ profile: linear

$$r(z) = \left(\frac{r_2 - r}{z_2 - z_1}\right) \cdot z + r_1$$



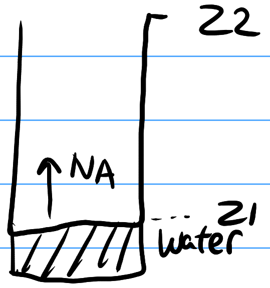
$$\frac{\overline{N_A}}{\pi r^2} = -\frac{D_{AB}}{RT} \frac{dp_A}{\left(1 - \frac{p_A}{p_T}\right)}$$

↳ Solve

$$\frac{\overline{N_A}}{\pi} \int_{z_1}^{z_2} \frac{dz}{\left[\left(\frac{r_2 - r_1}{z_2 - r_1}\right) z + r_1\right]^2} = -\frac{D_{AB}}{RT} \int_{p_{A1}}^{p_{A2}} \frac{dp_A}{1 - \frac{p_A}{P}}$$

Can you solve this ?

Example 3 (6.2-3) Diffusion with change path length



Water evaporates → level decrease

time of level drop from z_0 to z_F (t_F)

1. Draw scheme

2. which condition? Stagnant B

3. Which assumption?

$\boxed{\text{Pseudo steady state}}$ ⇒ 1) Flux at each t follows Stagnant B
2) $t \to t + \Delta t$ $z_2 - z_1$ increases

4. Governing eq (using log-mean pressure form)

at each t $\quad N_A = \dfrac{D_{AB}}{RT(z_2 - z_1)} \cdot \dfrac{P_T}{P_{Bm}} (P_{A1} - P_{A2})$

$P_{Bm} = \dfrac{P_{B1} - P_{B2}}{\ln \frac{P_{B1}}{P_{B2}}}$ $\quad P_{A1}$: vapor pressure $\quad P_{A2} = 0$ dry air

Mass balance

In − Out + Gen = Acc

$0 - N_A + 0 = -\dfrac{(\text{mass loss})}{(\text{time})}$

$\cancel{S} \cdot N_A \cdot dt = \dfrac{\cancel{S} \cdot dz \cdot \rho_A}{M_A}$ and sur

Integrate

$$\dot{N}_A \cdot dt = \frac{dz \cdot \rho_A}{M_A}$$

$$\frac{D_{AB}\ dt}{RT\ z} \cdot \frac{P_T}{P_{Bm}} \cdot (P_{A1} - P_{A2}) = \frac{\rho_A}{M_A} dz$$

$$\int_{z_0}^{z_F} z\, dz = \int_0^{t_F} \frac{D_{AB}\ M_A}{RT\ \rho_A} \cdot \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2})\, dt$$

$$\Rightarrow \frac{1}{2}(z_F^2 - z_0^2) = \frac{D_{AB}\ M_A}{RT\ \rho_A} \cdot \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2})\ t_F$$

Rearrange

$$t_F = \frac{\rho_A (z_F^2 - z_0^2) \cdot RT}{2 D_{AB}\ M_A} \cdot \frac{P_{Bm}}{P_T} \cdot \frac{1}{(P_{A1} - P_{A2})}$$

Unit check

$$\frac{\frac{\cancel{kg}}{m^3} \cdot \overset{m^2}{\cancel{(m^2 - m^2)}} \cdot \frac{J}{kg\ mol \cdot \cancel{K}} \cdot \cancel{K}}{\frac{m^2}{s} \cdot \frac{\cancel{kg}}{kg\ mol}} \cdot \frac{1}{1} \cdot \frac{1}{\frac{N}{m^2} - \frac{N}{m^2}}$$

$$\frac{1}{\cancel{m}} \cdot \frac{\cancel{N \cdot m}}{\cancel{kg\ mol}} \cdot \frac{s}{\cancel{m^2}} \cdot \cancel{kg\ mol} \cdot \frac{\cancel{m^2}}{\cancel{N}}$$

Final unit s ✓

Example 4 Determine diffusivity w/ evaporation

(From Griskey 10-2)

tube $D = 0.01128\,m$

A CCl_3NO_2 (chloropicrin)

B air 1atm

$t=0$ liquid from top $= 0.0388\ m$

$t=1$ day . . . . $= 0.0412\,m$

Vapor pressure ($P_{A1} = 3178.3\ N/m^2$)

$\rho_A = 1650\ kg/m^3$

$M_A = 164.39\ kg/kg\ mol$

Rearrange previous eq

$P_{A1} = 3178.3\ N/m^2$
$P_{A2} = 0\ N/m^2$
$P_{B1} = 101325 - 3178.3$
$P_{B2} = 101325$

$$D_{AB} = \frac{\rho_A (Z_F^2 - Z_0^2) \cdot RT}{2t\,M_A} \cdot \frac{P_{Bm}}{P_T} \cdot \frac{1}{(P_{A1} - P_{A2})}$$

$P_{Bm} = 99727.4$

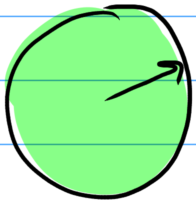
$$= \frac{1650 \cdot (0.0412^2 - 0.0388^2) \cdot 8314 \cdot 298}{2 \cdot 164.39 \cdot (3600 \cdot 24)} \cdot \frac{99727.4}{101325} \cdot \frac{1}{3178.3}$$

$$= 8.56 \times 10^{-6}\ m^2/s$$

(assuming constant N_A then $D_{AB} = 8.75 \times 10^{-6} m^2/s$)
+2.2% error

Example 6.2-4 Pseudo steady state through sphere

$r_1 = 2.0\,mm$



$T = 318K$

$P_{A1} = 0.555$ mm Hg

$D_{AB} = 6.92 \times 10^{-6}\ m^2/s$

evaporation rate ?

Use stagnant B case equ.

$$P_{A1} = 0.555\ mm\ Hg = 0.555 \times \frac{101325}{760} = 73.99\ Pa$$

$\therefore$ P_{B1}, P_{B2} very large

$$P_{Bm} \approx \frac{P_{B1}+P_{B2}}{2} = \frac{(101325-73.99)+101325}{2}$$

$$= 1.0129 \times 10^5\ Pa$$

$$N_A = \frac{D_{AB}}{RTr_1} \cdot \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2}^{\nearrow 0})$$

$$= \frac{6.92 \times 10^{-6}}{8314 \cdot 318 \cdot 0.002} \cdot \frac{101325}{101290} \cdot (74-0)$$

$$= 9.68 \times 10^{-8}\ kg\ mol/m^2/s$$

Same setup of naphthalene sphere
generalize. (r_1 radius, $P_{A1} \ll P_T$)
density of solid ρ

1) Derive t_F for r decrease $r_1 \to r_F$
2) Expression of t_F if $r_F = 0$ (fully evaporated)

Mass balance

In $-$ Out $+$ Gen $=$ Acc

$$0 - \bar{N}_A + 0 = + \frac{[4\pi \cdot r^2 \cdot \Delta r] \cdot \frac{\rho}{M_A}}{\Delta t}$$

$$\bar{N}_A = -4\pi r^2 \cdot \frac{\rho}{M_A} \cdot \frac{dr}{dt}$$

We have solution for $\bar{N}_A$ ($P_{A1} \ll P_{Bm}$)

$$N_A = \frac{\bar{N}_A}{4\pi r^2} = \frac{D_{AB}}{RT} \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2}) \cdot \frac{1}{r_1}$$

$$-\frac{\cancel{4\pi r^2} \cdot \frac{\rho}{M_A}}{\cancel{4\pi r^2}} \cdot \frac{dr}{dt} = \frac{D_{AB}}{RT} \cdot \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2}) \frac{1}{r}$$

$$-r\,dr = \frac{D_{AB}}{RT} \cdot \frac{M_A}{\rho} \cdot \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2})\, dt$$

$$\int_{r_0}^{r_F} -r\,dr = \int_0 \frac{D_{AB}}{RT} \cdot \frac{M_A}{\rho} \cdot \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2})\, dt$$

$$\frac{(r_0^2 - r_F^2)}{2} = \frac{D_{AB}}{RT} \cdot \frac{M_A}{\rho} \cdot \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2})\, dt$$

$$\frac{(r_0^2 - r_F^2)}{2} = \frac{D_{AB}}{RT} \cdot \frac{M_A}{\rho} \cdot \frac{P_T}{P_{Bm}} (P_{A1} - P_{A2}) dt$$

$$t_F(r=r_F) = \frac{\rho \; RT \; P_{Bm}}{2 M_A D_{AB} P_T} \cdot \frac{1}{(P_{A1} - P_{A2})} (r_0^2 - r_F^2)$$

2) if $r_F = 0 \Rightarrow$

$$t_F(r=0) = \frac{\rho RT P_{Bm} \; r_0^2}{2 M_A D_{AB} P_T (P_{A1} - P_{A2})}$$

Complete evap

Compare with solution to example 3 in this note!

$$t_F = \frac{\rho_A (z_F^2 - z_0^2) \cdot RT}{2 D_{AB} M_A} \cdot \frac{P_{Bm}}{P_T} \cdot \frac{1}{(P_{A1} - P_{A2})}$$