CHE 318 Lecture 02

Molecular Diffusion in Gases: Diffusive + Convective Mass Transport

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Recap

- Fick's 1st law of diffusion
$$J^*_{Az} = -D_{AB}\frac{dc_A}{dz}$$
- Diffusion and convection
$$N_A = J^*_{Az} + c_A v_m$$
- **Governing equation** for binary mixture system
$$N_A = -c_T D_{AB}\frac{dx_A}{dz} + x_A(N_A + N_B)$$
- We will learn how to solve this equation in this lecture!

Learning Outcomes

After today's lecture, you will be able to:

- **Distinguish** diffusion vs convection mechanisms
- **Recall** common cases in defining the N_A and N_B relation
- **Apply** constraints to select the right case
- **Solve**:
  - Equimolar counter diffusion (EMCD)
  - Diffusion through stagnant B
- **Analyze** different solutions for EMCD and stagnant B

Recap: Fick's 1st Law of Diffusion

Diffusion flux of A in B, z-direction follows:

$$J^*_{Az} = -D_{AB}\,\frac{dc_A}{dz}$$

Figure 1: *Adolf Fick (1829 - 1901), German physiologist*

- Fick was the first to propose the relation between diffusion and concentration gradient driving force
- Analog:
  - Heat transfer (**Fourier's law**)
  - Momentum transfer in fluid (**Newton equation**)

- Diffusivity D_{AB} was later linked to molecular Brownian motion by Albert Einstein
- D_{AB} has unit of $\mathrm{m^2\,s^{-1}}$

Behaviour of Molecular Diffusion

- Brownian motion (Bm) is the inherent motion of molecules
- Bm leads to redistribution of molecules until $\frac{dc_A}{dz} = 0$
- Non-zero flux only when $\frac{dc_A}{dz} \neq 0$
- Is diffusivity temperature dependent? pressure dependent?
- How fast is molecular diffusion?

Typical D_{AB} Range

A Common Misconception

Search for any youtube video with *"diffusion experiment dye"*

Example Video

Can we **verify** whether the scenario seen is Ficknian diffusion?

Diffusion vs Convection Length Scale

Length L traveled in time t:

- **Diffusion:** $L = 6\sqrt{D_{AB}\,t}$ *(Einstein, ~1905)*
- **Convection:** $L = v_m\,t$

What is typical D_{AB} in a liquid?
- Often $D_{AB} \sim 10^{-9}$ to $10^{-10}\,\mathrm{m^2/s}$

Assuming $D_{AB} = 10^{-10}\mathrm{m^2/s}$ $v_m = 10^{-3}\mathrm{m/s}$

Diffusion vs Convection Summary

Diffusion

- Driven by concentration gradient
- Associated with Diffusivity D_{AB}
- Diffusive velocity v_{Ad}
- **Slow** at large (industry) length scale

Convection

- Driven by bulk motion
- Can reinforce or oppose diffusion
- Bulk fluid motion v_m
- **Fast** at large (industry) length scale

A Note on Setups

Reference frame

- J^*_{Az} refers to the fluid plane frame (hence the $*$)
- N_A refers to the stationary frame (lab frame)
- We will be dealing with N_A in this course!

Mass balance in stationary frame

$$[\text{In}] - [\text{Out}] + [\text{Generate}] = [\text{Accumulation}]$$

Steady state (S.S)

- $[\text{Generate}] = [\text{Accumulation}] = 0$
- $[\text{In}] = [\text{Out}]$
- $\dfrac{dN_A}{dz} = 0$ (**S.S**)

Governing Equation for N_A and N_B

The common way of expressing the governing equation is

$$N_A = -c_T D_{AB} \frac{dx_A}{dz} + x_A(N_A + N_B) \quad (1)$$

$$N_B = -c_T D_{BA} \frac{dx_B}{dz} + x_B(N_A + N_B) \quad (2)$$

How can we solve these?

- For this course we assume D_{AB} and D_{BA} are constants
- For industrial purposes we want to know values of N_A and N_B
- We need relation between N_A and N_B to solve them!
- $x_A(z)$ can be solved as a by-product

Three Limiting Cases

Equimolar Counter Diffusion (EMCD)

Assumption

- $N_A + N_B = 0$
- $v_m = 0$

Example

- Two gases exchanging through a thin tube
- Idealized membrane diffusion

Diffusion with Stagnant B

Assumption

- $N_B = 0$
- $N_A \neq 0$

Example

- Evaporation of A through non-diffusing air
- Gas absorption into a liquid film

General Case

Assumption

- $N_A \neq 0$
- $N_A = kN_B$ $(k \neq -1)$

Example

- Catalyst reaction

Case 1: Equimolar Counter Diffusion (EMCD)

- Condition: $N_A + N_B = 0$
- No bulk fluid motion

$$\begin{aligned} N_A &= -N_B && (3)\\ &= J^*_{Az} && (4)\\ &= -c_T D_{AB} \frac{dx_A}{dz} && (5) \end{aligned}$$

Relation in EMCD gives:

$$c_T D_{BA} \frac{dx_B}{dz} = -c_T D_{AB} \frac{dx_A}{dz} \tag{6}$$

Since $x_A + x_B = 1$, we have $D_{AB} = D_{BA}$

Solving EMCD: Flux N_A

Assume S.S., constant D_{AB} and integrate from z_1 to z_2

$$\int_{c_{A1}}^{c_{A2}} dc_A = -\frac{N_A}{D_{AB}} \int_{z_1}^{z_2} dz \tag{7}$$
$$c_{A2} - c_{A1} = -\frac{N_A}{D_{AB}}(z_2 - z_1) \tag{8}$$
$$\tag{9}$$

$$\boxed{N_A = \frac{D_{AB}}{(z_2 - z_1)}(c_{A1} - c_{A2})} \tag{10}$$

For ideal gas:

$$\boxed{N_A = \frac{D_{AB}}{RT(z_2 - z_1)}(p_{A1} - p_{A2})} \tag{11}$$

Case 2: Diffusion Through Stagnant B

Definition: **stagnant** species B means zero molar flux in the lab frame:

$$N_B = 0$$

But diffusion in B phase **still occurs**!

The governing equation becomes:

$$N_A = -c_T D_{AB} \frac{dx_A}{dz} + x_A N_A \tag{12}$$
$$N_A(1 - x_A) = -c_T D_{AB} \frac{dx_A}{dz} \tag{13}$$

Solving Stagnant B Case

We again do an integration by separating variables:

$$\frac{dx_A}{1-x_A} = -\frac{N_A}{c_T D_{AB}}\,dz \tag{14}$$

$$\int_{x_{A1}}^{x_{A2}} \frac{dx_A}{1-x_A} = -\frac{N_A}{c_T D_{AB}} \int_{z_1}^{z_2} dz \tag{15}$$

$$[-\ln(1-x_A)]_{x_{A1}}^{x_{A2}} = -\frac{N_A}{c_T D_{AB}}(z_2 - z_1) \tag{16}$$

$$\ln\left(\frac{1-x_{A1}}{1-x_{A2}}\right) = -\frac{N_A}{c_T D_{AB}}(z_2 - z_1) \tag{17}$$

$$\boxed{N_A = \frac{c_T D_{AB}}{(z_2 - z_1)} \ln\left(\frac{1-x_{A2}}{1-x_{A1}}\right)} \tag{18}$$

Various Forms of Stagnant B Solution

- In concentration and molar fraction

$$N_A = \frac{c_T D_{AB}}{(z_2 - z_1)} \ln\left(\frac{1-x_{A2}}{1-x_{A1}}\right) \tag{19}$$

- Ideal gas with partial pressure

$$N_A = \frac{p_T D_{AB}}{RT(z_2 - z_1)} \ln\left(\frac{p_T - p_{A2}}{p_T - p_{A1}}\right) \tag{20}$$

Log-mean Form

Historically, engineers liked to write the stagnant B equation using linear terms.

$$\ln\left(\frac{p_T - p_{A2}}{p_T - p_{A1}}\right) = \ln\left(\frac{p_{B2}}{p_{B1}}\right) \tag{21}$$

$$(p_{B2} - p_{B1})\ln\left(\frac{p_T - p_{A2}}{p_T - p_{A1}}\right) = \ln\left(\frac{p_{B2}}{p_{B1}}\right)(p_{A1} - p_{A2}) \tag{22}$$

$$\ln\left(\frac{p_T - p_{A2}}{p_T - p_{A1}}\right) = \ln\left(\frac{p_{B2}}{p_{B1}}\right)\left(\frac{p_{A1} - p_{A2}}{p_{B2} - p_{B1}}\right) \tag{23}$$

Define $p_{Bm} = \dfrac{p_{B2} - p_{B1}}{\ln(p_{B2}/p_{B1})}$

We get

$$N_A = \frac{D_{AB}}{RT(z_2 - z_1)}\frac{p_T}{p_{Bm}}(p_{A1} - p_{A2}) \tag{24}$$

Solving Concentration Profiles in Stagnant B

- We will utilize the fact $dN_A/dz = 0$ (S.S).
- Do we have $dc_A/dz = 0$ like in EMCD?

$$dN_A/dz = -cD_{AB}\frac{d}{dx}\left[\frac{1}{1-x_A}\frac{dx_A}{dz}\right] \tag{25}$$

$$= 0 \tag{26}$$

$$\frac{1}{1-x_A}\frac{dx_A}{dz} = \text{Const} \tag{27}$$

$$\int_{x_{A1}}^{x}\frac{1}{1-x'_A}dx'_A = \int_{z_1}^{z}\text{Const}\,dz' \tag{28}$$

Can you solve the profile for $x_A(z)$?

Wrap-up

- "Case selection": choosing the right constraint
- Different **constraints** lead to different solvable cases
- **Equimolar counter diffusion (EMCD):** linear concentration profiles
- **Stagnant B:** non-linear profiles and logarithmic driving force
- **Stagnant no diffusion:** $N_B = 0$

Next lecture: we remove simplifying constraints and discuss the **general case**