CHE 318 Lecture 07

Steady State Mass Transfer – Other Geometries

Dr. Tian Tian

2026-01-19

Recap

- Examples of steady state diffusion
- Applying steady state flux equations to solid and liquid systems
- Examples for several special forms
  - weight % and average concentration in liquid
  - log mean form of concentration / molar fraction
  - pressure - solubility - permeability

Learning Outcomes

(Continue from Lecture 06) After today's lecture, you will be able to:

- **Identify** the difference between diffusion in various geometries
- **Describe** the approximations used for simplifying the soluton for N_A
- **Recall** the reason to choose stagnant B solution for spherical diffusion
- **Solve** pseudo-steady state diffusion problem
- **Analyze** solutions of P.S.S solution and calculate diffusivity through experiment

Diffusion Through Varying Cross-Sectional Area

Steady state mass balance

Many industrial applications involde 1D transport with variable area $A(z)$, with mass balance:

$$[\text{In}] - [\text{Out}] = 0 \tag{1}$$

$$N_{A1}A_1 - N_{A2}A_2 = 0 \tag{2}$$

Define the **total molar flow rate** of A:

$$\overline{N}_A = N_A \, A(z)$$

At steady state: - $\overline{N}_A$ is constant - N_A varies with position if $A(z)$ (or $A(r)$) varies

Applications of Variable-Area Diffusion

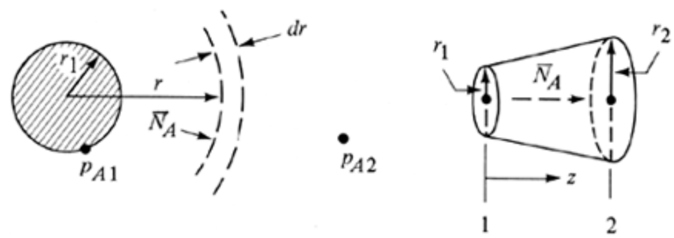

Figure 6.2-3. Diffusion through a varying cross-sectional area: (a) from a sphere to a surrounding medium, (b) through a circular conduit that is tapered uniformally.

This framework can be used to solve diffusion through:

- Sphere
- Cylinder
- Tube with varying diameter
- Any system with a known area function $A = A(z)$ or $A = A(r)$

Key ideas

- Do **not** solve as simple 1D Cartesian diffusion
- Geometry enters through $A(z)$
- Flux adjusts to maintain constant $\overline{N}_A$

Case Study 1: Diffusion Through a Sphere

Typical physical situations

- Evaporation of a liquid droplet
- Sublimation of a solid organic sphere

Conditions

- Steady state
- Stagnant B ($N_B = 0$)
- Radial symmetry

Governing equation (stagnant B): use the **ODE form**, not the full 1D Cartesian solution:

$$N_A = -\frac{D_{AB}}{RT}\frac{dp_A}{dr} + \frac{p_A}{p_T}N_A \tag{3}$$

$$N_A\left(1 - \frac{p_A}{p_T}\right) = -\frac{D_{AB}}{RT}\frac{dp_A}{dr} \tag{4}$$

Stagnant B in a Sphere: Reformulation

For spherical symmetry, $N_A(r)$ varies with r and **cannot** appear alone in the balance equation L.H.S

Use the **constant molar flow rate**:

$$\overline{N}_A = N_A(r)\,4\pi r^2 = \text{constant}$$

$$\frac{\overline{N}_A}{4\pi r^2}\,dr = -\frac{D_{AB}}{RT}\frac{1}{1 - p_A/p_T}\,dp_A \tag{5}$$

Stagnant B in a Sphere: Final Results

$$\boxed{\frac{\overline{N}_A}{4\pi}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) = \frac{D_{AB}p_T}{RT}\ln\left(\frac{p_T - p_{A2}}{p_T - p_{A1}}\right)} \tag{6}$$

This looks very similar to the 1D stagnant B solution in cartesian coordinates. We can simplify it in several occations.

Stagnant B in a Sphere: Far-Field Limit ($r_2 \gg r_1$)

Special case: $r_2 \gg r_1$ (often $r_2 \to \infty$)

Typical examples: - Evaporating liquid droplet - Sublimation of a naphthalene (solid) sphere

From the general spherical stagnant-B result, use the **log-mean pressure** form:

$$\boxed{N_{A1} = \frac{D_{AB}p_T}{RTp_{Bm}}\,(p_{A1} - p_{A2})} \tag{7}$$

Where $N_{A1} = N_A(r = r_1)$. For liquid, another form is often used (considering $p_{Bm}/p_T \approx 1$ and use $p = cRT$)

$$\boxed{N_{A1} = \frac{D_{AB}}{r_1}\left(c_{A1} - c_{A2}\right)} \tag{8}$$

Spherical Diffusion: Thin Shell Limit $r_1 \approx r_2$

Special case: thin membrane / shell
$\Delta r = r_2 - r_1 \ll r_1$

Approximation:

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

Final result:

$$\boxed{N_{A1} = \frac{D_{AB}}{RT}\frac{p_T}{p_{Bm}}\frac{(p_{A1} - p_{A2})}{\Delta r}} \tag{9}$$

This acts like a 1D stagnant-B film with thickness Δr! (See lecture 3 wooclap question.)

Case 2: Diffusion Through a Non-uniform Area Conduit

Conditions:

- Stagnant B
- Steady state
- Variable radius $r(z)$

Assume **linear radius profile**:

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

Use the **ODE form** with $\dot{N}_A = N_A(z)\,A(z)$ and $A(z) = \pi r(z)^2$:

$$\frac{\dot{N}_A}{\pi}\int_{z_1}^{z_2}\frac{dz}{\left[r(z)\right]^2} = -\frac{D_{AB}}{RT}\int_{p_{A1}}^{p_{A2}}\frac{dp_A}{1 - p_A/p_T} \tag{10}$$

Can you solve for N_{A1}?

Examples for Pseudo Steady State (P.S.S)

Example 1: Diffusion Through Stagnant B with Changing Path Length

Adapted from Geankoplis 6.2-3

Water vapor diffuses through a stagnant gas in a narrow vertical tube, dry air is constantly blown at the top of tube.
At time t, the liquid level is a distance z from the tube top (i.e., the diffusion path length is z). As diffusion proceeds, the liquid level drops slowly, so z increases with time. The liquid has density ρ_A, and molecular weight M_A

1) Derive an expression for the time t_F required for the level to drop such that the diffusion path length changes from $z = z_0$ at $t = 0$ to $z = z_F$ at $t = t_F$.

Example 1: solutions

> Tip
>
> 1. Use pseudo steady-state assumption
> 2. N_A change over time!

Answer

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

Example 2: Determine D_{AB} Through Evaporation

Adapted from Griskey 10-2

Sample setup as example 4, a vertical tube of diameter $D = 0.01128$ m contains a liquid volatile species A (chloropicrin, CCl_3NO_2) evaporating into stagnant air (B) at 1 atm. The gas-phase diffusion of A occurs through the air column above the liquid surface.

At $t = 0$, the distance from the tube top to the liquid surface is $z_0 = 0.0388$ m, after $t = 1$ day, the distance is $z_1 = 0.0412$ m.

- Vapor pressure at the interface: $p_{A1} = 3178.3$ Pa
- Liquid density: $\rho_A = 1650$ kg/m^3
- Molecular weight: $M_A = 164.39$ kg/kmol

1) Use your expression from example 4, determine the binary diffusivity D_{AB} of A in air.

Example 2: solutions

> **Tip**
>
> Pseudo steady state solution and assuming $N_A = \text{const}$ solution differ very little. Why?

Answer:

1. Pseudo-steady state: $D_{AB} = 8.56 \times 10^{-6}$ m^2/s
2. N_A constant: $D_{AB} = 8.75 \times 10^{-6}$ m^2/s (+2.2% error)

Example 3: P.S.S For Diffusion Through Sphere

Adapted from Geankoplis Ex 6.2-4

A sphere of naphthalene having a radius of 2.0 mm is suspended in a large volume of still air at 318 K and 1.01325×10^5 Pa (1 atm). The surface temperature of the naphthalene can be assumed to be at 318 K and its vapor pressure at 318 K is 0.555 mm Hg. The D_AB of naphthalene in air at 318 K is 6.92×10^{-6} m^2/s.

1. Calculate the rate of evaporation of naphthalene from the surface.
2. Write the expression for the time t_F to evaporate a sphere from radius r_0 to r_F. The solid density for naphthalene is ρ and molecular weight is M_A.
3. What is the t_F value when the sphere is completely evaporated?

Example 3: solutions

> **Tip**
>
> Similar setup as example 5. N_A is time-dependent

Answer:

1) $N_A = 9.68 \times 10^{-8}$ kg mol/m^2/s
2) Expression for $t_F r = r_F$:

$$t_F(r = r_F) = \frac{\rho R T p_{Bm}}{2 M_A D_{AB} p_T} \frac{1}{(p_{A1} - p_{A2})} (r_0^2 - r_F^2)$$

3) Expression for $t_F r = 0$:

$$t_F(r = 0) = \frac{\rho R T p_{Bm} r_0^2}{2 M_A D_{AB} p_T} \frac{1}{(p_{A1} - p_{A2})}$$

Compare the solutions with Example 4. We can also measure the diffusivity of volatile organic molecules using the sphere evaporation methos!

Summary

- Solving diffusion through varying cross-section
- Pseudo-steady state solutions to diffusion-evaporation problems