CHE 318 Lecture 05

Diffusion in Liquid and Solid

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Recap

- Theories for predicting gas diffusivity D_{AB}:
  - Kinetic theory (inaccurate)
  - Chapman-Enkog theory (high accuracy, hard to use)
  - Fuller method (trade off)
- Estimating $\sum \nu_i$ using Fuller method table
- Extrapolating D_{AB} at different (T, P)
- Solving examples

Learning Outcomes

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

- **Recall** differences between diffusion in gas and in liquid
- **Describe** the limiting cases of mass transport in liquid
- **Solve** EMCD, stagnant B and general cases for transport in liquid
- **Analyze** analogs between mass transport solution in gas and liquid

Diffusion in Liquid

Recall our general transport phenomena equation in Lecture 1

$$[\text{rate of transfer process}] = \frac{[\text{driving force}]}{[\text{resistance}]}$$

Let A being a soluble species, B being the liquid. The resistance in liquid for diffusive transport is much larger than in gases:

Molecular density of liquid (*value*) is much higher than gas (*value*) !

- Intermolecular interaction in liquid is dominating (in comparison, kinetic effect in gases)
- $D_{AB}|_l \approx 10^{-5} D_{AB}|_g$
- $D_{AB}|_l \approx 10^{-12} \sim 10^{-10}\ \mathrm{m}^2 \cdot \mathrm{s}^-1$

Diffusion in Liquid (2)

Unlike in gas, $D_{AB}|_l$ is usually dependent on the molar fraction of A

- In this lecture we will use the diluted limit
- $D_{AB}|_l \neq f(c_A)$

Mass Transport in Liquid – Example 1 EMCD

The equimolar counter diffusion (EMCD) case in liquid also satisfies $N_A + N_B = 0$

From notes in Lecture 2, we can directly write the solution for N_A:

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

Often for dilute A solution, we can rewrite the EMCD solution using average concentration.

EMCD Solution in Liquid

$$\boxed{N_A = \frac{D_{AB} c_{A,v}}{z_2 - z_1}(x_{A1} - x_{A2})} \tag{1}$$

We define c_{av} as the average total concentration in A+B (*not A alone!*):

$$c_{av} = \left(\frac{\rho}{M}\right) = \frac{1}{2}\left(\frac{\rho_1}{M_1} + \frac{\rho_2}{M_2}\right)$$

- ρ_1 and ρ_2 are average density of solution at points 1 and 2
- M_1 and M_2 are average molecular weight of the solution at points 1 and 2
- What is the assumption if we can use the average c_{av} in this case?

Example 2 Stagnant B ($N_B = 0$)

- EMCD in liquid is very rare, stagnant B case more frequent
- Typical setup: diffusion through liquid films, where liquid molecules cannot permeate the barrier

Recall gas-phase equation:

$$N_A = \frac{D_{AB}\, p_T\, (p_{A1} - p_{A2})}{RT(z_2 - z_1)\, p_{B,m}}$$

We have similarly in liquid:

$$\boxed{N_A = \frac{D_{AB} c_{A,v}}{(z_2 - z_1)} \frac{(x_{A1} - x_{A2})}{x_{B,m}}}, \quad x_{B,m} = \frac{x_{B2} - x_{B1}}{\ln(x_{B2}/x_{B1})} \tag{2}$$

Stagnant B: Further Discussions

- $x_{B,m}$ is the log-mean value of x_B
- In diluted A through stagnant B, we often have $x_{B1} \approx x_{B2} \approx 1$
- A simpler approximation can be made $x_{B,m} \approx \frac{x_{B1}+x_{B2}}{2}$
- We can even roughly approximate $x_{B,m} = 1$!

$$N_A = \frac{D_{AB} c_{A,v}}{(z_2 - z_1)} \frac{(x_{A1} - x_{A2})}{x_{B,m}} \tag{3}$$

$$\approx \frac{D_{AB} c_{A,v}}{(z_2 - z_1)} \frac{(x_{A1} - x_{A2})}{(x_{B1} + x_{B2})/2} \tag{4}$$

$$\approx \frac{D_{AB}}{(z_2 - z_1)} (c_{A1} - c_{A2}) \tag{5}$$

Diffusivity in Liquid

Experimentally measured D_{AB} in liquid:

TABLE 6.3-1. *Diffusion Coefficients for Dilute Liquid Solutions*

Solute	Solvent	Temperature °C	Temperature K	Diffusivity $[(m^2/s)10^9$ or $(cm^2/s)10^5]$	Ref.
NH_3	Water	12	285	1.64	(N2)
		15	288	1.77	
O_2	Water	18	291	1.98	(N2)
		25	298	2.41	(V1)
CO_2	Water	25	298	2.00	(V1)
H_2	Water	25	298	4.8	(V1)
Methyl alcohol	Water	15	288	1.26	(J1)
Ethyl alcohol	Water	10	283	0.84	(J1)
		25	298	1.24	(J1)
n-Propyl alcohol	Water	15	288	0.87	(J1)
Formic acid	Water	25	298	1.52	(B4)
Acetic acid	Water	9.7	282.7	0.769	(B4)
		25	298	1.26	(B4)
Propionic acid	Water	25	298	1.01	(B4)
HCl (9 g mol/liter)	Water	10	283	3.3	(N2)
(2.5 g mol/liter)		10	283	2.5	(N2)
Benzoic acid	Water	25	298	1.21	(C4)
Acetone	Water	25	298	1.28	(A2)
Acetic acid	Benzene	25	298	2.09	(C5)
Urea	Ethanol	12	285	0.54	(N2)
Water	Ethanol	25	298	1.13	(H4)
KCl	Water	25	298	1.870	(P2)
KCl	Ethylene glycol	25	298	0.119	(P2)

Prediction of Diffusivity in Liquid

- Molecular diffusion in liquid encounters much more collision than gas phase!
- Kinetic theory is not applicable!
- A few semi-empirical laws exist:

Einstein-Stokes Equation

- Model molecules A as spheres through a fluid B
- Drag force of A in B predicted from Stoke's law

$$D_{AB} = \mu_{AB} k_B T$$

where μ_{AB} is the mobility of A in B

Einstein-Stokes Equation for D_{AB}

Stokes–Einstein correlation for diffusivity in liquids:

$$D_{AB} = \frac{9.96 \times 10^{-16}\, T}{\eta\, V_A^{0.333}}$$

- D_{AB} in m^2/s
- $T:$ temperature (K)
- η_B : viscosity of B (kg / m · s)
- V_A : molar volume of solute A
  - evaluated at **normal boiling point**
  - units: m^3/kg mol
- Good for:
  - Molecular weight > 1000
  - $V_A > 0.5$ m^3/kg mol
- Poor accuracy otherwise

Semi-Empirical Wilke–Chang Equation for Liquids

$$D_{AB} = \frac{1.173 \times 10^{-16}\, (\phi M_B)^{1/2}\, T}{\eta_B\, V_A^{0.6}}$$

- D_{AB} in m^2/s
- $T:$ temperature (K)
- η_B : viscosity of solvent B (kg / m · s)
- M_B : molecular weight of solvent B
- V_A : molar volume of solute A (m^3/kgmol)
- ϕ : solvent association parameter (see next slide)
- Typical error:

  - 10–15% for aqueous systems
  - ~25% for non-aqueous solvents

- Valid temperature range:

  - 278 K $< T <$ 313 K

Wilke–Chang Equation, ϕ values

Association parameter ϕ

- Water: $\phi = 2.6$

- Methanol: $\phi = 1.9$

- Ethanol: $\phi = 1.5$

- Benzene: $\phi = 1.0$

- Non-associating solvents: $\phi \approx 1.0$

Diffusion in Solids

- **Slowest** mode of mass transfer
- **Vital to industry**:

  - Packaging
  - Catalysts
  - Biological processes

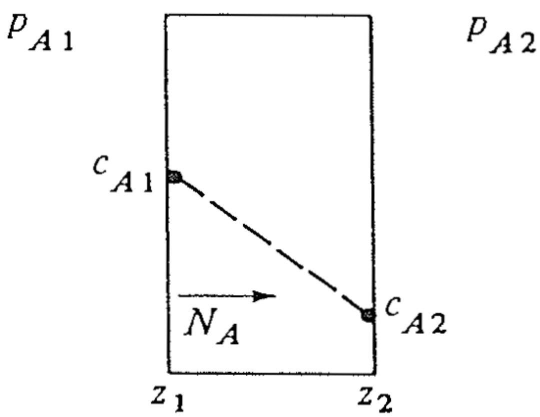
- We will focus on **two types of solids**

Type 1: Homogeneous Solids

- Uniform solid matrix
- Diffusion follows **Fick's law**
- Well-defined diffusion path

Examples

- O_2 diffusion through plastic
- H_2O diffusion through paint



Type 1: General Flux Equation for Solids

For diffusion of A in a **homogeneous solid**:

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

In solids:

- Solid matrix is stationary
- $v_m = 0 \Rightarrow (N_A + N_B) = 0$

$$\boxed{N_A = -c_T D_{AB} \frac{dx_A}{dz}}$$

Final Flux Expression (Concentration Form)

Key properties for diffusion in solids:

- D_{AB} is **independent of pressure**
- $D_{AB} \neq D_{BA}$

For steady-state diffusion through a slab:

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

Assumptions:

- Slab geometry
- Homogeneous solid matrix
- Constant D_{AB}

How Do We Know c_A?

For this type of problem, we are often interested in the gas solubility in solid, where $c_A \propto p_A$. When expressed using the solubility S :

$$\boxed{c_A = \frac{S p_A}{22.414}}$$

Unit:

- c_A: $\mathrm{kg\ mol \cdot m^{-3}}$
- S: $\mathrm{m^3}$ (STP at 0 ℃ and 1 atm)
- p_A: atm

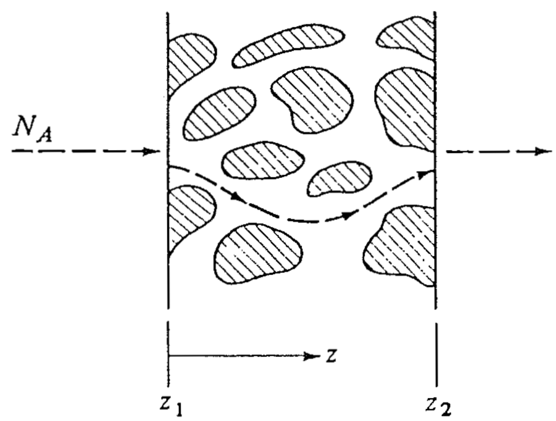
Often we also express the **permeability** of a gas (P_M) in solid using $P_M = SD_{AB}$

Type 2: Inhomogeneous Solids

- Non-uniform structure
- Diffusion through:
  - Pores
  - Fixed or **tortuous** paths in solid matrix
- Requires **modified Fick's law**

Examples:

- Brita water filter
- Porous catalysts



Flux in Porous Solids

Steady-state diffusion of A through a porous solid:

$$N_A = \frac{\varepsilon}{\tau} \frac{D_{AB}\,(c_{A1} - c_{A2})}{(z_2 - z_1)}$$

- ε: open void fraction
  - typically 0.1–0.9
- τ: tortuosity
  - typically 1.5–5 for solids

Effective Diffusivity

Porous-media effects are lumped into an **effective diffusivity**:

$$\boxed{D_{AB,\text{eff}} = \frac{\varepsilon}{\tau} D_{AB}}$$

- Accounts for reduced area and increased path length
- Used directly in Fick's law for porous solids

Example Problems

General Steps

See handwritten notes for step-by-step solutions.

1. Draw the physical scheme
2. Identify the diffusion case
3. List assumptions
4. Write the governing flux equation
5. Apply boundary conditions (optional)
6. Solve for the molar flux

Example 1: EMCD Basics

Adapted from Geankoplis 6.2-1

Ammonia (A) is diffusing through nitrogen (B) in a straight tube of length $L = 0.10$ m at steady state.
The system is maintained at a total pressure of $P_T = 1.0132 \times 10^5$ Pa and a temperature of $T = 298$ K.
The partial pressure of ammonia at z_1 is $p_{A1} = 1.013 \times 10^4$ Pa, and at z_2 is $p_{A2} = 0.507 \times 10^4$ Pa.
The binary diffusivity of ammonia in nitrogen is $D_{AB} = 0.230 \times 10^{-4}$ m^2/s.

1) Determine values for fluxes of A and B.

Example 2: EMCD in Two-Bulb Setup

Two bulbs with $V_1 = V_2$ are connected by a narrow tube of length $L = 0.15$ m and diameter $d = 1$ mm. The system is at $T = 25$ °C and $P = 1$ atm. Species A is N_2 and species B is H_2, with $D_{AB} = 0.784$ cm^2/s.

At $t = 0$:

- Left bulb: $x_{N_2} = 1.00$, $x_{H_2} = 0.00$
- Right bulb: $x_{N_2} = 0.00$, $x_{H_2} = 1.00$

At time $t = t_1$:

- Left bulb: $x_{N_2} = 0.80$
- Right bulb: $x_{N_2} = 0.25$

1) Determine the molar fluxes N_A and N_B at $t = t_1$ (include direction).
2) Find the value for v_{Ad} (diffusive velocity)

Example 3: 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.

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 $t = t_F$.

Hint: use pseudo steady-state assumption

Example 4: 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 3, determine the binary diffusivity D_{AB} of A in air.

Summary

- Compare diffusion in gas and in liquid
- $D_{AB}|_l \ll D_{AB}|_g$
  $D_{AB}|_s$
- Theories for predicting diffusivity in liquid, and when to apply them

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