CHE 318 Lecture 04

Molecular Diffusivity: Theories and Measurement

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Recap

- **General solution** for diffusion binary mixture gas systems ($N_B = kN_A$)
  - $k = -1$ reduces to EMCD solution
  - Total flux N_A is EMCD flux times a coefficient

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

- Brief discussion about diffusivity measurement: two-bulb setup

Demonstration of General Solution

Interaction Time!

participation link

Results and comments to be published after the class

Learning Outcomes

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

- **Recall** multiple theories of molecular diffusivity
- **Analyze** the diffusivity D_{AB} as function of (T, P)
- **Derive** new diffusivity values from standard table
- **Formulate** governing equations for different scenarios measuring the diffusivity

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Let's Look At The General Mass Transfer Equation (Again)

$$N_A = \frac{D_{AB} c_T}{(z_2 - z_1)} s \ln \left[\frac{s - \frac{c_{A2}}{c_T}}{s - \frac{c_{A1}}{c_T}} \right] \quad s = \frac{N_A}{N_A + N_B}$$

What values do we know from the system setup?

- Geometry: z_1, z_2, c_{A1}, c_{A2}, c_T
- Chemical reaction stoichiometry: k

What else value(s) do we need to solve N_A?

- D_{AB}: generally $D_{AB}(z) = \text{Const}$
- But $D_{AB} = f(T, P, \cdots)$

Motivation to Have Theory About Diffusivity

- Solving the general solution for gas mass transfer requires parameter D_{AB} (and D_{BA})!
- Measuring every D_{AB} pair for gases is tedious
- D_{AB} is dependent on conditions T, P
- We need to have theories that can **predict** diffusivity D_{AB} **without** doing all pair experiments and all (T, P) conditions!
- In the lease case, the theory should allow extrapolating a measured $D_{AB}(T_1, P_1)$ to $D_{AB}(T_2, P_2)$

Molecular Diffusivity Theory – Kinetic Theory

In dilute gas regime ($p_T \approx$ atm), the kinetic behaviour of gas molecules can be described using kinetic theory. A few assumptions are made:

1. Interdiffusion between A and B are dominated by **collision** between molecules (low p_T **only 2** molecules can collide at the same time)
2. The molecules are rigid spheres having particle masses m_A, m_B and diameters d_A and d_B

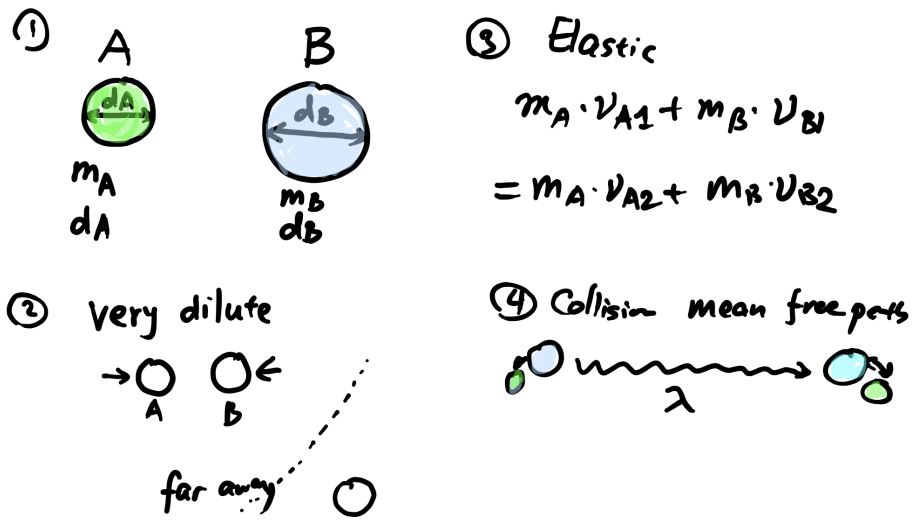

Figure 1: Scheme of gas kinetic theory

Kinetic Theory – Key Results

There are some results from the kinetic theory: [1]

1. Mean molecular speed $\overline{u}$

$$\overline{u} = \sqrt{\frac{8k_B T}{\pi \overline{m}_{AB}}}$$

2. Mean free path (between collisions): $\lambda_{A,B}$

$$\lambda_{AB} = \frac{1}{\sqrt{2}\pi d_{AB}^2 c_T}$$

[1] adapted from *BSL Transport Phenomena ch 17.3*

3. Frequency of molecule A colliding with wall (Z, unit $\mathrm{m}^{-2} \cdot \mathrm{s}^{-1}$):

$$Z_A = \frac{1}{4} c_A \overline{u}$$

where $d_{AB} = \frac{d_A + d_B}{2}$, $m_{AB}^{-1} = m_A^{-1} + m_B^{-1}$, k_B is the Boltzmann constant

4. We also have the average distance a to one plane from last collision:

$$a = \frac{2}{3} \lambda_{AB}$$

Kinetic Theory – Mass Transfer

When there is only molecular diffusion (no convection), at plane $z = 0$, the flux can be described by:

$$\begin{aligned} J_{Az}^*|_{z=0} &= [\mathrm{In}]|_{z=-a} - [\mathrm{Out}]|_{z=+a} && (2) \\ &= \frac{1}{4} c_T [x_A \overline{u}]|_{z=-a} && (3) \\ &\quad - \frac{1}{4} [c_T x_A \overline{u}]|_{z=+a} && (4) \\ &= -\frac{1}{4} c_T \cdot 2a \cdot \overline{u} \frac{dx_A}{dz} && (5) \\ &= -D_{AB} c_T \frac{dx_A}{dz} && (6) \end{aligned}$$

We can now link D_{AB} to microscopic properties!

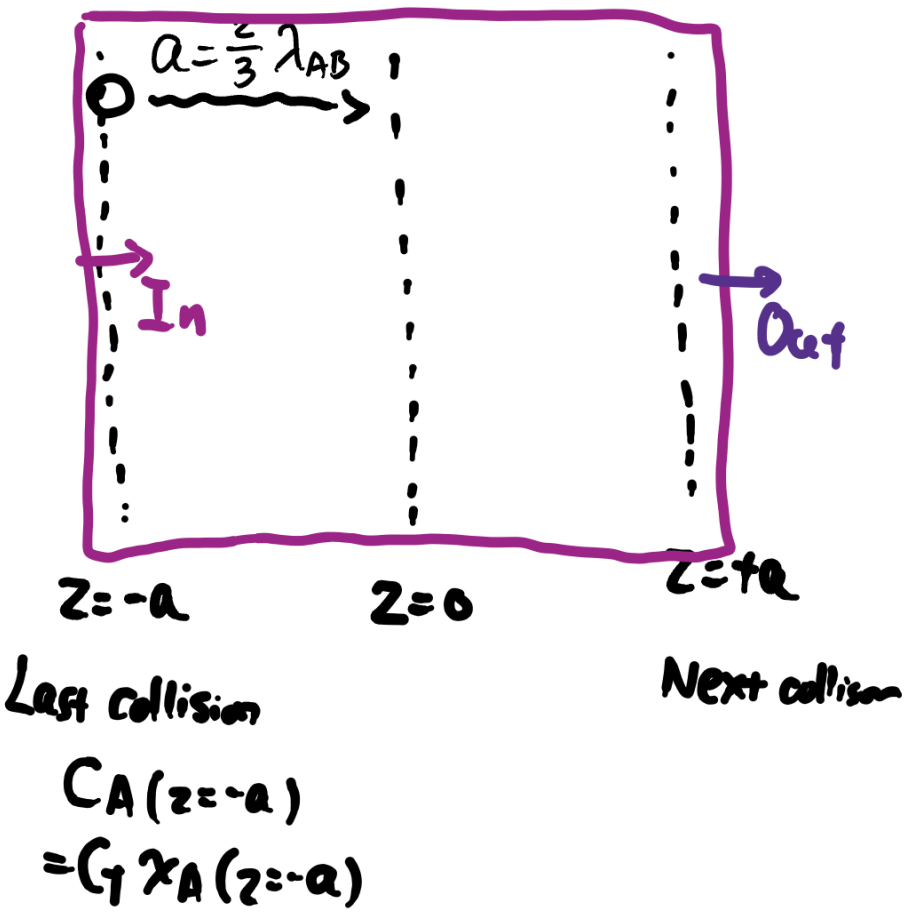

Figure 2: Mass balance in gas kinetic theory

Kinetic Theory of Diffusivity – Conclusion

Results:

$$D_{AB} = \frac{1}{3}\overline{u}\lambda_{A,B}$$

- $\overline{u}$: average molecular velocity
- λ: mean free path between collisions

Assumptions:

- Rigid sphere type molecules (what are they?)
- No interaction upon collisions
- Collisions are elastic (momentum conserved)
- Good for dilute gases (low P)
- Not accurate otherwise

Molecular Diffusivity – Chapman-Enskog Theory

We can take real interaction between molecules into the kinetic theory!

$$D_{AB} = \frac{1.8583 \times 10^{-7} T^{3/2}}{p_T \sigma_{AB}^2 \Omega_{D,AB}} \left(\frac{1}{m_A} + \frac{1}{m_B} \right)^{\frac{1}{2}} \tag{7}$$

$$\propto \frac{T^{\frac{3}{2}}}{p_T} \left(\frac{1}{m_A} + \frac{1}{m_B} \right)^{\frac{1}{2}} \tag{8}$$

- m_A, m_B, molecular weight
- σ_{AB}: average collision radius between A and B
- $\Omega_{D,AB}$: Lennard-Jones collision integral
  - $\Omega_{D,AB} = 1$ for elastic collision
  - Chapman-Enskog theory accounts for non-elastic collision using $\Omega_{D,AB} \neq 1$

Chapman-Enskog Theory: How to Use

$$D_{AB} = \frac{1.8583 \times 10^{-7} T^{3/2}}{p_T \sigma_{AB}^2 \Omega_{D,AB}} \left(\frac{1}{m_A} + \frac{1}{m_B} \right)^{\frac{1}{2}} \tag{9}$$

The Chapman-Enskog theory formula in *Geankoplis book* need to use the following units:

- T: absolute temperature in K
- m_A, m_B: molecular weight in $\text{kg} \cdot (\text{kg mol})^{-1}$ or $\text{g} \cdot (\text{g mol})^{-1}$
- p_T: absolute pressure in atm
- σ_{AB}: average collision diameter in Å

- $\Omega_{D,AB}$: collision integral (dimensionless)

Resulting D_{AB} is in $\mathrm{m}^2 \cdot \mathrm{s}^{-1}$

Chapman-Enskog Theory & Lennard Jones Potential

- Parameters σ_{AB} and $\Omega_{D,AB}$ can be derived using Lennard-Jones (LJ) potential
- LJ potential described the interaction energy U_{AB} between 2 molecules at distance r follows:

$$U_{AB}(r) = 4\epsilon_{AB}\left[(\frac{\sigma_{AB}}{r})^{12} - (\frac{\sigma_{AB}}{r})^{6}\right] \tag{10}$$

How to get the parameters from table:

- $\sigma_{AB} = (\sigma_A + \sigma_B)/2$
- $\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$
- $\Omega_{D,AB}$: get interpolated table values as function of $T^* = k_B T/\epsilon_{AB}$

> **Note**
>
> Check online course materials for the $\Omega_{D,AB}$ table!

Molecular Diffusivity Theory – Fuller Method

The Chapman Enskog theory can be difficult to use, engineers need some simplied empirical rules.

$$D_{AB} = \frac{1.0 \times 10^{-7} T^{1.75}}{p_T\left[(\sum \nu_A)^{1/3} + (\sum \nu_B)^{1/3}\right]^2}\left(\frac{1}{m_A} + \frac{1}{m_B}\right)^{\frac{1}{2}} \tag{11}$$

$$\propto \frac{T^{1.75}}{p_T} \tag{12}$$

- Mainly to overcome the complicated estimation of $\Sigma_{D,AB}$ in Chapman-Enskog Theory

- $\sum \nu_i$ sum of structural volume increments
- $\sum \nu_i$ can be estimated from individual atoms
- Easier to use than the Chapman-Enskog Theory, but less accurate

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Fuller Method: How to Use

$$D_{AB} = \frac{1.0 \times 10^{-7} T^{1.75}}{p_T \left[(\sum \nu_A)^{1/3} + (\sum \nu_B)^{1/3} \right]^2} \left(\frac{1}{m_A} + \frac{1}{m_B} \right)^{\frac{1}{2}} \tag{13}$$

The Fuller method formula in *Geankoplis book* need to use the following units:

- T: absolute temperature in K
- m_A, m_B: molecular weight in $\text{kg} \cdot (\text{kg mol})^{-1}$ or $\text{g} \cdot (\text{g mol})^{-1}$
- p_T: absolute pressure in atm
- ν_A, ν_B: structural volume increments (dimensionless)

Resulting D_{AB} is in $\text{m}^2 \cdot \text{s}^{-1}$

How to Use the Fuller Method From a Table

We need to determine $\sum \nu_A$ and $\sum \nu_B$, *Check Table 6.2-2 of Geankoplis 4th ed.*

- $\sum \nu_i$ are **dimensionless** numbers
- For known gases in the table, use its value in the table
  - Air: $\nu = 20.1$
  - O_2: $\nu = 16.6$
- For an unknown gas, use its chemical composition
  - For chemical formula $C_xH_yO_z$,

$$\sum \nu(C_xH_yO_z) = \nu(C) \cdot x + \nu(H) \cdot y + \nu(O) \cdot z$$

Estimating D_{AB} At Different (T, P)

For the same pair of (A, B), both the Chapman-Enskog and Fuller methods have the same form

$$D_{AB} \propto \frac{T^n}{P}$$

This means we can find one existing D_{AB} value from table and extrapolate:

$$\frac{D_{AB}|_1}{D_{AB}|_2} = \left(\frac{T_1}{T_2}\right)^n \left(\frac{P_2}{P_1}\right)$$

Fuller method is often used in chemical engineering, where $n = 1.75$.

Example 1: Chapman-Enskog Theory vs Fuller Method

Question: calculate the diffusivity D_{AB} for methan–ethan system at 313 K and 1 atm.

Chapman-Enskog Theory

- $m_A = 16.04$, $m_B = 30.07$
- $\rho_A(\text{Å}) = 3.822$, $\rho_B(\text{Å}) = 4.418$
- $\epsilon_A = k_B * (137\ \text{K})$, $\epsilon_B = k_B * (230\ \text{K})$
- $\Omega_{D,AB} = 1.125$ in this case

Fuller Method

- $m_A = 16.04$, $m_B = 30.07$
- $\nu(\text{C}) = 16.5$, $\nu(\text{H}) = 1.98$

The experimental value at this condition is $D_{AB} = 1.84 \times 10^{-5}\ \text{m}^2 \cdot s^{-1}$. Compare the percent errors in both methods.

Summary

- Diffusivity D_{AB} value is the key to solve the transport problem in gases
- D_{AB} can be measured from experiments, but not exhaustively
- Several theories predict the value for D_{AB} with certain accuracy
- Chapman-Enkog theory and Fuller method both have $D_{AB} \propto T^n/P$ form
- Fuller method more often used as it can approximate D_{AB} solely by taking values from table