CHE 318 Lecture 03

Molecular Diffusion in Gases: General Solutions

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2026-01-09

Recap

- **Governing equation** for diffusion binary mixture gas systems

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

- Case 1: equimolar counter diffusion (EMCD)
  - $N_A + N_B = 0$
  - $N_A = -c_T D_{AB} \frac{dx_A}{dz}$
  - Linear x_A, c_A and p_A profiles
  - $N_A = \frac{D_{AB}}{RT(z_2 - z_1)} (p_{A1} - p_{A2})$
- Case 2: diffusion through stagnant B
  - $N_B = 0$
  - $N_A (1 - x_A) = -c_T D_{AB} \frac{dx_A}{dz}$
  - Usually in log-mean pressure form
  - $N_A = \frac{D_{AB}}{RT(z_2 - z_1)} \frac{p_T}{p_{Bm}} (p_{A1} - p_{A2})$

Office Hour

- Wednesday 11:15 - 12:15
- DICE 12-245
- Can take place in other meeting rooms if many people are attending
- Please use seminar time wisely for assignment questions!

Learning Outcomes

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

- **Derive** general solution for mass transport in binary gas mixture
- **Define** the conditions for each cases we have studied so far
- **Formulate** governing equations for various case systems
- **Apply** general solution to defined problem
- **Analyze** pressure / concentration profile

Deriving the General Solution (I)

General case for steady state (S.S) transport

- $N_B = kN_A$ (k is a constant. *why?*)
- Only x_A (or c_A, p_A) dependent on z, not N_A or N_B separation of variables!

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

$$\frac{dz}{D_{AB}c_T} = -\frac{dx_A}{N_A - x_A(N_A + N_B)} \tag{2}$$

$$\int_{z_1}^{z_2} \frac{dz}{D_{AB}c_T} = \int_{x_{A1}}^{x_{A2}} -\frac{dx_A}{N_A - x_A(N_A + N_B)} \tag{3}$$

Deriving the General Solution (II)

- L.H.S.

$$\int_{z_1}^{z_2} \frac{dz}{D_{AB}c_T} = \frac{(z_2 - z_1)}{D_{AB}c_T}$$

- R.H.S.

Using substitution $u = N_A - x_A(N_A + N_B)$, $du = -(N_A + N_B)\,dx_A$

$$\int_{x_{A1}}^{x_{A2}} -\frac{dx_A}{N_A - x_A(N_A + N_B)} = - \cdot -\frac{1}{N_A + N_B}\ln[N_A - x_A(N_A + N_B)]\Big|_{x_{A1}}^{x_{A2}} \tag{4}$$

$$= \frac{1}{N_A + N_B}\ln\left[\frac{N_A - x_{A2}(N_A + N_B)}{N_A - x_{A1}(N_A + N_B)}\right] \tag{5}$$

Deriving the General Solution (III)

We want to solve for N_A

$$\frac{(z_2 - z_1)}{c_T D_{AB}} = \frac{1}{N_A + N_B} \ln\left[\frac{N_A - x_{A2}(N_A + N_B)}{N_A - x_{A1}(N_A + N_B)}\right] \tag{6}$$

$$N_A = \frac{c_T D_{AB}}{(z_2 - z_1)} \frac{N_A}{N_A + N_B} \ln\left[\frac{N_A - x_{A2}(N_A + N_B)}{N_A - x_{A1}(N_A + N_B)}\right] \tag{7}$$

We can gather all $N_A/(N_A + N_B)$ in the R.H.S since it's a constant

$$\boxed{N_A = \frac{c_T D_{AB}}{(z_2 - z_1)} \left(\frac{N_A}{N_A + N_B}\right) \% \ln\left[\frac{\frac{N_A}{N_A+N_B} - x_{A2}}{\frac{N_A}{N_A+N_B} - x_{A1}}\right]} \tag{8}$$

- This is the general solution for binary gas transport.
- Also works for $N_A = -N_B$ (EMCD), with a little bit trick

Relation Between Gen. Sol. and EMCD

The general solution is not applicable $N_B = -N_A$, but we can prove $N_B/N_A \to -1$ reduces to the EMCD equation.

- Let $s = N_A/(N_A + N_B)$, so $s \to \infty$ when $N_B/N_A \to -1$
- Use the Taylor expansion that $\lim_{u\to 0} \ln(1 - u) = -u$

$$\lim_{s\to\infty} \left(\frac{N_A}{N_A + N_B}\right) \ln\left[\frac{\frac{N_A}{N_A+N_B} - x_{A2}}{\frac{N_A}{N_A+N_B} - x_{A1}}\right] = s \ln\left(\frac{s - x_2}{s - x_1}\right) \tag{9}$$

$$= s \ln\left(\frac{1 - x_2/s}{1 - x_1/s}\right) \tag{10}$$

$$= s[(-\frac{x_2}{s}) - (-\frac{x_1}{s})] \tag{11}$$

$$= x_1 - x_2 \tag{12}$$

This **is** the EMCD result!

Three Forms of Gass Mass Transport Equations (I)

In c_A form

- Case 1: EMCD
  - $N_A + N_B = 0$

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

- Case 2: stagnant B
  - $N_B = 0$

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

- General solution
  - $N_B = kN_A$

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

Three Forms of Gass Mass Transport Equations (II)

In x_A form

- Case 1: EMCD
  - $N_A + N_B = 0$

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

- Case 2: stagnant B
  - $N_B = 0$

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

- General solution
  - $N_B = \lambda N_A$

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

Three Forms of Gass Mass Transport Equations (III)

In p_A form (ideal gas)

- Case 1: EMCD
  - $N_A + N_B = 0$

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

- Case 2: stagnant B
  - $N_B = 0$

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

- General solution
  - $N_B = \lambda N_A$

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

General Solution – $x_A(z)$ Profile

In all the cases we study the S.S. condition:

$$\frac{dN_A}{dz} = 0$$

For the general case $s = N_A/(N_A + N_B)$, we have

$$\frac{dN_A}{dz} = \frac{d}{dz} \left[\frac{D_{AB} c_T}{s - x_A} \frac{dx_A}{dz} \right] = 0 \tag{13}$$

$$\frac{D_{AB} c_T}{s - x_A} \frac{dx_A}{dz} = \text{Const} \tag{14}$$

$x_A(z)$ has a general solution with exponential form (with K_1 and K_2 being constants)

$$\boxed{x_A = s - K_1 e^{K_2 z}} \tag{15}$$

$x_A(z)$ Profile

Notes on the Relation Between N_A and N_B (1)

Using steady state condition, we need to know relation between N_A and N_B *before* solving the general EQ.

It depends on the system setup and mass balance.

Let's consider the same chemical reaction of hydrogen dissociation by a solid catalst

$$\mathrm{H_2}\ (A, \mathrm{gas}) \rightarrow 2\mathrm{H}^*\ (B, \mathrm{gas}) \tag{16}$$

- Case 1: reaction through a solid catalyst at bottom of a tube
  - The flux of A and B have **opposite** signs
  - $N_B = -2N_A$

Notes on the Relation Between N_A and N_B (2)

- Case 2: gas flow through a solid catalyst inside a tube
  - The flux of A and B have the **same** sign
  - $N_B = 2N_A$

Take home question: - How do the flux directions affect the general solution?

Measuring Diffusivity D_{AB} In Gases

- Several experimental methods exist for gases, evaporated liquid and sublimated solids (see *Geankoplis* Ch 6.2E)
- We will introduce the two-bulb method for gases
- Typical setup see Duncan & Toor *AIChE J.* 1962, 8, 38-41
- Which case should we apply?

Two-Bulb Experiment: Conditions

Conditions for the two-bulb experiment

- Initially, pure A in bulb 1 and pure B and bulb 2
- $t = 0$, the valve is opened slowly to minimize convection
- $t = t_e$, the valve is closed and the composition in 1 and 2 are analyzed
- The valve open time is much shorter than $t_2 - t_1$
- The tube is a very thin capillary   no convection
- Constant p_T and T throughout experiment

Two-Bulb Experiment: Pseudo Steady State

We can apply:

- EMCD condition (no convection)
- *Pseudo*-steady state (P.S.S) assumption
  - At each time step, we assume N_A or J^*_{Az} is constant (linear c_A profile)
  - But net N_A flux accumulates A molecules in bulb 2
  - c_A in bulb 2 **changes** over time

Two-Bulb Experiment: Governing Equations

We use the mass balance of the system

$$
\begin{aligned}
[\text{Mass In}] &= [\text{Accumulation}] \\
S \cdot J^*_{Az} &= V_2 \frac{dc_{A2}}{dt} \\
D_{AB} \frac{c_{A1} - c_{A2}}{L} \cdot S &= V_2 \frac{dc_{A2}}{dt}
\end{aligned}
$$

Since the total pressure p_T is constant, the average concentration of c_A in the system, $c_{A,av}$ is also constant

$$
\begin{aligned}
V_T c_{A,av} &= (V_1 + V_2) c_{A,av} \\
&= V_1 c_{A1}(t = 0) + V_2 c_{A2}(t = 0) \\
&= V_1 c_{A1}(t \neq 0) + V_2 c_{A2}(t \neq 0)
\end{aligned}
$$

Two-Bulb Experiment: Solutions

We are interested in c_{A2}, so substitute c_{A1} with relation to $c_{A,av}$:

$$
c_{A1} = \frac{V_T c_{A,av} - V_2 c_{A2}}{V_1}
$$

After the substitution, rearrangement and integration we get:

$$
\ln \left[\frac{c_{A,av} - c_{A2}(t = t_e)}{c_{A,av} - c_{A2}(t = 0)} \right] = -\frac{D_{AB} V_T S}{V_1 V_2 L} \cdot t
$$

We can extract D_{AB} usingt the slope of the plot!

Some Typical Diffusivity Measurements

Table 6.2-1. Diffusion Coefficients of Gases at 101.32 kPa Pressure

	Temperature		Diffusivity [(m^2/s)10^4	
System	°C	K	or cm^2/s]	Ref.
Air–NH_3	0	273	0.198	(W1)
Air–H_2O	0	273	0.220	(N2)
	25	298	0.260	(L1)
	42	315	0.288	(M1)
Air–CO_2	3	276	0.142	(H1)
	44	317	0.177	
Air–H_2	0	273	0.611	(N2)
Air–C_2H_5OH	25	298	0.135	(M1)

[1]

Summary

- General solution for $N_B = kN_A$

[1] Geankoplis Table 6.2-1

- Like stagnant B case, general solution take a **logarithm** form for N_A
- When x_{A1} and x_{A_2} are determined, the flux N_A is controlled by the relation between N_B and N_A
- The ratio between N_B and N_A depends on the system and setup
- Diffusivity D_{AB} can be determined by EMCD through two-bulb setup

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Preview of Next Class: Theories for predicting D_{AB}

- Kinetic theory

$$D_{AB} = \frac{1}{3}\overline{u}\lambda$$

- Chapman-Enskog theory

$$D_{AB} \propto \frac{T^{\frac{3}{2}}}{P}\left(\frac{1}{m_A} + \frac{1}{m_B}\right)^{\frac{1}{2}}$$

- Fuller method

$$D_{AB} \propto \frac{T^{1.75}}{P}\left(\frac{1}{m_A} + \frac{1}{m_B}\right)^{\frac{1}{2}}$$