CHEN3001-TP
Mass Transport - 2

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Outline

- Steady-state mass transfer
  - Continuity equation
  - Application of the continuity equation
    - Case-1: Diffusion of A through non-diffusing B
    - Case-2: Steady-state mass transfer with a chemical reaction
    - Case-3: Diffusion with a homogeneous zero-order chemical reaction
    - Case-4: Diffusion with a homogeneous first-order chemical reaction

Continuity eqution

$$\left\{\begin{array}{c}\text{Rate of}\\ \text{mass of}\\ \text{A } in\end{array}\right\}-\left\{\begin{array}{c}\text{Rate of}\\ \text{mass of}\\ \text{A } out\end{array}\right\}+\left\{\begin{array}{l}\text{Rate of production of}\\ \text{mass of A by}\\ homogeneous \text{ reaction}\end{array}\right\}=\left\{\begin{array}{c}\text{Rate of}\\ \text{increase of}\\ \text{mass of A}\end{array}\right\}$$

For mass flux in the x-direction:

$$n_{Ax}\big|_{x}\Delta y\Delta z - n_{Ax}\big|_{x+\Delta x}\Delta y\Delta z \quad + \quad r_{Ax}\Delta x\Delta y\Delta z \quad = \quad \left(\frac{\partial \rho_A}{\partial t}\right)\Delta x\Delta y\Delta z$$

Mass flux ----> *(Also in other direction: n_{Ay} and n_{Az})*

Equation of continuity for A:

$$\frac{\partial \rho_A}{\partial t} = -\left(\frac{\partial n_{Ax}}{\partial x}+\frac{\partial n_{Ay}}{\partial y}+\frac{\partial n_{Az}}{\partial z}\right)+r_A$$

Convection + diffusion ⇒ $n_{Ax} = \rho_A v_x + j_{Ax}$

Continuity equation

$$\frac{\partial \rho_A}{\partial t} = -\left(\frac{\partial n_{Ax}}{\partial x} + \frac{\partial n_{Ay}}{\partial y} + \frac{\partial n_{Az}}{\partial z} \right) + r_A$$

$$\Leftrightarrow \quad \frac{\partial \rho_A}{\partial t} = -\left(\frac{\partial \rho_A v_x}{\partial x} + \frac{\partial \rho_A v_y}{\partial y} + \frac{\partial \rho_A v_z}{\partial z} \right) - \left(\frac{\partial j_{Ax}}{\partial x} + \frac{\partial j_{Ay}}{\partial y} + \frac{\partial j_{Az}}{\partial z} \right) + r_A$$

$$\Leftrightarrow \quad \frac{\partial \rho_A}{\partial t} = -\nabla \cdot \rho_A \boldsymbol{v} - \nabla \cdot \boldsymbol{j}_A + r_A$$

If the above equation is summed up for all of the species in the mixture:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \rho \boldsymbol{v}$$ ⇒ Law of conservation of mass: $$\sum_{\alpha=1}^{n} r_\alpha = 0$$

If mixture density is constant:

$$\nabla \cdot \boldsymbol{v} = 0$$

Continuity equation

Equation of continuity for A in *molar* units:

$$\frac{\partial c_A}{\partial t} = -\left(\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z}\right) + R_A$$

$$\Leftrightarrow \quad \frac{\partial c_A}{\partial t} = -\left(\frac{\partial c_A v_x}{\partial x} + \frac{\partial c_A v_y}{\partial y} + \frac{\partial c_A v_z}{\partial z}\right) - \left(\frac{\partial J_{Ax}}{\partial x} + \frac{\partial J_{Ay}}{\partial y} + \frac{\partial J_{Az}}{\partial z}\right) + R_A$$

$$\Leftrightarrow \quad \frac{\partial c_A}{\partial t} = -\nabla \cdot c_A \boldsymbol{v} - \nabla \cdot \boldsymbol{J}_A + R_A$$

If the above equation is summed up for all of the species in the mixture:

$$\frac{\partial c}{\partial t} = -\nabla \cdot c \boldsymbol{v} + \sum_{\alpha=1}^{N} R_\alpha$$

No law of conservation of moles, unless reaction is A → B

Equation of continuity for A in mass units:

$$\frac{\partial \rho_A}{\partial t} + \left(\frac{\partial \rho_A v_x}{\partial x} + \frac{\partial \rho_A v_y}{\partial y} + \frac{\partial \rho_A v_z}{\partial z}\right) = -\left(\frac{\partial j_{Ax}}{\partial x} + \frac{\partial j_{Ay}}{\partial y} + \frac{\partial j_{Az}}{\partial z}\right) + r_A$$

Equation of continuity for A in *molar* units:

$$\frac{\partial c_A}{\partial t} = -\left(\frac{\partial c_A v_x}{\partial x} + \frac{\partial c_A v_y}{\partial y} + \frac{\partial c_A v_z}{\partial z}\right) - \left(\frac{\partial J_{Ax}}{\partial x} + \frac{\partial J_{Ay}}{\partial y} + \frac{\partial J_{Az}}{\partial z}\right) + R_A$$

Continuity equation

Simplifications

1. For binary systems of dilute liquid solutions @ constant T & P → constant ρ, D_{AB}

Fick's law: $j_{Ax} = -D_{AB}\frac{d\rho_A}{dx} = -\rho D_{AB}\frac{d\omega_A}{dx}$ ← (As $\rho_A = \rho\omega_A$)

$$\frac{\partial \rho_A}{\partial t} + v_x\frac{\partial \rho_A}{\partial x} + v_y\frac{\partial \rho_A}{\partial y} + v_z\frac{\partial \rho_A}{\partial z} = D_{AB}\left(\frac{\partial^2 \rho_A}{\partial x^2} + \frac{\partial^2 \rho_A}{\partial y^2} + \frac{\partial^2 \rho_A}{\partial z^2}\right) + r_A$$

Divide by the molecular weight of A:

$$\frac{\partial c_A}{\partial t} + v_x\frac{\partial c_A}{\partial x} + v_y\frac{\partial c_A}{\partial y} + v_z\frac{\partial c_A}{\partial z} = D_{AB}\left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2}\right) + R_A$$

Continuity equation

Simplifications

2. For binary systems of low-density gases @ constant T & P → constant c, D_{AB}

$$\frac{\partial c_A}{\partial t} + \left(v_x \frac{\partial c_A}{\partial x} + v_y \frac{\partial c_A}{\partial y} + v_z \frac{\partial c_A}{\partial z} \right) = D_{AB} \left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2} \right) + R_A$$

3. For binary systems zero velocity & no chemical reaction

$$\frac{\partial c_A}{\partial t} = D_{AB} \left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2} \right)$$

Continuity equation

Cylindrical:

$$\frac{\partial c_A}{\partial t} = -\left(\frac{1}{r}\frac{\partial}{\partial r}\left(rN_{Ar}\right) + \frac{1}{r}\frac{\partial N_{A\theta}}{\partial \theta} + \frac{\partial N_{Az}}{\partial z} \right) + R_A$$

Spherical:

$$\frac{\partial c_A}{\partial t} = -\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 N_{Ar}\right) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}\left(N_{A\theta}\sin\theta\right) + \frac{1}{r\sin\theta}\frac{\partial N_{A\phi}}{\partial \phi} \right) + R_A$$

Case-1: Diffusion of A through non-diffusing B

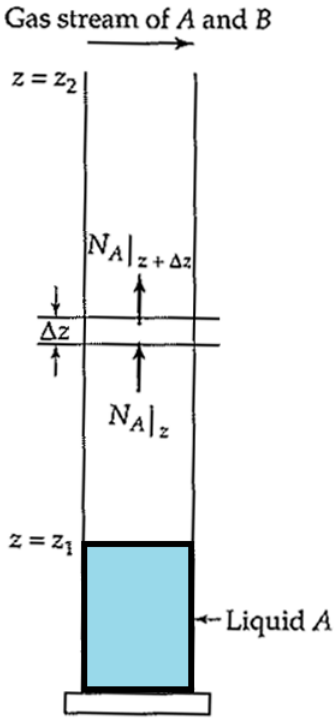
- In both systems, the continuity equation applies:

$$\frac{\partial c_A}{\partial t} = -\left(\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z}\right) + R_A$$

Steady-state analysis

Diffusion in z-direction only

No reaction (no homogeneous reaction in the bulk fluid for case 2)



$$\frac{\partial N_{Az}}{\partial z} = 0$$

- Then, substitute in the diffusion equation:

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

Follow the same procedure and analysis from here

Classroom example-1 (using cylindrical coordinates)

A given gas A can diffuse through the solid wall of a tube in which it flows. Find the rate of gas diffusion in terms of the tube dimensions (inside wall radius R_i, outside wall radius R_o), the gas-solid diffusivity, and the gas concentrations at the walls.

- Assumptions:
- steady state
- flux in r direction only
- no chemical reaction
- A concentration in gas is quite dilute → $x_A \sim 0$
- Constant D_{AB}

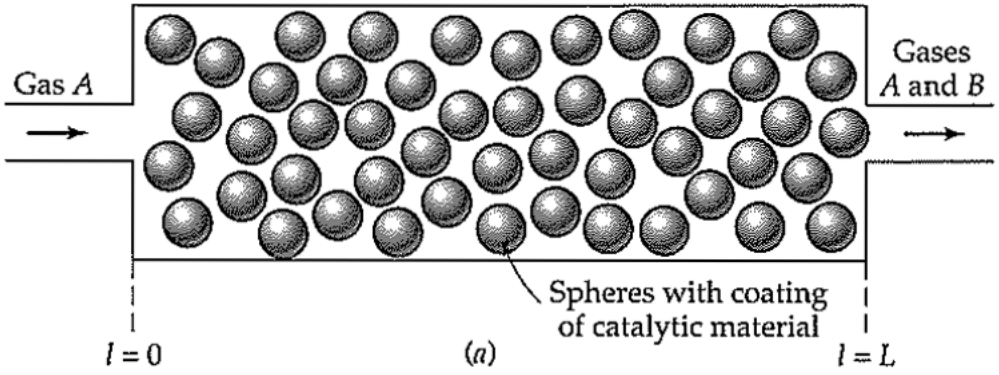
Classroom example-2 (using spherical coordinate)

A spherical ball of solid, nonporous naphthalene is suspended in still air. The naphthalene ball slowly sublimes, releasing naphthalene into the surrounding air. It may be assumed that the sublimation occurs as a molecular diffusion-limited process. Through consideration of the diffusion equation, estimate the time required to reduce the diameter of the ball from 2 to 0.5 cm when the surrounding air is at 347 K and 1 atm.

- Data for naphthalene:
- MW = 128 g/mol
- Density = 1.145 g/cm^3
- Diffusivity in air = 8.19 × 10-6 m^2/s
- Vapour pressure = 666 Pa at 347 K

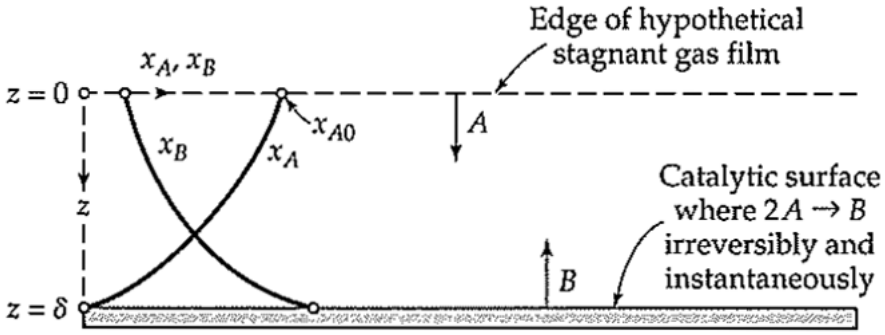
Case-2: With a chemical reaction

- Catalytic reactor
- Reaction: 2A → B
- Catalyst particle surrounded by stagnant gas film through which A has to diffuse to reach the catalyst surface
- (Assumption) reaction occurs instantaneously at the catalyst surface
- Product B diffuses back out through the gas film to the main stream
- (Assumption) isothermal conditions, constant pressure & diffusion constant



Case-2: With a chemical reaction

Consider a layer of stagnant gas film on the surface of a catalyst particle



1 mole of B *removed* from catalyst surface for every 2 moles of A *moving towards* the catalyst surface:

$$N_{Bz} = -\frac{1}{2} N_{Az}$$

Consider the diffusion equation: $N_A = -cD_{AB}\frac{dx_A}{dz} + x_A(N_A + N_B)$

$$N_{Az} = -cD_{AB}\frac{dx_A}{dz} + x_A\left(N_{Az} - \frac{1}{2}N_{Az}\right) \quad \Rightarrow \quad N_{Az} = -\frac{cD_{AB}\dfrac{dx_A}{dz}}{\left(1 - \dfrac{1}{2}x_A\right)}$$

Case-2: With a chemical reaction

Follow the same procedure of shell balance as before, to get: $\frac{dN_{Az}}{dz} = 0$

$$\Leftrightarrow \frac{d}{dz}\left(\frac{cD_{AB}}{(1-0.5x_A)}\frac{dx_A}{dz}\right) = 0 \quad \Rightarrow \frac{d}{dz}\left(\frac{1}{(1-0.5x_A)}\frac{dx_A}{dz}\right) = 0$$

(As cD_{AB} is constant)

First integration: $\frac{1}{(1-0.5x_A)}\frac{dx_A}{dz} = C_1$

Second integration: $-2\ln(1-0.5x_A) = C_1 z + C_2$

$$-2\ln(1-0.5x_A) = C_1 z + C_2 \quad \Rightarrow \quad (1-0.5x_A) = K_1{}^z K_2$$

Use: $C_1 = -2\ln K_1$; $C_2 = -2\ln K_2$

Analyse using boundary conditions:

- $z = 0 \rightarrow x_A = x_{A0}$
- $z = \delta \rightarrow x_A = 0$

Case-2: With a chemical reaction

Previously → a case of diffusion-controlled reaction.

What happens of reaction of 2A → B is not instantaneous? *→ Not so much diffusion controlled anymore…*

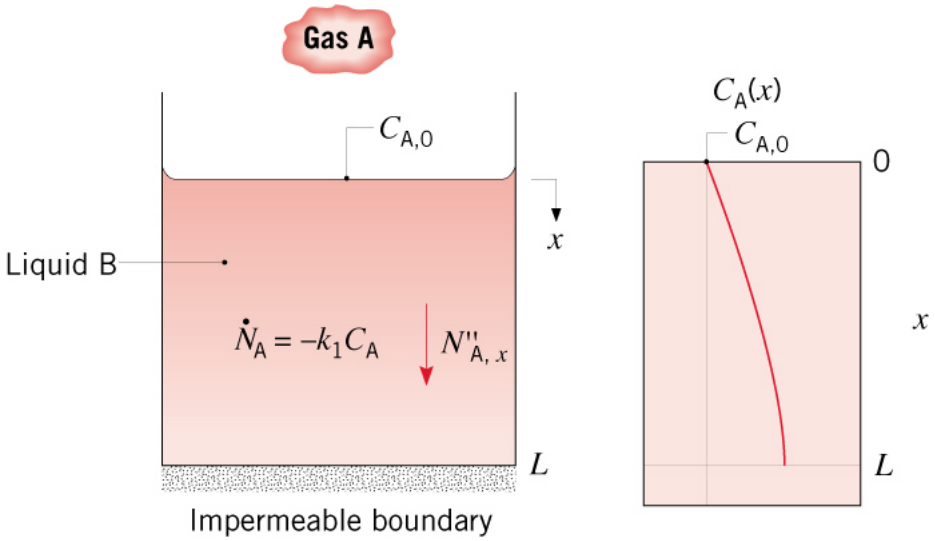
- Assume the reaction is 1st order → Rate of disappearance of A:

$$N_{Az} = k_1'' c_A = k_1'' c x_A$$

- Approach: Similar as before, BUT we use the following boundary conditions:

$$z = 0 \rightarrow x_A = x_{A0} \quad \text{AND} \quad z = \delta \rightarrow x_A = \frac{N_{Az}}{k_1'' c}$$

Case-3: Diffusion with a homogeneous chemical reaction



- Gas A dissolves in liquid B and diffuses isothermally into the liquid phase
- A undergoes irreversible zero-order homogeneous reaction: A+B → AB
- (Assumption) Concentration of AB is low/negligible
- (Assumption) Concentration of A is low → $x_A \sim 0$
- (Assumption) Constant T, D_{AB}.

Case-3: Diffusion with a homogeneous chemical reaction

$$\frac{\partial c_A}{\partial t} = -\left(\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z} \right) + R_A$$

$$-\frac{\partial N_{Ax}}{\partial x} + R_A = 0$$

Rate of disappearance of A: $-k_0$ ⇒ $-\frac{\partial N_{Ax}}{\partial x} - k_0 = 0$

Equation for N_{Ax}: $N_{Ax} = -cD_{AB}\frac{dx_A}{dx} + x_A(N_{Ax} + N_{Bx}) = -cD_{AB}\frac{dx_A}{dx}$ (As x_A is assumed to be a small number)

So, with constant D_{AB}, $D_{AB}\frac{\partial^2 c_A}{\partial x^2} - k_0 = 0$

Case-3: Diffusion with a homogeneous chemical reaction

$$D_{AB}\frac{\partial^2 c_A}{\partial x^2} - k_0 = 0$$

General solution for this equation: $c_{A,x} = \frac{k_0}{2D_{AB}}x^2 + ax + b$

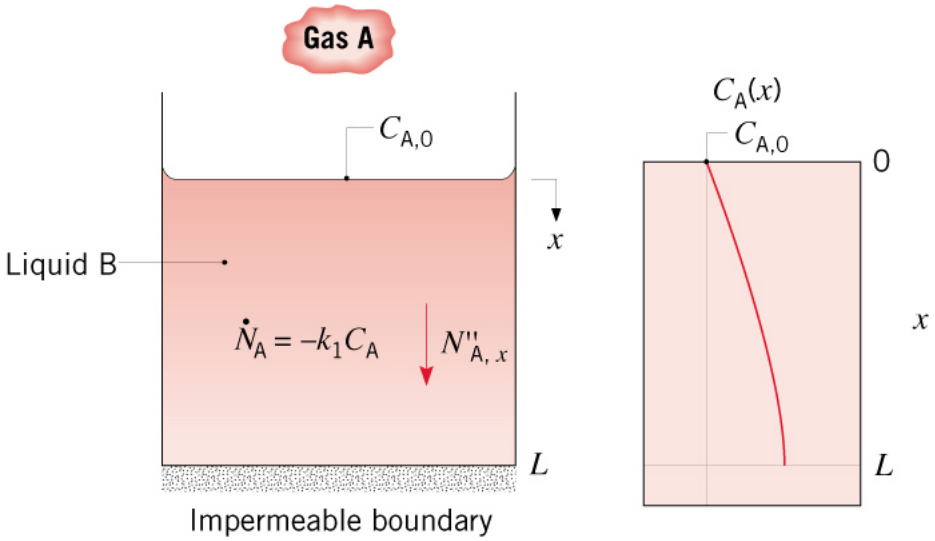
Boundary condition:

z = 0 → $c_A = c_{A0}$

z = L → $N_{Az} = 0$ (impermeable boundary) OR $\left.\frac{\partial c_A}{\partial x}\right|_{x=L} = 0$

$$c_{A,x} = \frac{k_0}{2D_{AB}}\left(x^2 - 2Lx\right) + c_{A,0}$$

Case-4: Diffusion with a homogeneous chemical reaction



- Gas A dissolves in liquid B and diffuses isothermally into the liquid phase
- A undergoes irreversible first-order homogeneous reaction: A+B → AB
- (Assumption) Concentration of AB is low/negligible
- (Assumption) Concentration of A is low → $x_A \sim 0$
- (Assumption) Constant T, D_{AB}.

Case-4: Diffusion with a homogeneous chemical reaction

$$\frac{\partial c_A}{\partial t} = -\left(\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z} \right) + R_A$$

$$-\frac{\partial N_{Ax}}{\partial x} + R_A = 0$$

Rate of disappearance of A= $-k_1''' c_A$ ⇒ $-\frac{\partial N_{Ax}}{\partial x} - k_1''' c_A = 0$

Equation for N_{Ax}: $N_{Ax} = -cD_{AB}\frac{dx_A}{dx} + x_A(N_{Ax} + N_{Bx}) = -cD_{AB}\frac{dx_A}{dx}$ (As x_A is assumed to be a small number)

So, with constant D_{AB}, $D_{AB}\frac{\partial^2 c_A}{\partial x^2} - k_1''' c_A = 0$

Case-4: Diffusion with a homogeneous chemical reaction

$$D_{AB}\frac{\partial^2 c_A}{\partial x^2} - k_1''' c_A = 0$$

General solution for this equation: $c_{A,x} = C_1 e^{mx} + C_2 e^{-mx}$ $\quad m = \left(k_1 / D_{AB}\right)^{1/2}$

Boundary condition:

z = 0 → $c_A = c_{A0}$

z = L → $N_{Az} = 0$ (impermeable boundary) OR $\left.\frac{\partial c_A}{\partial x}\right|_{x=L} = 0$

$$c_{A,x} = c_{A,0}\left(\cosh mx - \tanh mL \sinh mx\right)$$

Concentration of A at the bottom of the tank is therefore:

$$c_{A,L} = c_{A,0}\left(\cosh mL - \tanh mL \sinh mL\right)$$

The flux at the liquid-gas interface:

$$N_{Ax} = -D_{AB}\left.\frac{dc_A}{dx}\right|_{x=0} = -D_{AB}\frac{d}{dx}\left(c_{A,0}\left(\cosh mx - \tanh mL \sinh mx\right)\right)\Big|_{x=0}$$

$$= -c_{A,0} D_{AB} m\left(\sinh mx - \tanh mL \cosh mx\right)\Big|_{x=0}$$

$$= -c_{A,0} D_{AB} m \tanh mL$$

Classroom example: Governing equations for convection and diffusion problems

Consider a catalytic tubular reactor, where a dilute solution of solute A in solvent S is in fully developed, laminar flow in the region $z < 0$. It encounters the catalytic wall in the region $0 \leq z \leq L$, where solute A is instantaneously and irreversibly rearranged to an isomer B. Write the appropriate diffusion equation (in differential form) for this problem, along with the boundary conditions. Assume that the flow is isothermal and neglect the presence of B.

