TRANSPORT PHENOMENA II (0905342)

02- GENERAL FLUX EQUATIONS

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Outline

- Existence of Gradients
- Stefan-Maxwell Formalism
- The Molar-Average Velocity and Relative Velocity
- The Molar Diffusive Flux
- Bulk Velocity and Total Molar Flux
- Total Molar Flux of Species and Net Velocity
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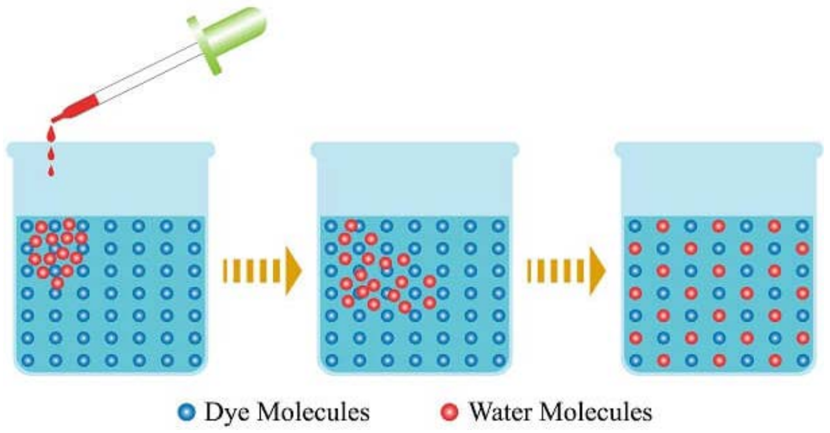
Existence of Gradients

- When a concentration gradient exists for one component of a binary mixture in any direction, there must be a concentration difference for the other component of the mixture in the opposite direction.
- As a result of these concentration differences, both components of the mixture diffuse in the opposite directions.
- If the rates of these diffusions are not equal in molar units, then the mixture itself drifts in the direction of the component whose molar diffusional rate is greater.
- So, it is obvious that total molar flux of each component for a fixed observer will be different than the diffusional fluxes of the components.



Stefan-Maxwell Formalism

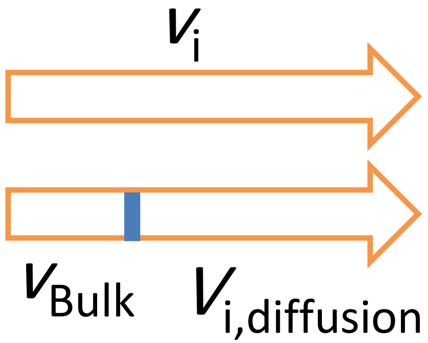
- Early experimental investigations of molecular diffusion were unable to verify Fick's law of diffusion.
  - Attributed to mass is often transferred simultaneously by two possible means:
    - as a result of the concentration differences as postulated by Fick, and
    - by convection induced by the density differences resulting from the concentration variation.
- Stefan (1872) and Maxwell (1877), using the kinetic theory of gases, showed that the mass flux relative to a fixed coordinate evolves as a result of two contributions: the concentration gradient contribution and the bulk motion contribution;

$$\begin{pmatrix}\text{Total mass}\\ \text{transported}\end{pmatrix} = \begin{pmatrix}\text{mass transported}\\ \text{by diffusion}\end{pmatrix} + \begin{pmatrix}\text{mass transported}\\ \text{by bulk motion of fluid}\end{pmatrix}$$

The Molar-Average Velocity and Relative Velocity

- The molar-average velocity (bulk velocity relative to stationary coordinates) for a multicomponent mixture is defined in terms of the molar concentrations of all components by:

$$v = \frac{\sum_{i=1}^{n} c_i v_i}{\sum_{i=1}^{N} c_i} = \frac{\sum_{i=1}^{n} c_i v_i}{c} = \sum_{i=1}^{n} x_i v_i$$



- Where v_i is the velocity of each type of molecule in the specified direction.
- The velocity of a particular species relative to the molar-average velocity is termed *diffusion velocity* .

$$v_{i,\text{diffusion}} = v_i - v_{\text{Bulk}}$$

The Molar Diffusive Flux

- The molar diffusive flux of A in B (in a binary mixture) is given by:

$$J_{AZ}^{*} = -D_{AB} \frac{dc_A}{dz}$$

- The velocity of the diffusive flux of A in B (diffusion velocity of A) can be given by:

$$v_{A,\text{diffusion}}(m/s) = \frac{J_A^{*}(\text{mol/m}^2\text{.s})}{c_A(\text{mol/m}^3)}$$

Bulk Velocity and Total Molar Flux

- The bulk velocity for a binary mixture is given by:

$$v_{\text{Bulk}}(\text{m/s}) = \frac{(c_A v_A + c_B v_B)(\text{mol/m}^2.\text{s})}{c_T\,(\text{mol/m}^3)}$$

- The total molar flux of components A and B relative to fixed coordinates is:

$$N_A = c_A v_A \quad \text{and} \quad N_B = c_B v_B$$

- Hence, the bulk velocity is:

$$\Rightarrow \quad v_{\text{Bulk}}(\text{m/s}) = \frac{(N_A + N_B)(\text{mol/m}^2.\text{s})}{c_T\,(\text{mol/m}^3)}$$

Total Molar Flux of Species and Net Velocity

- The total molar flux of species *i* (N_i) by **convection** (diffusion plus advection) with respect to a stationary point is defined as the rate of transfer by unit area:

$$N_i\,(\text{mol/m}^2.\text{s}) = \frac{\overline{N}_i\,(\text{mol/s})}{A\,(\text{m}^2)}$$

- Hence, the velocity of the net flux of A in B (relative to stationary coordinates) can be given by:

$$v_A\,(\text{m/s}) = \frac{N_A\,(\text{mol/m}^2.\text{s})}{c_A\,(\text{mol/m}^3)}$$

General Flux Equation

- Hence, for species A,

$$v_A = v_{A,\text{ diffusion}} + v_{\text{Bulk}}$$

- Multiplying by C_A provides the general flux equation

$$\underbrace{}_{}c_A v_A = \underbrace{c_A v_{A,\text{diffusion}}}_{\text{Molecular Diffusion}} + \underbrace{c_A v_{\text{Bulk}}}_{\text{Bulk Flow Flux}}$$

$$N_A = J_A^* + c_A \frac{(N_A + N_B)}{c_T}$$

$$N_A = J_A^* + x_A (N_A + N_B)$$

General Flux Equation

- Substituting J_A^* for the diffusive flux from Fick's first law yields:

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

Molecular Diffusion flux of A — Bulk Flow Flux of A

$$\begin{pmatrix}\text{Total mass}\\ \text{transported}\end{pmatrix} = \begin{pmatrix}\text{mass transported}\\ \text{by diffusion}\end{pmatrix} + \begin{pmatrix}\text{mass transported}\\ \text{by bulk motion of fluid}\end{pmatrix}$$

- A special case arises when the mixture is dilute in A which results in neglecting the bulk flow term and the flux reduces to:

$$N_A \approx J_A^* = -D_{AB}\frac{dc_A}{dz}$$

General Flux Equation: Gases at Low Pressures

- Making use of the definition of partial pressure and ideal gas equation of state provides a general flux equation suitable for gases at low pressures:

$$c_A = \frac{n_A}{V} = \frac{p_A}{RT} \qquad c_T = \frac{n_T}{V} = \frac{P}{RT}$$

- Hence the general flux equation becomes

$$N_A = -\frac{D_{AB}}{RT}\frac{dp_A}{dz} + \frac{p_A}{P}(N_A + N_B)$$

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

Net Diffusional Flux of All Species

- Sum the general flux equation to obtain

$$\sum N_i = \sum J_i^* + x_i N_T = \sum J_i^* + \sum x_i N_T = \sum J_i^* + N_T$$

$$\text{but } \sum N_i = N_T$$

$$N_T = \sum J_i^* + N_T$$

$$\sum J_i^* = 0$$

- **<u>The net diffusional flux of all species is zero</u>**

$$\sum J_i^* = 0$$

- Provides a relationship between various diffusion coefficients.

Example: what will be the relation between diffusion coefficients D_{AB} and D_{BA} for a binary system along the x-dimension?

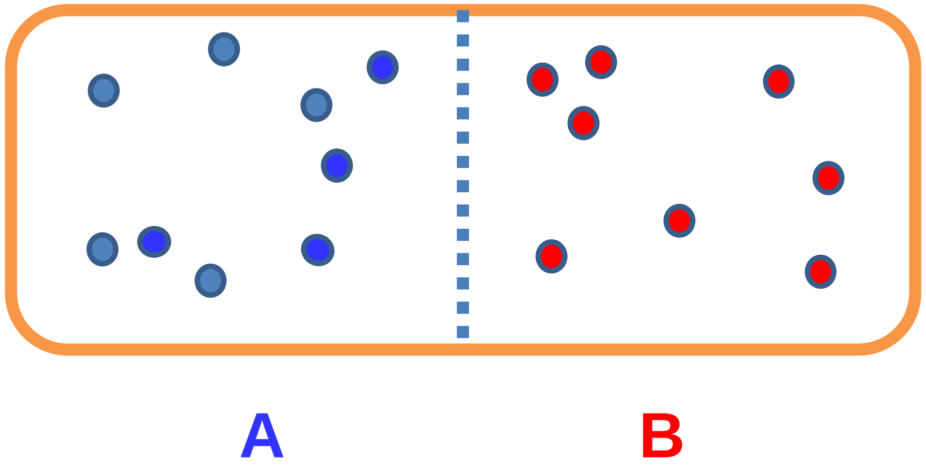
$$\sum J_i^* = 0 = \sum -D_{ik} \frac{dc_i}{dx}$$

$$-D_{AB} c \frac{dy_A}{dx} - D_{BA} c \frac{dy_B}{dx} = 0$$

$$y_A + y_B = 1 \Rightarrow dy_A = -dy_B$$

$$\left(-D_{AB} + D_{BA}\right) c \frac{dy_A}{dx} = 0$$

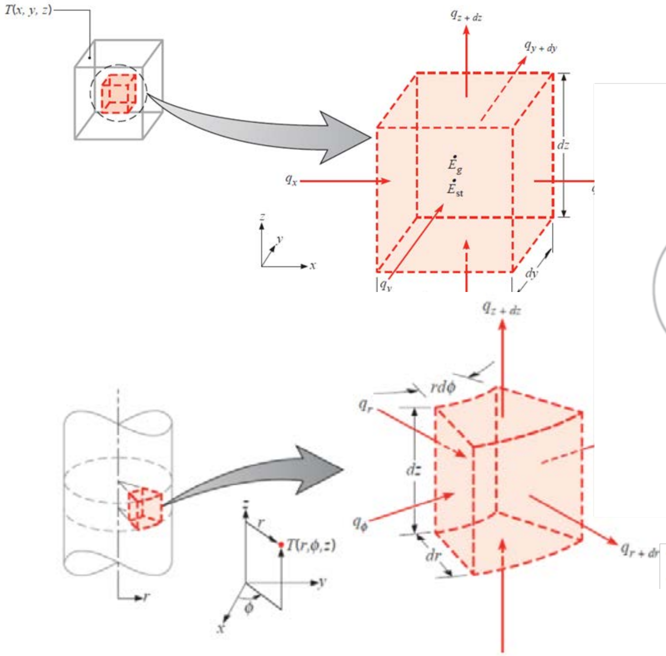
$$D_{AB} = D_{BA}$$



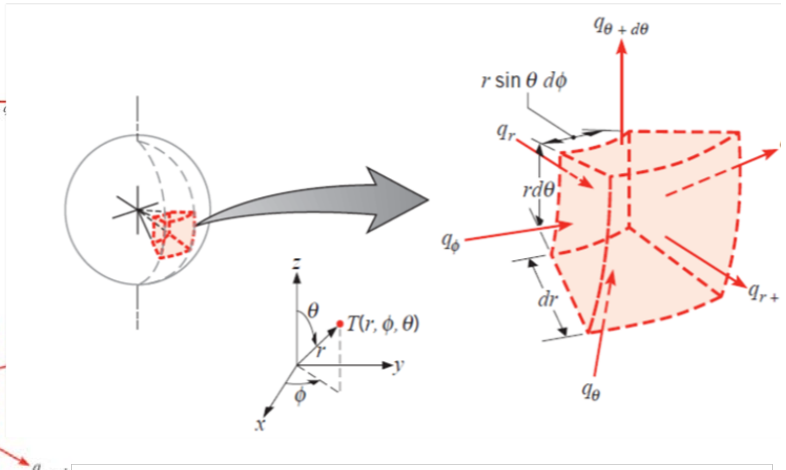
Diffusional Flux in 3D

- The extension from one dimension to 3D is straightforward using the ∇ (del) operator.

$$J_i^* = -D_{ik} \nabla c_i$$



Differential control volume, $dr \cdot r\, d\phi \cdot dz$



Differential control volume, $dr \cdot r \sin\theta\, d\phi \cdot r\, d\theta$

$$\nabla = \frac{\partial}{\partial x}\hat{\mathbf{x}} + \frac{\partial}{\partial y}\hat{\mathbf{y}} + \frac{\partial}{\partial z}\hat{\mathbf{z}}$$

$$\nabla = \frac{\partial}{\partial r}\hat{\mathbf{r}} + \frac{1}{r}\frac{\partial}{\partial \theta}\hat{\boldsymbol{\theta}} + \frac{\partial}{\partial z}\hat{\mathbf{z}}$$

$$\nabla = \frac{\partial}{\partial r}\hat{\mathbf{r}} + \frac{1}{r}\frac{\partial}{\partial \theta}\hat{\boldsymbol{\theta}} + \frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}\hat{\boldsymbol{\phi}}$$