MASS DIFFUSION EQUATIONS

DERIVATIONS AND APPLICATIONS
& UNSTEADY STATE DIFFUSION

Introduction

- The derivation of the general diffusion equation will include the spatial and time variable. On other words, the derived equation will include the accumulation term in order to account the unsteady state problems.
- To simplify the derivation, assume one directional differential element (control volume).
- In general, I-D S.S. (Fick'sFirst Law of Diffusion is written as follows when C_A is only a function of z)equation is:

$$J_A^* = - D_{AB} \frac{dC_A}{dz}$$

Introduction

- I-D unsteady State equation of Fick's 1st law becomes

$$J_A^* = - D_{AB} \frac{\partial C_A}{\partial z}$$

C_A is a function of z plus other variables such as time t

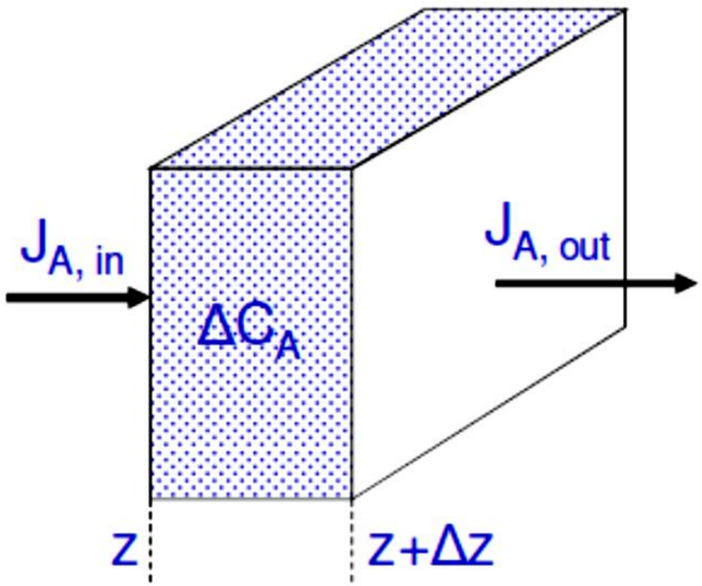
- **Note: Observe the use of ordinary and partial derivatives as appropriate.**

DERIVATION OF BASIC EQUATION

- The derivation of general mass transfer equation is similar to that be done for the derivation of heat transfer equation.
- We make mass balance on component A in terms moles for no generation.

$$\text{rate of input} = \text{rate of output} + \text{rate of accumulation}$$

One-dimensional Unsteady-state Diffusion



A: cross-sectional area

M_A: molecular weight of species *A*

Mass flow of species *A* **into** the control volume:

$$= J_{A,\,in} \times A \times M_A$$

where

$$J_{A,\,in} = -\,D_{AB}\left.\frac{\partial C_A}{\partial z}\right|_{\text{at } z}$$

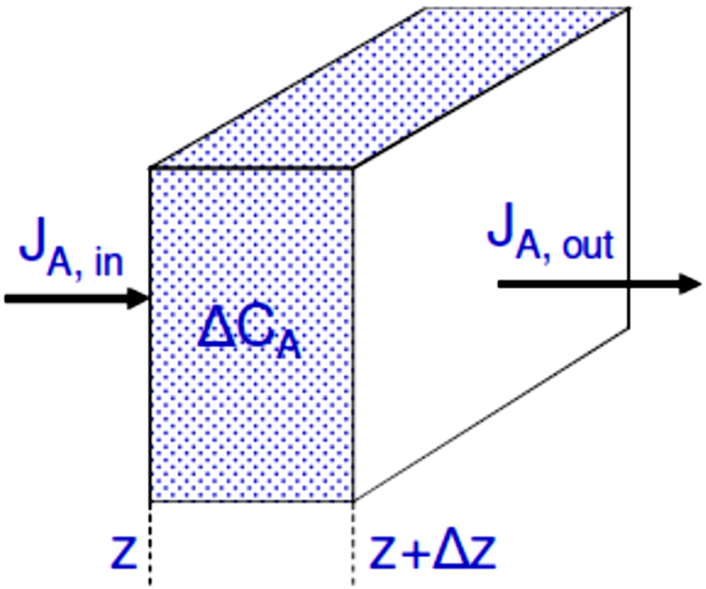
Mass flow of species *A* **out** of the control volume:

$$= J_{A,\,out} \times A \times M_A$$

where

$$J_{A,\,out} = -\,D_{AB}\left.\frac{\partial C_A}{\partial z}\right|_{\text{at } z+\Delta z}$$

One-dimensional Unsteady-state Diffusion



A: cross-sectional area

M_A: molecular weight of species *A*

Accumulation of species *A* in the control volume:

$$= \frac{\partial C_A}{\partial t} \times (A \times \Delta z) \times M_A$$

Mass balance for species *A* in the control volume gives:

$$J_{A, in}\, A\, M_A = J_{A, out}\, A\, M_A + \frac{\partial C_A}{\partial t}\,(A\, \Delta z)\, M_A$$

One-dimensional Unsteady-state Diffusion

Mass balance can be simplified to:

$$- D_{AB} \left. \frac{\partial C_A}{\partial z} \right|_{\text{at } z} = - D_{AB} \left. \frac{\partial C_A}{\partial z} \right|_{\text{at } z+\Delta z} + \frac{\partial C_A}{\partial t} \Delta z$$

The above can be rearranged to give

$$\frac{\partial C_A}{\partial t} = D_{AB} \left[\frac{(\partial C_A/\partial z)_{z+\Delta z} - (\partial C_A/\partial z)_z}{\Delta z} \right]$$

One-dimensional Unsteady-state Diffusion

In the limit as Δz goes to 0:

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial z^2} \qquad (1)$$

which is known as the **Fick's Second Law**.

Fick's second law in the above form is applicable strictly for constant D_{AB} and for diffusion in solids, and also in stagnant liquids and gases when the medium is dilute in *A*.

One-dimensional

Fick's second law, applies to one-dimensional unsteady-state diffusion, is given below:

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial z^2} \tag{2}$$

Fick's second law for one-dimensional diffusion in radial direction only for **cylindrical** coordinates:

$$\frac{\partial C_A}{\partial t} = \frac{D_{AB}}{r} \frac{\partial}{\partial r}\left[r \frac{\partial C_A}{\partial r} \right] \tag{3}$$

Fick's second law for one-dimensional diffusion in radial direction only for **spherical** coordinates:

$$\frac{\partial C_A}{\partial t} = \frac{D_{AB}}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial C_A}{\partial r} \right] \tag{4}$$

Three-dimensional

Fick's second law, applies to three-dimensional unsteady-state diffusion, is given below:

$$\frac{\partial C_A}{\partial t} = D_{AB}\left(\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right) \quad (5a)$$

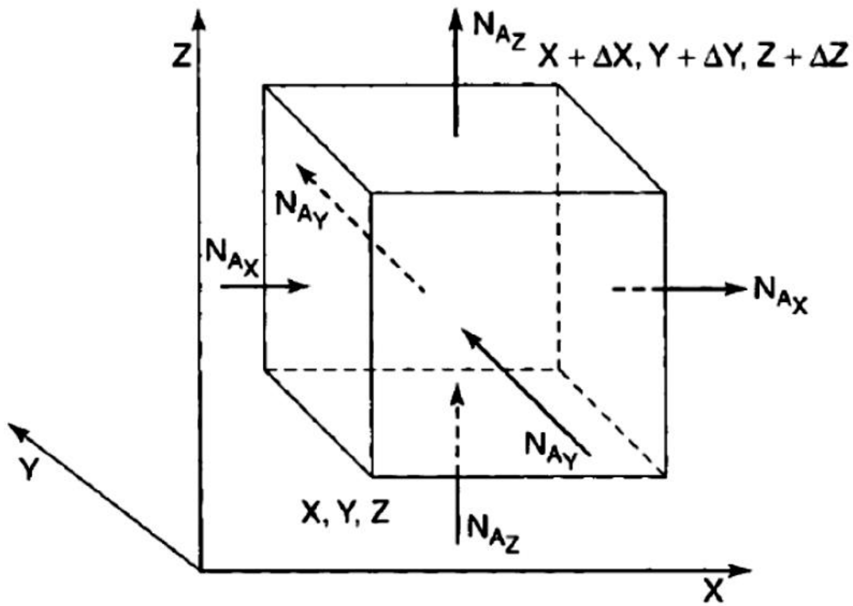
Fick's second law for three-dimensional diffusion in **cylindrical** coordinates:

$$\frac{\partial C_A}{\partial t} = \frac{D_{AB}}{r}\left(\frac{\partial}{\partial r}\left[r\frac{\partial C_A}{\partial r}\right] + \frac{\partial}{\partial \theta}\left[\frac{\partial C_A}{r\,\partial \theta}\right] + \frac{\partial}{\partial z}\left[r\frac{\partial C_A}{\partial z}\right]\right) \quad (5b)$$

Fick's second law for three-dimensional diffusion in **spherical** coordinates:

$$\frac{\partial C_A}{\partial t} = \frac{D_{AB}}{r^2}\left(\frac{\partial}{\partial r}\left[r^2\frac{\partial C_A}{\partial r}\right] + \frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left[\sin\theta\frac{\partial C_A}{\partial \theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2 C_A}{\partial^2 \Phi}\right)$$

Note 2_ Alterative approach



Mass balance on a volume in space

Note that the principal terms will include accumulation, the balance of the mass fluxes, and chemical reaction

The equation of continuity of A in various coordinate systems

- If we consider this in a differential element that we shrink to an infinitesimal basis, we obtain (in rectangular coordinates)

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

- Likewise, for cylindrical coordinates we obtain

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

- While for spherical coordinates the form is

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

Note 3

- Note that similar equations would be written for each of the molecular species present in the system.
- If you consider that N_A = Fick's Law = $-D_{AB}$ dc/dz, then you will get the same equations as before, for example (non reacting system)

$$\frac{\partial C_A}{\partial t} = D_{AB}\left[\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}\right]$$

$-D_{AB}$ dc/dz

convection

- But if you consider $N_A = J_A^* + c_A v_m$, in this case you will get the following equation:

The equation of continuity of A for constant ρ and $\mathcal{D}_{AB}$

rectangular coordinates

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

cylindrical coordinates

$$\frac{\partial c_A}{\partial t} + \left(v_r \frac{\partial c_A}{\partial r} + v_\theta \frac{1}{r} \frac{\partial c_A}{\partial \theta} + v_z \frac{\partial cA}{\partial z} \right) = D_{AB} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_A}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 c_A}{\partial \theta^2} + \frac{\partial^2 c_A}{\partial z^2} \right)$$

spherical coordinates

$$\frac{\partial c_A}{\partial t} + \left(v_r \frac{\partial c_A}{\partial r} + v_\theta \frac{1}{r} \frac{\partial c_A}{\partial \theta} + v_\phi \frac{1}{r \sin\theta} \frac{\partial c_A}{\partial \phi} \right)$$

$$= D_{AB} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_A}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial c_A}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 c_A}{\partial \phi^2} \right]$$

density and diffusivity are constant

Generalized Solution Procedure

1. Sketch the problem.
2. Write the suitable assumptions for the given problem.
3. Select a suitable coordination system.
4. Select the appropriate general mass diffusion equation "differential form" .
5. Cancel the not needed terms in the differential equation according to the assumptions in step 2.
6. Identify the boundary conditions.
7. Write the **flux equation** with respect to species of interest.
8. Substitute the flux from step 5 in the differential equation of step 5.
9. Integrate using the boundary conditions to get the concentration distribution.
10. Apply the Fick's law to obtain the rate of diffusion.