Chap. 25. Differential equations of mass transfer

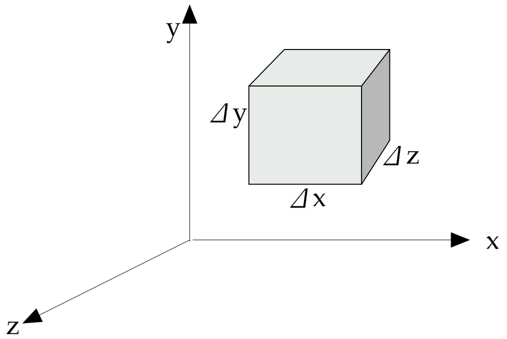
mass balance for control volume ~ continuity equation

1. Differential equation for mass transfer

· the conservation of mass for multi-component system

- molecular diffusion
- bulk motion

· control volume method



$$\int\int_{c.s}\rho(\vec{v}\cdot\vec{n})\,dA+\frac{\partial}{\partial t}\int\int\int_{c.v.}\rho\,dV=0$$

(Efflux) + (Accumulation) = 0 where efflux = output - input

net rate of mass efflux from control volume	+	net rate of accumulation of mass within control volume	-	rate of chemical production of A in control volume	= 0

For species A, mass flux $\vec{n}_A=\rho_A\ \vec{v}_A$

i) Effulx

x-direction : $n_{A,x}\Delta y\Delta z\,|_{\ x+\Delta x}-n_{A,x}\Delta y\Delta z\,|_{\ x}$

y-direction : $n_{A,y}\Delta x\Delta z\,|_{\ y+\Delta y}-n_{A,y}\Delta x\Delta z\,|_{\ y}$

z-direction : $n_{A,z}\Delta x\Delta y\,|_{\ z+\Delta z}-n_{A,z}\Delta x\Delta y\,|_{\ z}$

ii) Accumulation : $\Delta x\Delta y\Delta z\,\frac{\partial\rho_A}{\partial t}$

iii) Rate of production : $r_A\,\Delta x\Delta y\Delta z$

$$\frac{n_{A,x}|_{\ x+\Delta x}-n_{A,x}|_{\ x}}{\Delta x}+\frac{n_{A,y}|_{\ y+\Delta y}-n_{A,y}|_{\ y}}{\Delta y}+\frac{n_{A,z}|_{\ z+\Delta z}-n_{A,z}|_{\ z}}{\Delta z}+\frac{\partial\rho_A}{\partial t}-r_A=0$$

As Δx, Δy, Δz → 0, then $\frac{\partial}{\partial x}n_{A,x}+\frac{\partial}{\partial x}n_{A,y}+\frac{\partial}{\partial x}n_{A,z}+\frac{\partial\rho_A}{\partial t}-r_A=0$

$\nabla\cdot\ \vec{n}_A+\frac{\partial\rho_A}{\partial t}-r_A=0$ ....i) where $\nabla=\frac{\partial}{\partial x}\vec{i}+\frac{\partial}{\partial y}\vec{j}+\frac{\partial}{\partial z}\vec{k}$

For species B in a binary system (A & B), similarly

$\nabla\cdot\ \vec{n}_B+\frac{\partial\rho_B}{\partial t}-r_B=0$ ....ii), $\vec{n}_A+\vec{n}_B=\rho\vec{v}$, $\rho_A+\rho_B=\rho$ & $r_A=-r_B$

i) + ii) ⇒ $\nabla\cdot\rho\vec{v}+\frac{\partial\rho}{\partial t}=0$: the equation of continuity cf) mole production A → nB

$$\vec{n}_A = c_A \vec{v}_A \quad , \quad \vec{n}_B = c_B \vec{v}_B$$

$$\nabla \cdot \vec{n}_A + \frac{\partial c_A}{\partial t} - R_A = 0 \quad , \qquad \nabla \cdot \vec{n}_B + \frac{\partial c_B}{\partial t} - R_B = 0$$

$$\nabla \cdot c\vec{v} + \frac{\partial c}{\partial t} - (R_A + R_B) = 0$$, 여기서 $R_A = -R_B$ 이 아닌 경우가 있다.

2. Special forms of the differential mass-transfer equation

- Objective: 지역적인 농도값 즉, 농도분포를 정량적으로 구하기 위한 모델식 구성
- Basics: Fick's equation for binary system

$$\vec{N}_A = -C D_{AB} \nabla y_A + y_A (\vec{N}_A + \vec{N}_B)$$

or $$\vec{N}_A = \underbrace{-C D_{AB} \nabla y_A}_{(\text{분자이동})} + \underbrace{C_A \vec{V}}_{(\text{bulk이동})}$$

$$\vec{N}_A = -\rho D_{AB} \nabla w_A + w_A (\vec{n}_A + \vec{n}_B) = -\rho D_{AB} \nabla w_A + \rho_A \vec{v}$$

- Continuity equation : $\nabla \cdot \vec{n}_A + \frac{\partial \rho_A}{\partial t} - r_A = 0$
- Differential mass-transfer equation

$$-\nabla \cdot \rho D_{AB} \nabla w_A + \nabla \cdot (\rho_A \vec{v}) + \frac{\partial \rho_A}{\partial t} - r_A = 0$$

$$-\nabla \cdot C D_{AB} \nabla y_A + \nabla \cdot (c_A \vec{V}) + \frac{\partial C_A}{\partial t} - R_A = 0$$

- Simplified forms under specific assumptions

i) ρ, D_{AB} ~ constant, incompressible fluid → $\nabla \cdot \vec{v} = 0$

$$\underline{\vec{v} \cdot \nabla c_A + \frac{\partial c_A}{\partial t}} = D_{AB} \nabla^2 c_A + R_A$$

↓

$$\underline{\frac{D c_A}{Dt} = [\frac{\partial}{\partial t} + \vec{v} \cdot \nabla] c_A} = D_{AB} \nabla^2 c_A + R_A$$

substantional derivative or material derivative for flowing system

$$\frac{D(\cdot)}{Dt} = \frac{\partial(\cdot)}{\partial t} + \vec{v} \cdot \nabla(\cdot)$$

ii) without generation (or production)

$$\frac{\partial c_A}{\partial t} + \underline{\vec{v} \cdot \nabla c_A} = D_{AB} \nabla^2 c_A$$

↓

$\vec{v} = 0$ 이면분자만의이동(*bulk*유동이없다):

$$\frac{\partial c_A}{\partial t} = D_{AB} \nabla^2 c_A$$

iii) without production & accumulation in steady state($\frac{\partial(\cdot)}{\partial t} = 0$)

$\nabla^2 c_A = 0$: Laplace equation

· Laplace Operator

$$\nabla^2 = \nabla \cdot \nabla$$

$$\nabla = (\frac{\partial}{\partial x})\vec{i} + (\frac{\partial}{\partial y})\vec{j} + (\frac{\partial}{\partial z})\vec{k}$$

Rectangular coordinate (x, y, z)

$$\nabla^2 = \nabla \cdot \nabla = (\frac{\partial^2}{\partial x^2}) + (\frac{\partial^2}{\partial y^2}) + (\frac{\partial^2}{\partial z^2})$$

$$\vec{i} \cdot \vec{i} = \vec{j} \cdot \vec{j} = \vec{k} \cdot \vec{k} = 1, \quad \vec{i} \cdot \vec{j} = 0, \quad \vec{j} \cdot \vec{k} = 0, \quad \vec{k} \cdot \vec{i} = 0$$

$$\begin{aligned} \nabla^2 \vec{v} &= (\frac{\partial^2}{\partial x^2}\vec{v}) + (\frac{\partial^2}{\partial y^2}\vec{v}) + (\frac{\partial^2}{\partial z^2}\vec{v}) \\ &= (\frac{\partial^2}{\partial x^2}\vec{v}_x + \frac{\partial^2}{\partial y^2}\vec{v}_x + \frac{\partial^2}{\partial z^2}\vec{v}_x)\vec{i} + (\frac{\partial^2}{\partial x^2}\vec{v}_y + \frac{\partial^2}{\partial y^2}\vec{v}_y + \frac{\partial^2}{\partial z^2}\vec{v}_y)\vec{j} \\ &\quad + (\frac{\partial^2}{\partial x^2}\vec{v}_z + \frac{\partial^2}{\partial y^2}\vec{v}_z + \frac{\partial^2}{\partial z^2}\vec{v}_z)\vec{k} \end{aligned}$$

Cylindrical coordinate (γ, θ, z)

$$\nabla^2 = \frac{1}{r}\frac{\partial}{\partial r}(r\frac{\partial}{\partial r}) + \frac{1}{r^2}(\frac{\partial^2}{\partial \theta^2}) + \frac{\partial^2}{\partial z^2}$$

Spherical coordinate (r, θ, ϕ)

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{rsin\theta}\frac{\partial}{\partial \theta}(\sin\theta\frac{\partial}{\partial \theta}) + \frac{1}{r^2\sin\theta}\frac{\partial^2}{\partial \phi^2}$$

3. Boundary conditions

∇ → geometry (surface or volume) : boundary conditions

$\frac{\Delta}{\Delta t} \sim \frac{\partial}{\partial t} \sim$ time setup : initial condition

· kinds of boundary

i) fixed boundary: constant value of concentration at the surface

$c_A = c_{A_1}$ (상수) $y_A = y_{A_1}$

cf) $p_A = p_B = y_A P$

ii) free boundary: constant mass flux at the surface

$$\vec{j}_A = \vec{j}_{A_1} = 상수 = -D_{AB}\frac{\partial c_A}{\partial z} \quad \text{or} \quad \vec{n}_A = \vec{n}_{A_1}$$

ex) zero on impermentable surface

$$j_{A,z\,surface} = -\rho D_{AB}\frac{d\omega_A}{dz}\Big|_{z=0}$$

iii) chemical reaction : instantaneous reaction at a surface

$N_A = -k_{c_1}c_{A_1}$ (first - order reaction)

iv) flowing system near the surface : convective mass transfer

$N_A = -k_c(c_{A_1} - c_{A_\infty})$

· Quantitative methods to find concentration distribution

Step 1: Draw a schematics of the system

Step 2: Make a list of assumptions

Step 3: Mathematical formulation in a proper coordinate (modeling under mass balance)

Governing equation (ex.: $\frac{\partial c_A}{\partial t} = D_{AB}\frac{\partial^2 c_A}{\partial x^2}$)

Step 4: Boundary conditions and initial condition

$0 \le x \le L$ $\quad c_A = c_A$ at $x = 0$ → surface boundary

$-D_{AB}\frac{\partial c_A}{\partial x} = 0$ at $x = L$ → Free boundary

$c = c_{A_1}$ at $t = 0$ initial condition

Step 5: Solution $\quad c_A = c_A(\ t\ ,\ x\ )$

Example 2 Combustion of carbon and oxygen transfer

chemical reaction at the carbon surface: $3C + 2O_2 \rightarrow 2CO + CO_2$

oxygen diffusion through air film near the flat surface of carbon in a steady-state process

mass balance equation: $\nabla \cdot \overrightarrow{N_{O_2}} + \frac{\partial O_2}{\partial t} - R_{O_2} = 0 \quad \rightarrow \quad \frac{dN_{O_{2,z}}}{dz} = 0$ under proper assumptions

Fick's law : $\quad N_{O_{2,z}} = -cD_{O_2-mixture}\frac{dy_{O_2}}{dz} + y_{O_2}(N_{O_{2,z}} + N_{CO,z} + N_{CO_{2,z}} + \cancel{N_{N_{2,z}}})$

$$N_{O_2,z} = -\frac{cD_{O_2-mixture}}{1+\frac{y_{O_2}}{2}}\frac{dy_{O_2}}{dz} \qquad \because\ N_{O_2,z} = -N_{CO,z} = -2N_{CO_2,z}$$

concentration profile: $\quad \frac{dN_{O_2,z}}{dz} = -\frac{d}{dz}\left(\frac{cD_{O_2-mixture}}{1+y_{O_2}/2}\frac{dy_{O_2}}{dz}\right) = 0$

B.C.'s: $y_{O_2,z} = 0$ at $z = 0$ (가정)

$y_{O_2,z} = 0.21$ at $z = \delta$

$$\int \frac{dy_{O_2}}{1+\frac{y_{O_2}}{2}} = \int A_1 dz \quad \rightarrow \quad 2\ln(1+\frac{y_{O_2,z}}{2}) = A_1 z + \cancel{A_2}\ ,\ A_1 = \frac{2\ln(1.105)}{\delta}$$

$$y_{O_2,z} = 2(\exp(0.0998\frac{z}{\delta}) - 1) \quad \text{for} \quad 0 \le z \le \delta$$

이 예제에 대하여 생각해보기로 할까요?

(1) $N_{O_2,z}$ 은 $0 \le z \le \delta$ 에서 어떤관계로 상수값을 유지할까?

(2) 가정한 필름두께 δ 의 실질적인 수치는 어느정도 일까? 그렇다면 농도식의 유효범위는?

(3) 탄소의 표면과 벌크 공기간의 물질전달을 생각한다면, 필름두께와 물질전달계수와의 관계는?