Chap. 26. Steady-state molecular diffusion

- mass balance for control volume ~ continuity equation
- diffusion(확산)~분자만의 움직임으로 계에 주어져 있는 농도구배를 최소화 하려는 물질전달 현상

  cf.) Heat conduction(열전도) & 열확산계수

- Governing Equation

$$\nabla \cdot \vec{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0, \qquad \frac{\partial c_A}{\partial t} = D_{AB}\nabla^2 c_A + R_A$$

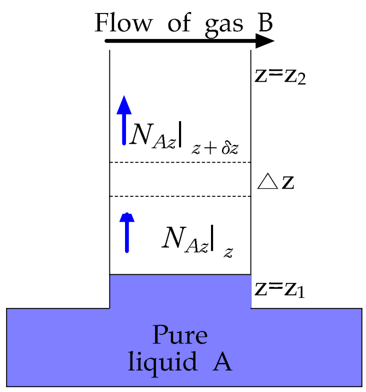
여기서 R_A 는 물질전달이 이루어지고 있는 phase 내에서 화학반응에 의한 생성속도를 나타낸다.

1. One-dimensional mass transfer without chemical reaction

1차원 방향(z-direction) 과 이성분(A & B)의 기상계(y_A, y_B)

$$N_A = -c\,D_{AB}\frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z}) \sim \text{Fick's law}$$

1) Arnold (diffusion) cell : stagnant gas film



- mass balance for control volume

  → no accumulation

$$S\,N_{A,z}|_{z+\Delta z} - S\,N_{A,z}|_{z} = 0$$

$$\frac{d}{dz}N_{A,z} = 0\ ,\quad N_{A,z_1} = N_{A,z} = N_{A,z_2} = \text{상수}$$

- general equation for steady state

$$\nabla \cdot \vec{N}_A + \frac{\partial c_A}{\partial t} - R_A = 0 \quad \text{without chemical reaction}$$

$$\nabla \cdot \vec{N}_A = \frac{\partial N_{A,x}}{\partial x} + \frac{\partial N_{A,y}}{\partial y} + \frac{\partial N_{A,z}}{\partial z} = 0$$

$$\frac{dN_{A,z}}{dz} = 0,\quad N_{A,z} = \text{상수} \neq 0; \qquad \frac{dN_{B,z}}{dz} = 0,\quad N_{B,z} = 0 \text{ for stagnant gas}$$

- Fick's law :

$$N_A = -c\,D_{AB}\frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z})$$

$$N_A = \frac{-c\,D_{AB}}{(1-y_A)}\frac{dy_A}{dz} \quad (= \text{상수} \quad \because \text{정상상태})$$

at $z = z_1$, $y_A = y_{A_1}$ & at $z = z_2$, $y_A = y_{A_2}$

$$N_{A,z}\int_{z_1}^{z_2} dz = -cD_{AB}\int_{y_{A_1}}^{y_{A_2}} \frac{dy_A}{1-y_A}, \qquad N_{A,z} = \frac{cD_{AB}}{(z_2-z_1)}\ln\frac{(1-y_{A_2})}{(1-y_{A_1})}$$

For a binary system of $y_{A_1} + y_{B_1} = 1$ & $y_{A_2} + y_{B_2} = 1$, $y_{B,lm} = \dfrac{y_{B_2} - y_{B_1}}{\ln(y_{B_2}/y_{B_1})}$

$$N_{A,z}=\frac{cD_{AB}}{(z_2-z_1)}\frac{(y_{A_1}-y_{A_2})}{y_{B,lm}}=\frac{D_{AB}P}{RT(z_2-z_1)}\frac{(p_{A_1}-p_{A_2})}{p_{B,lm}} \quad \text{as} \quad y_A=\frac{P_A}{P}$$

Ex.: Absorption or humidification process

정상상태에 대하여 $N_{A,z}$ 를 먼저 구하고, 면적 (S)를 곱하면, 이 공정에서 시간당 전달되는 물질의 량이 쉽게 구해진다.

· Concentration distribution

$$N_A=-\frac{c\,D_{AB}}{(1-y_A)}\frac{dy_A}{dz} \quad \& \quad \frac{dN_{A,z}}{dz}=0 \rightarrow \quad \frac{d}{dz}\left(-\frac{c\,D_{AB}}{1-y_A}\frac{dy_A}{dz}\right)=0$$

$$-\frac{1}{1-y_A}\frac{dy_A}{dz}=c_1 \quad \& \quad -\ln(1-y_A)=c_1 z+c_2 \quad ,$$

B.C.'s: at $z=z_1$, $y_A=y_{A_1}$ and at $z=z_2$, $y_A=y_{A_2}$

$$\left(\frac{1-y_A}{1-y_{A_1}}\right)=\left(\frac{1-y_{A_2}}{1-y_{A_1}}\right)^{\frac{z-z_1}{z_2-z_1}} \quad \text{or} \quad y_A=1-(1-y_{A_1})\left(\frac{1-y_{A_2}}{1-y_{A_1}}\right)^{\frac{z-z_1}{z_2-z_1}}$$

· Film theory

· "Film concept": 물질전달의 모든 저항이 경계면 근처에 국한되어 있다. 이때 가상적인 매우 작은 길이로서 δ 가 정의되고, 이 길이는 정지상태로서 일정한 값으로 가정된다. 따라서 이 모델에서는 δ 내에서의 유동이 정상상태의 층류 흐름으로 가정된다.

· Film 외부에서는 eddy 또는 eddy보다는 큰 크기인 대류에 의한 혼합이 있게 된다. 한편, film의 깊이 δ 를 추산하면, 기체의 경우 10^{-4}m 정도, 그리고 액체의 경우 10^{-5}m 정도로 알려져 있다.

· 분자확산에 의한 저항 ~ 유동하는 유체의 혼합에 의한 대류 저항

$$N_{A,z}=\frac{D_{AB}P}{RT(z_2-z_1)}\frac{(p_{A_1}-p_{A_2})}{p_{B,lm}} \quad \sim \quad N_{A,z}=k_c(c_{A_1}-c_{A_2})=\frac{k_c}{RT}(p_{A_1}-p_{A_2})$$

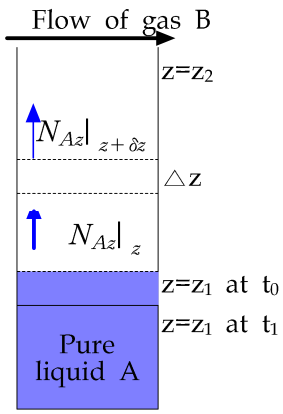
$$k_c=\frac{D_{AB}P}{p_{B,lm}\delta} \rightarrow \text{convective mass transfer coefficient} \propto \text{mass diffusivity}$$

actually, $k_c \propto D_{AB}^{0.5\sim1}$ 즉, film 내에서 농도분포가 선형으로 주어지는 경우에는 지수승이 1이 되고, 비선형일 경우 1보다는 작은 지수승을 갖는다. 따라서, film 내에서는 선형의 농도분포를 갖은 정상상태의 양상을 보이게 된다.

2) Pseudo-steady-state system

For long time period, one of the boundaries may move with time.

The length of the diffusion path changes a small amount over long period of time.



$$N_{A,z} = \frac{cD_{AB}}{(z_2 - z_1)} \frac{(y_{A_1} - y_{A_2})}{y_{B,lm}} \quad \text{at any instant}$$

let $(z_2 - z_1) = z(t)$, & $N_{A,z} = \frac{\rho_{A,L}}{M_A}\frac{dz}{dt}$: liquid surface

$$\therefore \frac{\rho_{A,L}}{M_A}\frac{dz}{dt} = \frac{cD_{AB}}{z}\frac{(y_{A_1} - y_{A_2})}{y_{B,lm}}$$

$$t = \frac{\rho_{A,L}\; y_{B,lm}/M_A}{cD_{AB}\,(y_{A_1} - y_{A_2})}\left(\frac{z_t^{\,2} - z_{t_0}^{\,2}}{2}\right)$$

$$D_{AB} = \frac{\rho_{A,L}\; y_{B,lm}/M_A}{c\,(y_{A_1} - y_{A_2})t}\left(\frac{z_t^{\,2} - z_{t_0}^{\,2}}{2}\right)$$

3) Equimolar counterdiffusion

- distillation of two constituents whose molar latent heats of vaporization are equal
- equimolar counterdiffusion, $N_{A,z} = -N_{B,z}$ & without reaction
- molar flux for a binary system: $N_A = -D_{AB}\frac{dc_A}{dz} + y_A(N_{A,z} + N_{B,z}) = -D_{AB}\frac{dc_A}{dz}$

G.E.: $\frac{dN_{A,z}}{dz} = 0 \rightarrow \frac{d^2c_A}{dz^2} = 0$ with B.C.'s: $c_A = c_{A1}$ $at\ z = z_1$; $c_A = c_{A2}$ $at\ z = z_2$

$$\frac{c_A - c_{A_1}}{c_{A_1} - c_{A_2}} = \frac{z - z_1}{z_1 - z_2} \quad \& \quad N_{A,z} = \frac{D_{AB}}{(z_2 - z_1)}(c_{A_1} - c_{A_2}) = \frac{D_{AB}}{RT(z_2 - z_1)}(p_{A_1} - p_{A_2})$$

- film concept

$$k^0 = \frac{D_{AB}}{\delta}$$

2. One-dimensional diffusion systems with chemical reactions

- simultaneous diffusion and disappearance or appearance of species through chemical reaction
- homogeneous reaction : reaction occurs uniformly throughout a given phase
- heterogenous reaction : reaction occurs within or at a boundary of the phase
- general differential equation : $\nabla \cdot \overrightarrow{N_A} + \frac{\partial c_A}{\partial t} - R_A = 0$

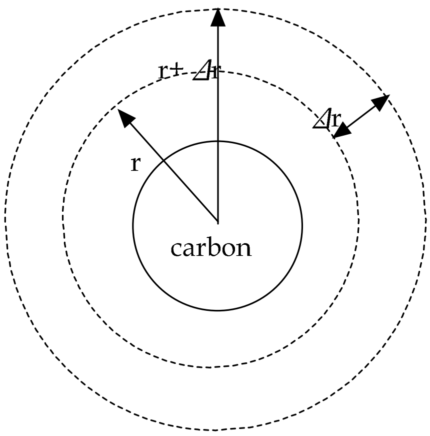
1) Simultaneous diffusion and heterogeneous, 1st-order chemical reactions

~ diffusion with varying area

- diffusion-controlled process : (reaction rate) >> (the rate of diffusion)
- reaction-controlled process : (reaction rate) >> (the rate of diffusion)

Example: diffusion of oxygen to the surface of spherical particle of coal

Reaction 1: 2C + O_2 → 2CO : diffusion-controlled process



Assume : no reaction between O_2 & CO, steady state

Balance on O_2 : $N_{O_2,r}4\pi r^2 |_r - N_{O_2,r}4\pi r^2 |_{r+\Delta r} = 0 \rightarrow \frac{1}{r^2}\frac{d}{dr}(r^2 N_{O_2,r}) = 0$

$$r^2 N_{O_2,r}|_{r_1} = r^2 N_{O_2,r}|_{r_2} = r^2 N_{O_2,r}|_r$$

similarly, $\frac{d}{dr}(r^2 N_{CO,r}) = 0$ & $-N_{CO,r} = 2N_{O_2,r}$ by stoichiometry

$$N_{O_2,r} = -cD_{O_2,air}\frac{dy_{O_2}}{dr} + y_{O_2}(N_{O_2,r} + N_{CO,r} + N_{N_2,r}) = -\frac{cD_{O_2-air}}{1+y_{O_2}}\frac{dy_{O_2}}{dr}$$

at $r = R$ $y_{O_2} = y_{O_2}|_R$ & at $r = \infty$ $y_{O_2} = 0.21$

Rate of mass transfer of O_2 : $W_{O_2} = 4\pi r^2 N_{O_2,r}|_R = 4\pi cD_{O_2-air}R\ln(\frac{1+y_{O_2}|_R}{1+0.21})$

→ O_2가 얼마만큼 전달되는가? (소모량)

(rate of oxygen transfer, rate of combustion of coal, rate of energy released)

Reaction 2: $C + O_2 \rightarrow CO_2$, $N_{O_2,r} = -N_{CO_2,r}$

$$N_{O_2,r} = -cD_{O_2,air}\frac{dy_{O_2}}{dr} + y_{O_2}(N_{O_2,r} + N_{CO,r} + N_{N_2,r}) = -cD_{O_2-air}\frac{dy_{O_2}}{dr}$$

at $r = R$ $y_{O_2} = y_{O_2}|_R$ & at $r = \infty$ $y_{O_2} = 0.21$

$W_{O_2} = 4\pi cD_{O_2-air}R(y_{O_2}|_R - 0.21)$: rate of oxygen transfer

cf) Heterogeneous reaction

at $r = R$, $N_{A,r}|_R = -k_s c_A|_R$ where k_s is reaction rate constant

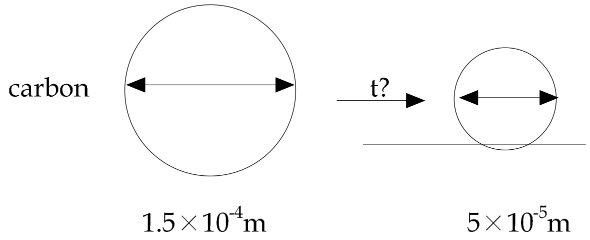
· instantaneous reaction 인 경우: $c_A|_R = 0$ 즉, 확산성분=0 & 반응만 진행된다.

$W_{O_2} = 4\pi cD_{O_2-air}R\ln(\frac{1}{1+0.21}) < 0$: Oxygen → negative direction(disapearing)

· instantaneous reaction 이 아닌 경우: $y_A|_R = \frac{-N_A|_R}{k_s c}$

$$W_{O_2} = 4\pi cD_{O_2-air}R\ln[\frac{1-\frac{N_{O_2,r}|_R}{ck_s}}{1+0.21}] \simeq \frac{4\pi cD_{O_2-air}}{1-\frac{D_{O_2,r}|_R}{k_s R}}\ln[\frac{1}{1+0.21}]$$ by Taylor expansion

ex 4. diffusion-limited → instantaneous reaction : $c_A|_R = 0$



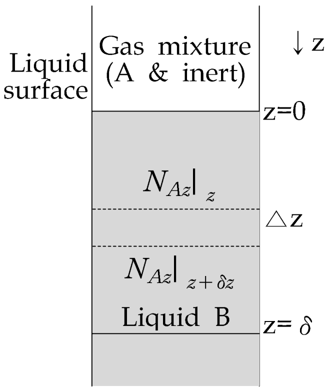
$D_{AB} = 1.3\times10^{-4} m^2/s$

$2C + O_2 \rightarrow 2CO$

$$W_c = -2cN_{O_2} = 2[4\pi c D_{O_2-air} R \ln 0.21], \qquad \frac{\rho_c}{M_c}\frac{dr}{dt} = \frac{\rho_L}{M_L} - 4\pi R^2 \frac{dR}{dt}$$

$$\therefore \ t = \frac{\rho_c(R_i^2 - R_f^2)}{4M_c c D_{O_2-air} \ln(1.21)}$$

2) Diffusion with a homogeneous, first-order chemical reaction



gas absorption

Absorption of gas : $c_{A0}|_{z=0}$ & $c_{A_\delta} = 0$

$$N_{A,z} = -D_{AB}\frac{dc_A}{dz}$$

$$\nabla \cdot N_A + \frac{\partial c_A}{\partial t} - R_A = 0 \quad \rightarrow \quad \frac{d}{dz}N_{A,z} - R_A = 0$$

$$-\frac{d}{dz}\left(D_{AB}\frac{dc_A}{dz}\right) + k_1 c_A = 0 \ \rightarrow \ D_{AB}\frac{d^2 c_A}{dz^2} - k_1 c_A = 0$$

$$c_A = c_1 \cosh\sqrt{\frac{k_1}{D_{AB}}}z + c_2 \sinh\sqrt{\frac{k_1}{D_{AB}}}z$$

· concentration profile : $c_A = c_{A_0}\cosh\sqrt{\frac{k_1}{D_{AB}}}z - \frac{c_{A_0}\sinh\sqrt{k_1/D_{AB}}\,z}{\tanh\sqrt{k_1/D_{AB}}\,\delta}$

· mass flux: $N_{A,z}|_{z=0} = \frac{D_{AB}c_{A_0}}{\delta}\left[\frac{\sqrt{k_1/D_{AB}}\delta}{\tanh\sqrt{k_1/D_{AB}}\delta}\right]$

↓

Hattta number ~ influence of chemical reaction

$$N_{A,z} = \frac{D_{AB}c_{AB}}{\delta}$$

$$k_1 \sim \tanh\sqrt{\frac{k_1}{D_{AB}}}\delta \sim 1$$

$N_{A,z}|_{z=0} = \sqrt{D_{AB}k_1}\,(c_{A_0} - 0) \ \leftrightarrow \ N_{A,z} = k_c\,(c_{A_1} - c_{A_2})$

↓

대류전달계수

· $k_c \propto \sqrt{D_{AB}}$: penetration theory model

first-order reaction : disappearance of A

cf) film model : $k_c \propto D_{AB}$