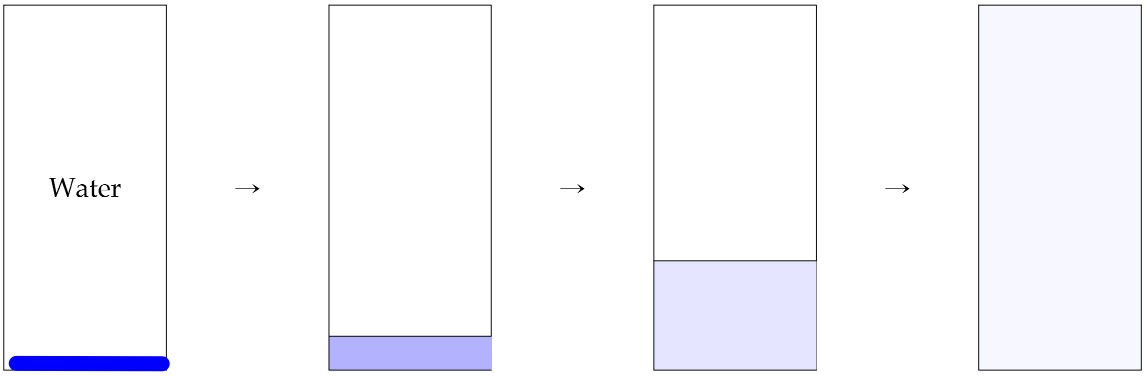
Chap. 24. Fundamentals of mass transfer

1. Molecular mass transfer

· Diffusion mass transfer : random molecular movement at a state ~ Fick's concept



Copper Sulfate   1 day   1 week   1 month

The Fick Rate Equation

· Concentration: amount(mass or mole) of a species in an elementary volume containing multi-component mixture, 정량화의 기본요건

i) mass concentration for species A (or density),

$$\rho_A = \frac{m_A}{V} \text{ : mass of A per unit volume of the mixture}$$

$$\rho = \sum_{i=1}^{n} \rho_i \text{ (total or bulk mass)}, \quad w_A = \frac{\rho_A}{\rho} \;\&\; \sum_{i=i}^{n} w_i = 1 \text{ (weight fraction)}$$

ii) molar concentration for species A : $c_i = \frac{n_i}{V} = \frac{m_i / M_i}{V} = \frac{\rho_i}{M_i}$

$$c = \sum_{i=1} c_i \text{ (bulk concentration)}, \quad x_i = \frac{c_i}{c}, \quad \sum_{i=1}^{n} x_i = 1 \text{ (mole fraction)}$$

기체의 경우(이상기체로 가정): $c_i = \frac{P_i}{RT}$, $y_i = \frac{c_i}{c} = \frac{p_i}{P}$, $\sum_{i=1}^{n} y_i = 1$

· Velocity

absolute velocity of species i : $\vec{v_i}$

mass-average velocity: $\vec{v} = \frac{\sum \rho_i \vec{v_i}}{\sum \rho_i} = \frac{\sum \rho_i \vec{v_i}}{\rho}$

mole-average velocity: $\vec{V} = \frac{\sum c_i \vec{v_i}}{\sum c_i} = \frac{\sum c_i \vec{v_i}}{c}$

diffusion velocity of species i relative to $\vec{v}$: $\vec{v_i} - \vec{v}$

diffusion velocity of species i relative to $\vec{V}$: $\vec{v_i} - \vec{V}$

· Fick's law: 1. 농도구배가 존재하는 계에서 물질은 분자의 움직임에 의한 확산속도를 갖는다.

2. 이때 발생하는 물질의 flux 는 농도구배(농도차/거리)에 비례한다.

※ Flux : 단위시간당, 단위면적당 이동하는 물질의 량(질량 또는 몰수)

$$J_{A,z} = -D_{AB}\frac{d\,c_A}{dz} = -c\,D_{AB}\frac{d\,y_A}{dz} \text{ : molar flux}$$

(The total concentration c is constant under isothermal and isobaric condition.)

D_{AB} : Mass diffusivity or diffusion coefficient for a binary system

$\overrightarrow{J_A} = J_{A,x}\vec{i} + J_{A,y}\vec{j} + J_{A,z}\vec{k}$ in a rectangular coordinate

$j_{A,z} = -D_{AB}\dfrac{d\rho_A}{dz} = -\rho D_{AB}\dfrac{dw_A}{dz}$: mass flux

$$J_{A,z} = -cD_{AB}\frac{dy_A}{dz} = c_A(v_{A,z} - V_z)$$

$$c_A v_{A,z} = -cD_{AB}d\frac{y_A}{dZ} + c_A V_z, \qquad V_z = \frac{1}{c}(c_A v_{A,z} + c_B v_{B,z})$$

let $\vec{N}_A = c_A\vec{v}_A$ & $\vec{N}_B = c_B\vec{v}_B$

$$N_{A,Z} = -cD_{AB}\frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z})$$

분자만의 움직임에 의한 확산 　 bulk 유동현상의 A성분의 물질전달

vector form of molar flux

$\vec{N}_A = -cD_{AB}\nabla y_A + y_A(\vec{N}_A + \vec{N}_B)$: A & B binary system

$\vec{N}_A = -cD_{A-Mix}\nabla y_A + y_A\sum_{i=1}^{n}\vec{N}_i$: A in multi-component system

concentration gradient contribution 　 bulk motion contribution

where $\nabla = \dfrac{\partial}{\partial x}\vec{i} + \dfrac{\partial}{\partial y}\vec{j} + \dfrac{\partial}{\partial z}\vec{k}$.

mass flux : $\vec{n}_A = -D_{AB}\nabla\rho_A + w_A(\vec{n}_A + \vec{n}_B)$

$\vec{n}_A = -\rho D_{AM}\nabla w_A + w_A(\overrightarrow{n_A} + \overrightarrow{n_B})$ for isothermal & isobaric condition

Related types of molecular mass transfer

chemical potential in terms of concentration: $\mu_c = \mu^0 + RT\ln c_A$

Nernst-Einstein relation : diffusion velocity ∝ (mobility; u_A)×(potential gradient; $\dfrac{d\mu_c}{dz}$)

$$v_{A,z} - V_z = u_A\frac{d\mu_c}{dz} = -\frac{D_{AB}}{RT}\frac{d\mu_c}{dz}$$

molar mass flux: $J_{A,z} = c_A(v_{A,z} - V_z) = -D_{AB}\dfrac{c_A}{RT}\dfrac{d\mu_c}{dz} = -D_{AB}\dfrac{dc_A}{dz}$

points of thermodynamics: 열역학 제2법칙에 의하면, 평형에서 벗어나 있는 계는 평형에 도달하려고 함을 알려준다. 열역학의 법칙에서는 그와 같은 과정의 필연성과 순서를 제시할 뿐, 평형으로 진행하는 속도 또는 평형에 도달하는데 소요되는 시간을 알 수가 없다. 열역학적 함수로서 화학포텐셜(chemical potential)은 주어진 계에 물질의 량이 변화할 때, 성분의 변화량에 대한 포텐셜에너지의 차로 정의된다. 이를 정량적으로 설명하면, 많은 량의 혼합물로부터 A 성분 1 mole을 가역적으로 분리하는데 소요되는 일이 바로 화학포텐셜에 대한 성분의 기여를 나타낸다.

2. Diffusion coefficient : D_{AB}

· Fick's Law : $J_{A,z} = -D_{AB}\frac{dc_A}{dz}$ ~ molar flux

차원: $[\frac{Mole}{L^2 t}] = [X]\frac{[Mole/L^3]}{[L]}$ $\therefore [X]=[\frac{L^2}{t}]$ or m^2/s

유사성: $D_{AB} \sim \alpha\ (=\frac{k}{\rho C_P}) \sim \nu\ (=\frac{\mu}{\rho}) = [\frac{L^2}{t}]$

thermal diffusivity, kinematic viscosity

$$\frac{\partial c_A}{\partial t} = D_{AB}\frac{\partial^2 c_p}{\partial z^2}, \quad \frac{\partial T}{\partial t} = \alpha\frac{\partial^2 T}{\partial z^2}, \quad \frac{\partial v}{\partial t} = \nu\frac{\partial^2 v}{\partial z^2}$$

크기정도: Gas $5 \times 10^{-6} \sim 10^{-5}\ m^2/s$

Liquid $10^{-10} \sim 10^{-9}\ m^2/s$

Solid $10^{-14} \sim 10^{-10}\ m^2/s$

· Gas mass diffusivity of binary system (A & B)

$$D_{AB} = \frac{0.001858\,T^{3/2}[\frac{1}{M_A}+\frac{1}{M_B}]^{1/2}}{P\sigma_{AB}{}^2\Omega_D}$$ by kinetic theory

$$D_{AB} \propto T^{3/2}, \frac{1}{\sqrt{M}}, \frac{1}{P}$$

· Gas mixture (more than 2 components: 1 & mixture)

$$D_{1-mix} = \frac{1}{\frac{y'_2}{D_{1-2}}+\frac{y'_3}{D_{1-3}}+\cdots\cdots+\frac{y'_n}{D_{1-n}}}$$

· Liquid mass diffusivity

~ order of magnitude smaller than gas

~ 경우에 따라서 농도와 점도에 의존한다.

$$D_{AB} = \frac{kT}{\sigma\pi r\mu_B}$$: Stokes-Einstein Law

· Solid mass diffusivity

Pore diffusions : $\vec{J}_A = -cD_{A,eff}\nabla y_A$ (effective diffusion coefficient)

Fick diffusion → diffusion in large-size pore

Knudsen diffusion → size of pore～mean free path of molecules

Surface diffusion → diffusion of absorbed molecules along surface

Atomic movements(vacancy, interstitial, interstitialcy, direct interchange)

3. Convective mass transfer

"Convection" ~ 복합성분 유체의 bulk motion이 있는 경우, 경계면에서의 물질전달량

Forced convection : external force to drive flow of fluids

Free convection : body force (gravity 등)

$$N_A = k_c\,\Delta c_A = k_c(c_{A,surface} - c_{A,bulk})$$

k_c : convective mass transfer coefficient [L/t]