Chap. 27. Unsteady-state molecular diffusion

- transient process, unsteady-state process, time-dependent processes
  - ~ concentration (and mass flux) at a given point varies with time
  - ~ an initial startup, a batch (or closed-system operation)
- equation of continuity for component A,

$$\nabla \cdot \overrightarrow{n_A} + \frac{\partial \rho_A}{\partial t} - r_A = 0, \qquad \nabla \cdot \overrightarrow{N_A} + \frac{\partial c_A}{\partial t} - R_A = 0$$

- $\rho = \rho(t, x, y, z)$, $c_A = c_A(t, x, y, z)$ in a rectangular coordinate
- requirements of solution : *mathematical details! (G.E., B.C. & I.C.)*

1. Analytical solutions

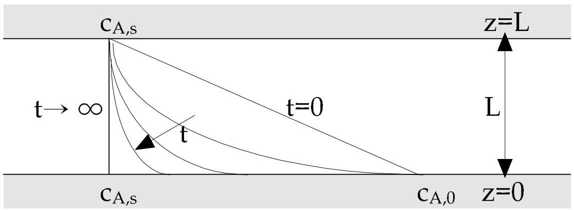
- one-dimensional(~z) mass transfer in Fick's 2nd law of diffusion ~ governing equation

$$\frac{\partial c_A}{\partial t} = D_{AB} \frac{\partial^2 c_A}{\partial z^2}$$; w/out bulk motion($\vec{v} = 0$), w/out chemical reaction($R_A = 0$)

cf.) $\frac{\partial \rho_A}{\partial t} = D_{AB} \frac{\partial^2 \rho_A}{\partial z^2}$, $\frac{\partial w_A}{\partial t} = D_{AB} \frac{\partial^2 w_A}{\partial z^2}$; $\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2}$ ~Fourier's 2nd law

- mathematical techniques: separation of variables, similarity method, Laplace transforms

(1) Transient diffusion under conditions of negligible surface resistance



G.E.: $\frac{\partial c_A}{\partial t} = D_{AB} \frac{\partial^2 c_A}{\partial z^2}$

B.C.'s: $c_A = c_{A,s}$ at z=0

$c_A = c_{A,s}$ at z=L

I.C.: $c_A = c_{A,0} - (c_{A,0} - c_{A,s}) \frac{z}{L}$ at t=0

Solution : G.E.: $\frac{\partial \theta}{\partial t} = D_{AB} \frac{\partial^2 \theta}{\partial z^2}$, when $\theta = \theta(t, z) = \frac{c_A - c_{A,s}}{c_{A,0} - c_{A,s}}$.

B.C.'s: $\theta = 0$ for z=0 & L, I.C.: $\theta = 1 - \frac{z}{L}$ at t=0

Separation of variables: $\theta = T(t) Z(z)$, $\frac{Z''}{Z} = \frac{T'}{D_{AB} T} = -\lambda^2 < 0$

$$Z'' + \lambda^2 Z = 0 \quad \text{with } Z(0) = Z(L) = 0$$

$$Z(z) = \cancel{a_1} \cos \lambda z + a_2 \sin \lambda z \quad \rightarrow \quad Z_n = a_n^* \sin \frac{n\pi z}{L} \quad \& \quad T_n = a_3 \exp\left(-D_{AB} \left(\frac{n\pi}{L}\right)^2 t\right)$$

as $Z(0) = 0$ & $Z(L) = a_2 \sin(\lambda L) = 0 \rightarrow \lambda = \frac{n\pi}{L}$: eigenvalue

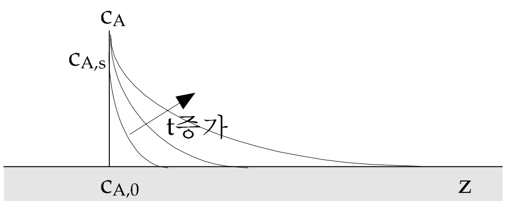
$$\theta = \sum_{n=1}^{\infty} a_n \sin\left(\frac{n\pi z}{L}\right) \exp\left(-D_{AB} \left(\frac{n\pi}{L}\right)^2 t\right) \rightarrow \theta(0, z) = 1 - \frac{z}{L} = \sum_{n=1}^{\infty} a_n \sin\left(\frac{n\pi z}{L}\right)$$

$$a_n = \frac{2}{L} \int_0^L \left(1 - \frac{z}{L}\right) \sin\left(\frac{n\pi z}{L}\right) dz \rightarrow a_n = \frac{2}{n\pi}$$

$$\theta = \frac{c_A - c_{A,s}}{c_{A,0} - c_{A,s}} = \sum_{n=1}^{\infty} \frac{2}{n\pi} \sin\left(\frac{n\pi z}{L}\right) \exp\left(-D_{AB} \left(\frac{n\pi}{L}\right)^2 t\right),$$

$$N_{A,z} = -D_{AB} \frac{\partial c_A}{\partial z} = \frac{2 D_{AB}}{L} (c_{A,s} - c_{A,0}) \sum_{n=1}^{\infty} \cos\left(\frac{n\pi z}{L}\right) \exp\left(-D_{AB} \left(\frac{n\pi}{L}\right)^2 t\right)$$

(2) Transient diffusion in a semi-infinite medium



G.E.: $\dfrac{\partial c_A}{\partial t} = D_{AB}\dfrac{\partial^2 c_A}{\partial z^2}$

B.C.'s: $c_A = c_{A,s}$ at z=0

$c_A = c_{A,0}$ as z→∞

I.C.: $c_A = c_{A,0}$ at t=0

Solution : Similarity method

$$Y = \frac{c_A - c_{A,0}}{c_{A,s} - c_{A,0}} = f\left(\frac{z}{z_1}, \frac{D_{AB}t}{z_1^2}\right) = f\left(\frac{D_{AB}t}{z^2}\right)$$

$$Y = Y(t, z) = Y(\eta) \quad \& \quad \eta = \frac{z}{2\sqrt{D_{AB}t}} : \text{similarity variable}$$

$$\frac{\partial Y}{\partial t} = \frac{\partial \eta}{\partial t}\frac{dY}{d\eta} = -\frac{\eta}{2t}\frac{dY}{d\eta}; \quad \frac{\partial^2 Y}{\partial z^2} = \left(\frac{\partial \eta}{\partial z}\right)^2 \frac{d^2Y}{d\eta^2} = \frac{1}{4D_{AB}t}\frac{d^2Y}{d\eta^2}$$

G.E.: $\dfrac{\partial c_A}{\partial t} = D_{AB}\dfrac{\partial^2 c_A}{\partial z^2}$ (PDE) → $\dfrac{d^2Y}{d\eta^2} + 2\eta\dfrac{dY}{d\eta} = 0$ (ODE)

B.C.'s & I.C. → $Y=1$ at $\eta=0$ & $Y=0$ as $\eta\to\infty$

let $p(\eta) = \dfrac{dY}{d\eta} = b_1 e^{-\eta^2}$ $\qquad Y = b_2 + b_1\int e^{-\xi^2}d\xi$

$$Y = \frac{c_A - c_{A,0}}{c_{A,s} - c_{A,0}} = 1 - \frac{2}{\sqrt{\pi}}\int_0^{\eta} e^{\xi^2}d\xi = 1 - erf\left(\frac{z}{2\sqrt{D_{AB}t}}\right)$$

cf.: Error function: $erf(\phi) = \dfrac{2}{\sqrt{\pi}}\displaystyle\int_0^x e^{y^2}dy \approx x$ for $x<0.4$ (부록 L)

$$erf(0) = 0, \quad erf(\infty) = 1, \quad erf(-\phi) = -erf(\phi)$$

2. Concentration-time chart for simple geometric shapes

Gurney-Lurie chart : flat plate, long cylinder, sphere (부록 F, p. 734)

→ partial differential equations for heat conduction and molecular diffusion

Four dimensionless ratios:

Y=unaccomplished concentration change $= \dfrac{c_{A,s} - c_A}{c_{A,s} - c_{A,0}}$, X_D=relative time $= \dfrac{D_{AB}t}{x_1^2}$

$n=$ relative position $= \dfrac{x}{x_1}$, $m=$ relative resistance $= \dfrac{D_{AB}}{k_c x_1}$

where x : distance from center to any point

k_c : convective mass transfer coefficient

(x_1 은 대상계의 중간에서 경계면까지의 거리임에 유의할 것!)

Assumptions

· Fick's 2nd law of diffusion: w/out fluid motion, w/out production & uniform D_{AB}

· Initial uniform concentration, c_{A0}

· Boundary remains constant with time

3. Numerical methods for transient mass transfer analysis

· Fick's 2nd law of diffusion : $\frac{\partial c_A}{\partial t} = D_{AB}\frac{\partial^2 c_A}{\partial z^2}$

· Finite Difference Method: (partial differential)→(finite difference) 연립방정식의 형태로 구성

$$\frac{\partial c_A}{\partial t} = \frac{c_{A,z}|_{t+\Delta t} - c_{A,z}|_t}{\Delta t}$$

$$\frac{\partial^2 c_A}{\partial z^2} = \frac{\frac{c_{A,t}|_{z+\Delta z} - c_{A,t}|_z}{\Delta z} - \frac{c_{A,t}|_z - c_{A,t}|_{z-\Delta z}}{\Delta z}}{\Delta z} = \frac{c_{A,t}|_{z+\Delta z} - 2c_{A,t}|_z + c_{A,t}|_{z-\Delta z}}{(\Delta z)^2}$$

$$\therefore \frac{c_{A,z}|_{t+\Delta t} - c_{A,z}|_t}{\Delta t} = D_{AB}\frac{c_{A,t}|_{z+\Delta z} - 2c_{A,t}|_z + c_{A,t}|_{z-\Delta z}}{(\Delta z)^2}$$

· $c_{A,z}|_{t+\Delta t} = c_{A,z}|_t + \frac{D_{AB}\Delta t}{(\Delta z)^2}[\, c_{A,t}|_{z+\Delta z} - 2c_{A,t}|_z + c_{A,t}|_{z-\Delta z}]$

· Diffusion number: $\frac{D_{AB}\Delta t}{(\Delta z)^2} \le \frac{1}{2}$ for stable solution

· when $\frac{D_{AB}\Delta t}{(\Delta z)^2} = \frac{1}{2}$, $c_{A,z}|_{t+\Delta t} = \frac{1}{2}(\, c_{A,t}|_{z+\Delta z} + c_{A,t}|_{z-\Delta z})$

· $N_{A,z}|_t = \frac{D_{AB}(c_{A,s} - c_{A1,t})}{\Delta x}$