

Fundamentals of Mass Transfer

When a system contains two or more components whose concentrations vary from point to point, there is natural tendency for mass to be transferred, minimizing the concentration differences within the system.

Mechanisms of mass transfer

Molecular Transfer ~ random molecular motion in quiescent fluid

Convective Transfer ~ transferred from surface into a moving fluid

Analogy between heat and mass transfer

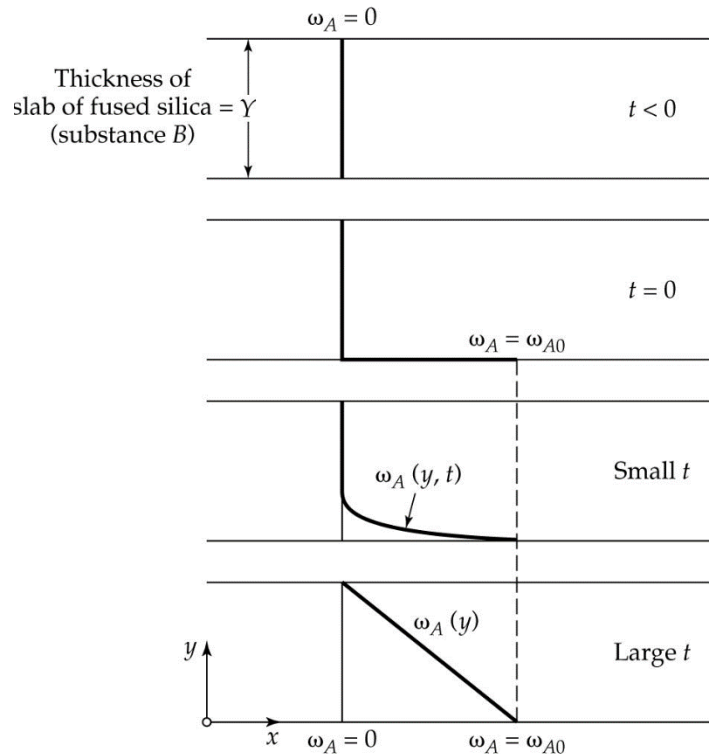
Mass transfer

Heat transfer

| | | |
|---------------------|--------|-----------------|
| Molecular transfer | —————> | Heat conduction |
| Convective transfer | —————> | Heat convection |

Molecular Mass Transfer(Molecular Diffusion)

Fick's law



$$j_{Az} = -\rho \mathcal{D}_{AB} \frac{d\omega_A}{dz}$$

$$J_{Az} = -C \mathcal{D}_{AB} \frac{dx_A}{dz}$$

In vector form $\underline{j}_A = -\rho \mathcal{D}_{AB} \nabla \omega_A$

$$\underline{J}_A = -C \mathcal{D}_{AB} \nabla x_A$$

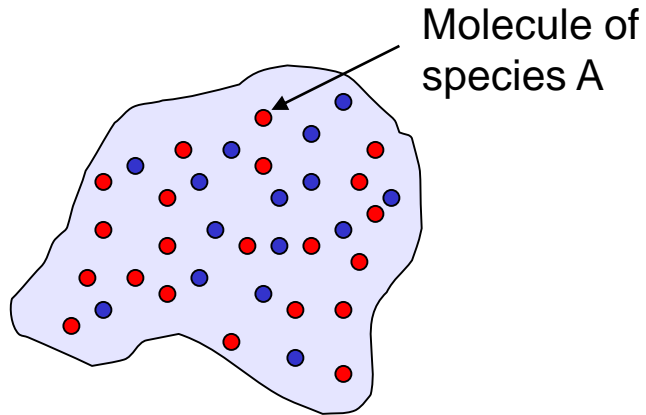
Mass diffusivity \mathcal{D}_{AB}

Prandtl number $Pr = \frac{\nu}{\alpha}$

Schmidt number $Sc = \frac{\mu}{\rho \mathcal{D}_{AB}} = \frac{\nu}{\mathcal{D}_{AB}}$

Lewis number $Le = \frac{k}{\rho C_p \mathcal{D}_{AB}} = \frac{\alpha}{\mathcal{D}_{AB}}$

Mass Concentration



dV in multicomponent
mixture

a) mass concentration (ρ_A)

the mass of A per unit volume of mixture

- Total mass concentration (density)

$$\rho = \sum_i \rho_i$$

- mass fraction

$$\omega_A = \frac{\rho_A}{\sum_i \rho_i} = \frac{\rho_A}{\rho}$$

$$\sum_i \omega_i = 1$$

Molar Concentration

b) molar concentration(C_A) ~ the number of moles of A present per unit volume of mixture

$$C_A = \frac{\rho_A}{M_A} \quad M_A - \text{molecular weight of A}$$

For ideal gas $P_A V = n_A RT$

$$C_A = \frac{n_A}{V} = \frac{P_A}{RT} \quad P_A - \text{partial pressure of A}$$

- Total molar concentration $C = \sum_i C_i$

$$\text{for ideal gas } C = \frac{n_{total}}{V} = \frac{P}{RT}$$

- Mole fraction

$$\text{for liquid } x_A = \frac{C_A}{C} \quad \sum_i x_i = 1 \quad \text{for gas } y_A = \frac{C_A}{C} \quad \sum_i y_i = 1$$

for ideal gas mixture

$$y_A = \frac{C_A}{C} = \frac{P_A/RT}{P/RT} = \frac{P_A}{P} \quad \text{Dalton's law of gas mixture}$$

Mass Average and Molar Average Velocity

a) mass average velocity

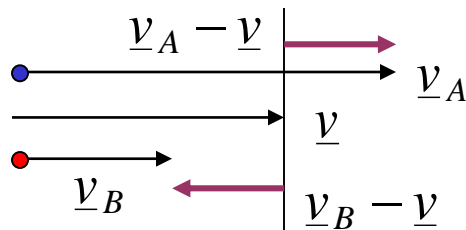
$$\underline{v} = \frac{\sum_i \rho_i \underline{v}_i}{\sum_i \rho_i} = \frac{\sum_i \rho_i \underline{v}_i}{\rho} = \sum_i \omega_i \underline{v}_i$$

\underline{v}_i - the absolute velocity of species i relative to stationary coordinate axes

b) molar average velocity

$$\underline{V} = \frac{\sum_i C_i \underline{v}_i}{\sum_i C_i} = \frac{\sum_i C_i \underline{v}_i}{C} = \sum_i x_i \underline{v}_i$$

c) diffusion velocity - the velocity of a particular species relative to the mass average or molar average velocity



$$\underline{v}_i - \underline{v} \quad \text{and} \quad \underline{v}_i - \underline{V}$$

A species can have a diffusion velocity only if gradients in the concentration exist

Mass Diffusivity

$$\mathcal{D}_{AB} = \frac{-J_A}{dC_A/dz} = \left(\frac{M}{L^2 t} \right) \left(\frac{1}{M/L^3 \cdot 1/L} \right) = \frac{L^2}{t}$$

$$\mathcal{D}_{AB} = f(\text{Temp.}, \text{Pressure}, \text{Composition})$$

Gases $5 \times 10^{-6} \sim 10^{-5}$ m²/s

Liquids $10^{-10} \sim 10^{-9}$

Solids $10^{-14} \sim 10^{-10}$

Molecular Mass and Molar Fluxes

Molar flux

$$\underline{J}_A = C_A(\underline{v}_A - \underline{V}) = -C\mathcal{D}_{AB}\nabla x_A$$

\mathcal{D}_{AB} mass diffusivity(diffusion coefficient) for component A diffusing through component B

\underline{J}_A the molar flux relative to the molar average velocity

Mass flux

$$\underline{j}_A = \rho_A(\underline{v}_A - \underline{v}) = -\rho\mathcal{D}_{AB}\nabla\omega_A$$

Convective Mass and Molar Fluxes

Molar flux

$$\underline{J}_A = C_A(\underline{v}_A - \underline{V}) = -C\mathcal{D}_{AB}\nabla x_A$$

$$C_A \underline{v}_A = -C\mathcal{D}_{AB}\nabla x_A + C_A \underline{V} \quad \underline{V} = \frac{\sum_i C_i \underline{v}_i}{\sum_i C_i} = \frac{\sum_i C_i \underline{v}_i}{C} = \sum_i x_i \underline{v}_i$$

$$C_A \underline{v}_A = -C\mathcal{D}_{AB}\nabla x_A + x_A \sum_i C_i \underline{v}_i$$

define $\underline{N}_A = C_A \underline{v}_A$ the molar flux relative to a set of stationary axes

$$\underline{N}_A = -C\mathcal{D}_{AB}\nabla x_A + x_A \sum_i \underline{N}_i = \underline{J}_A + x_A \sum_i \underline{N}_i$$

concentration gradient contribution bulk motion contribution

Mass flux relative to a fixed spatial coordinate system

$$\underline{n}_A = \rho \underline{v}_A = -\rho\mathcal{D}_{AB}\nabla \omega_A + \rho_A \underline{v} = -\rho\mathcal{D}_{AB}\nabla \omega_A + \omega_A \sum_i \underline{n}_i = \underline{j}_A + \omega_A \sum_i \underline{n}_i$$

Related Types of Molecular Mass Transfer

According to 2nd law of thermodynamics, system not equilibrium will tend to move toward equilibrium with time

—————> Driving force = chemical potential

Nernst-Einstein Relation

$$\underline{v}_A - \underline{V} = u_A \nabla \mu_c = -\frac{\mathcal{D}_{AB}}{RT} \nabla \mu_c$$

u_A Mobility of component A, or the resultant velocity of the molecule under a unit driving force

$$\underline{J}_A = C_A (\underline{v}_A - \underline{V}) = -C_A \frac{\mathcal{D}_{AB}}{RT} \nabla \mu_c$$

in homogeneous ideal solution at constant T & P

$$\mu_c = \mu^0 + RT \ln C_A$$

$$\underline{J}_A = -\mathcal{D}_{AB} \nabla C_A \quad \text{Fick's Equation}$$

Mass Transfer by Other Physical Conditions

~ produce a chemical potential gradient

Thermal diffusion(Soret diffusion)

Mass transfer by applying a temperature gradient to a multicomponent system
Small relative to other diffusion effects in the separation of isotopes

Pressure diffusion

Mass fluxes being induced in a mixture subjected to an external force field
Separation by sedimentation under gravity
Electrolytic precipitation due to an electrostatic force field
Magnetic separation of mineral mixtures by magnetic force
Component separation in a liquid mixtures by centrifugal force

Knudsen diffusion

If the density of the gas is low, or if the pores through which the gas traveling are quite small

- ⇒ the molecules will collide with the wall more frequently than each other (wall collision effect increases)
- ⇒ the molecules are momentarily absorbed and then given off in the random directions
- ⇒ gas flux is reduced by the wall collisions

Differential Equations of Mass Transfer

Conservation of Mass(overall)

$$\int_A \rho(\underline{v} \cdot \underline{n}) dA + \frac{\partial}{\partial t} \int_V \rho dV = 0$$

Conservation of Mass of Component A

$$\begin{aligned} & n_{A,x} \Delta y \Delta z \Big|_{x+\Delta x} - n_{A,x} \Delta y \Delta z \Big|_x + n_{A,y} \Delta z \Delta x \Big|_{y+\Delta y} - n_{A,y} \Delta z \Delta x \Big|_y \\ & + n_{A,z} \Delta x \Delta y \Big|_{z+\Delta z} - n_{A,z} \Delta x \Delta y \Big|_z + \frac{\partial \rho_A}{\partial t} \Delta x \Delta y \Delta z - r_A \Delta x \Delta y \Delta z = 0 \end{aligned}$$

$$\nabla \cdot \underline{n}_A + \frac{\partial \rho_A}{\partial t} - r_A = 0$$

Equation of Continuity for Component A

$$\nabla \cdot \underline{N}_A + \frac{\partial C_A}{\partial t} - R_A = 0$$

In binary mixture

$$\nabla \cdot \underline{n}_A + \frac{\partial \rho_A}{\partial t} - r_A = 0$$

$$\nabla \cdot \underline{n}_B + \frac{\partial \rho_B}{\partial t} - r_B = 0$$

$$\nabla \cdot (\underline{n}_A + \underline{n}_B) + \frac{\partial (\rho_A + \rho_B)}{\partial t} - (r_A + r_B) = 0$$

$$\underline{n}_A + \underline{n}_B = \rho_A \underline{v}_A + \rho_B \underline{v}_B = \rho \underline{v}$$

$$\rho_A + \rho_B = \rho$$

$$r_A = -r_B$$

$$\nabla \cdot \rho \underline{v} + \frac{\partial \rho}{\partial t} = 0$$

Equation of Continuity for the Mixture

$$\underline{n}_A = \underline{j}_A + \omega_A \rho \underline{v}$$

$$\nabla \cdot \underline{n}_A = \nabla \cdot \underline{j}_A + \nabla \cdot (\omega_A \rho \underline{v})$$

$$\nabla \cdot \underline{n}_A + \frac{\partial \rho_A}{\partial t} - r_A = 0$$

$$\Rightarrow \nabla \cdot \underline{j}_A + \frac{\partial \rho \omega_A}{\partial t} + \nabla \cdot (\rho \omega_A \underline{v}) - r_A = 0$$

$$\rho \frac{\partial \omega_A}{\partial t} + \omega_A \frac{\partial \rho}{\partial t} + \rho \underline{v} \cdot \nabla \omega_A + \omega_A \nabla \cdot \rho \underline{v} = 0$$

$$\rho \frac{D\omega_A}{Dt} + \nabla \cdot \underline{j}_A - r_A = 0$$

in terms of molar unit

$$\nabla \cdot \underline{N}_A + \frac{\partial C_A}{\partial t} - R_A = 0$$

$$\nabla \cdot \underline{N}_B + \frac{\partial C_B}{\partial t} - R_B = 0$$

$$\nabla \cdot (\underline{N}_A + \underline{N}_B) + \frac{\partial (C_A + C_B)}{\partial t} - (R_A + R_B) = 0$$

$$\underline{N}_A + \underline{N}_B = C_A \underline{v}_A + C_B \underline{v}_B = C \underline{V}$$

$$C_A + C_B = C$$

But R_A is not always $-R_B$

for only stoichiometry reaction ($A \rightleftharpoons B$) $R_A = -R_B$

$$\nabla \cdot C \underline{V} + \frac{\partial C}{\partial t} - (R_A + R_B) = 0$$

$$\underline{N}_A = -C\mathcal{D}_{AB}\nabla y_A + y_A(\underline{N}_A + \underline{N}_B)$$

or
$$\underline{N}_A = -C\mathcal{D}_{AB}\nabla y_A + C_A\underline{V}$$

$$\underline{n}_A = -\rho\mathcal{D}_{AB}\nabla\omega_A + \omega_A(\underline{n}_A + \underline{n}_B)$$

or
$$\underline{n}_A = -C\mathcal{D}_{AB}\nabla\omega_A + \rho_A\underline{v}$$

$$\rho\frac{D\omega_A}{Dt} + \nabla \cdot \underline{j}_A - r_A = 0$$

$$\left(\frac{\partial\rho_A}{\partial t} + \nabla \cdot \rho_A\underline{v}\right) = \mathcal{D}_{AB}\nabla^2\omega_A + r_A$$

If ρ and \mathcal{D}_{AB} are constant

$$\rho\frac{\partial\omega_A}{\partial t} + \omega_A\frac{\partial\rho}{\partial t} + \omega_A\nabla \cdot \rho\underline{v} + \rho\underline{v} \cdot \nabla\omega_A = \rho\mathcal{D}_{AB}\nabla^2\omega_A + r_A \quad \rho\left(\frac{\partial\omega_A}{\partial t} + \underline{v} \cdot \nabla\omega_A\right) = \rho\mathcal{D}_{AB}\nabla^2\omega_A + r_A$$

$$\frac{\partial C_A}{\partial t} + \underline{V} \cdot \nabla C_A = \mathcal{D}_{AB}\nabla^2 C_A + R_A$$

$$\frac{\partial}{\partial t} \rho \omega_A = -\nabla \cdot \underline{\mathbf{n}}_A + \underline{\mathbf{r}}_A$$

$$\underline{\mathbf{n}}_A = \underline{\mathbf{j}}_A + \rho \underline{\mathbf{v}} \omega_A$$

$$\frac{\partial}{\partial t} \rho \underline{\mathbf{v}} = -[\nabla \cdot \underline{\underline{\phi}}] + \rho \underline{\mathbf{g}}$$

$$\underline{\underline{\phi}} = \underline{\underline{\pi}} + \rho \underline{\mathbf{v}} \underline{\mathbf{v}}$$

$$\frac{\partial}{\partial t} \rho \left(\hat{\mathbf{U}} + \frac{1}{2} \mathbf{v}^2 \right) = -\nabla \cdot \underline{\mathbf{e}} + (\rho \underline{\mathbf{v}} \cdot \underline{\mathbf{g}})$$

$$\underline{\mathbf{e}} = \underline{\mathbf{q}} + [\underline{\underline{\pi}} \cdot \underline{\mathbf{v}}] + \rho \underline{\mathbf{v}} \left(\hat{\mathbf{U}} + \frac{1}{2} \mathbf{v}^2 \right)$$

$$\begin{aligned} \rho(\mathbf{T}, \omega_A) &= \bar{\rho} + \left. \frac{\partial \rho}{\partial \mathbf{T}} \right|_{\bar{\mathbf{T}}, \bar{\omega}_A} (\mathbf{T} - \bar{\mathbf{T}}) + \left. \frac{\partial \rho}{\partial \omega_A} \right|_{\bar{\mathbf{T}}, \bar{\omega}_A} (\omega_A - \bar{\omega}_A) + \dots \\ &\approx \bar{\rho} - \bar{\rho} \bar{\beta} (\mathbf{T} - \bar{\mathbf{T}}) - \bar{\rho} \bar{\zeta} (\omega_A - \bar{\omega}_A) \end{aligned}$$

$$\rho \frac{D \underline{\mathbf{v}}}{Dt} = \left(-\nabla \underline{\mathbf{p}} + \bar{\rho} \underline{\mathbf{g}} \right) - [\nabla \cdot \underline{\underline{\tau}}] - \bar{\rho} \underline{\mathbf{g}} \bar{\beta} (\mathbf{T} - \bar{\mathbf{T}}) - \bar{\rho} \underline{\mathbf{g}} \bar{\zeta} (\omega_A - \bar{\omega}_A)$$

Boundary Conditions

Initial Conditions $at\ t = 0, \ C_A = C_{A0}$ or $\rho_A = \rho_{A0}$

Boundary Conditions

Case 1) The concentration of the surface may be specified

$$C_A = C_{A1}, \quad y_A = y_{A1}, \quad x_A = x_{A1}, \quad \rho_A = \rho_{A0}, \quad \omega_A = \omega_{A1},$$

Case 2) The mass flux at the surface may be specified

$$\underline{j}_A = \underline{j}_{A1}, \quad \underline{N}_A = \underline{N}_{A1}, \quad \underline{j}_A = 0(\text{impermeable}), \quad \underline{j}_{A,z\ surface} = -\rho D_{AB} \left. \frac{d\omega_A}{dz} \right|_{z=0}$$

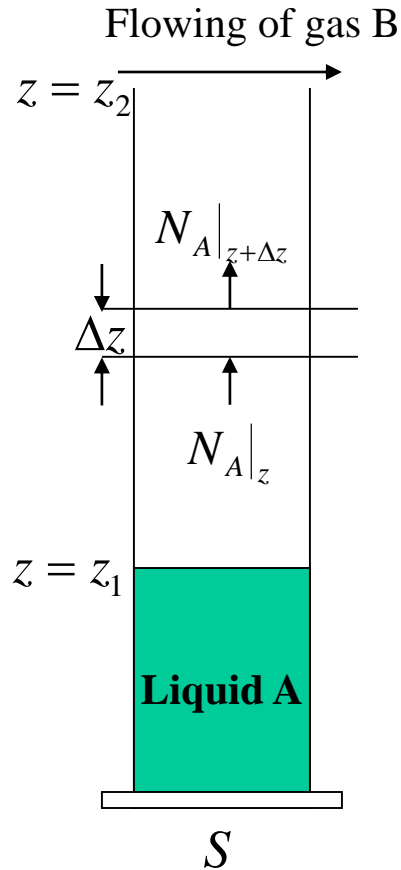
Case 3) The rate of heterogeneous chemical reaction may be specified

$$\underline{N}_{A,z\ surface} = k_n C_A^n \Big|_{surface}$$

Case 4) The species may be lost from the phase of interest by convective mass transfer

$$\underline{N}_{A,z\ surface} = k_c (C_{A,surface} - C_{A,\infty})$$

Steady State Diffusion of A through Stagnant B



Mass Balance Equation

$$SN_{A,z}|_{z+\Delta z} - SN_{A,z}|_z = 0$$

$$\frac{dN_{A,z}}{dz} = 0 \quad \frac{dN_{B,z}}{dz} = 0$$

At $z=z_1$, gas B is insoluble in liquid A $\therefore N_{B,z} = 0$

~ Component B is stagnant

$$N_{A,z} = -C\mathcal{D}_{AB} \frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z})$$

$$N_{B,z} = 0$$

$$N_{A,z} = -\frac{C\mathcal{D}_{AB}}{1-y_A} \frac{dy_A}{dz}$$

$$\text{at } z = z_1, \quad y_A = y_{A1}$$

$$\text{at } z = z_2, \quad y_A = y_{A2}$$

$$N_{A,z} \int_{z_1}^{z_2} dz = C \mathcal{D}_{AB} \int_{y_{A1}}^{y_{A2}} - \frac{dy_A}{1 - y_A}$$

$$N_{A,z} = \frac{C \mathcal{D}_{AB}}{z_2 - z_1} \ln \frac{1 - y_{A2}}{1 - y_{A1}} = \frac{C \mathcal{D}_{AB}}{z_2 - z_1} \frac{y_{A1} - y_{A2}}{y_{B,\ln}} = \frac{C \mathcal{D}_{AB}}{(z_2 - z_1) y_{B,\ln}} (y_{A1} - y_{A2})$$

$$y_{B,\ln} = \frac{y_{B2} - y_{B1}}{\ln y_{B2}/y_{B1}} = \frac{(1 - y_{A2}) - (1 - y_{A1})}{\ln(1 - y_{A2})/(1 - y_{A1})}$$

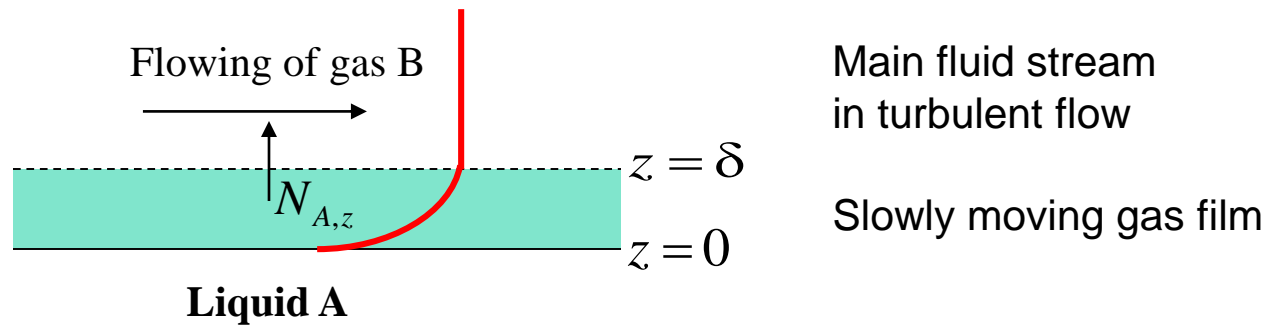
For ideal gas $C = \frac{n}{V} = \frac{P}{RT}$ and $y_A = \frac{P_A}{P}$

$$N_{A,z} = \frac{\mathcal{D}_{AB} P}{RT(z_2 - z_1)} \frac{P_{A1} - P_{A2}}{P_{B,\ln}}$$

Steady state diffusion of one gas through a second gas
~ absorption, humidification

Film Theory

~ a model in which the entire resistance to diffusion from the liquid surface to the main gas stream is assumed to occur in a stagnant or laminar film of constant thickness δ .



$$N_{A,z} = \frac{\mathcal{D}_{AB} P}{RT\delta} \frac{P_{A1} - P_{A2}}{P_{B,\ln}}$$

Convective Mass Transfer

$$N_{A,z} = k_c (C_{A1} - C_{A2}) = \frac{k_c}{RT} (P_{A1} - P_{A2})$$

$$k_c = \frac{\mathcal{D}_{AB} P}{P_{B,\ln} \delta} \longrightarrow \text{actual } k_c \propto \mathcal{D}_{AB}^{0.5-1.0}$$

Concentration Profile

$$\frac{dN_{A,z}}{dz} = 0 \qquad \frac{d}{dz} \left(\frac{C \mathcal{D}_{AB}}{1 - y_A} \frac{dy_A}{dz} \right) = 0$$

$$N_{A,z} = - \frac{C \mathcal{D}_{AB}}{1 - y_A} \frac{dy_A}{dz}$$

If C and \mathcal{D}_{AB} are constant under isothermal and isobaric conditions

$$\frac{d}{dz} \left(\frac{1}{1 - y_A} \frac{dy_A}{dz} \right) = 0$$

$$-\ln(1 - y_A) = C_1 z + C_2 \qquad \begin{array}{l} \text{at } z = z_1, \quad y_A = y_{A1} \\ \text{at } z = z_2, \quad y_A = y_{A2} \end{array}$$

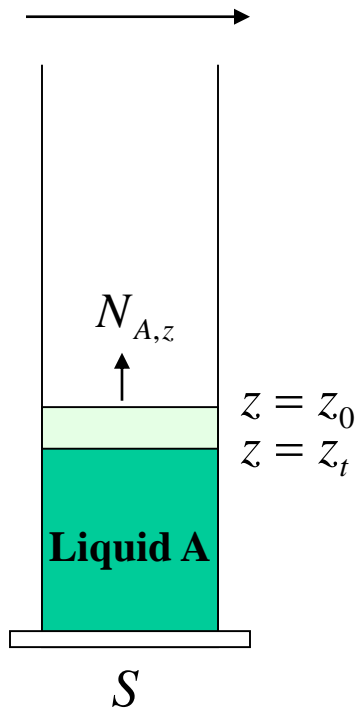
$$\frac{1 - y_A}{1 - y_{A1}} = \left(\frac{1 - y_{A2}}{1 - y_{A1}} \right)^{(z - z_1)/(z_2 - z_1)}$$

$$\bar{y}_B = \frac{\int y_B dz}{\int dz} = \frac{y_{B2} - y_{B1}}{\ln y_{B2}/y_{B1}} = y_{B,\ln}$$

Pseudo Steady State Diffusion through a Stagnant Gas Film

the length of the diffusion path changes a small amount over a long period of time ~ pseudo steady state model

Flowing of gas B



$$N_{A,z} = \frac{C \mathcal{D}_{AB}}{z_2 - z_1} \ln \frac{1 - y_{A2}}{1 - y_{A1}} = \frac{C \mathcal{D}_{AB}}{z_2 - z_1} \frac{y_{A1} - y_{A2}}{y_{B,ln}}$$

$$N_{A,z} = \frac{\rho_{A,L}}{M_A} \frac{dz}{dt}$$

Molar density of A in the liquid phase

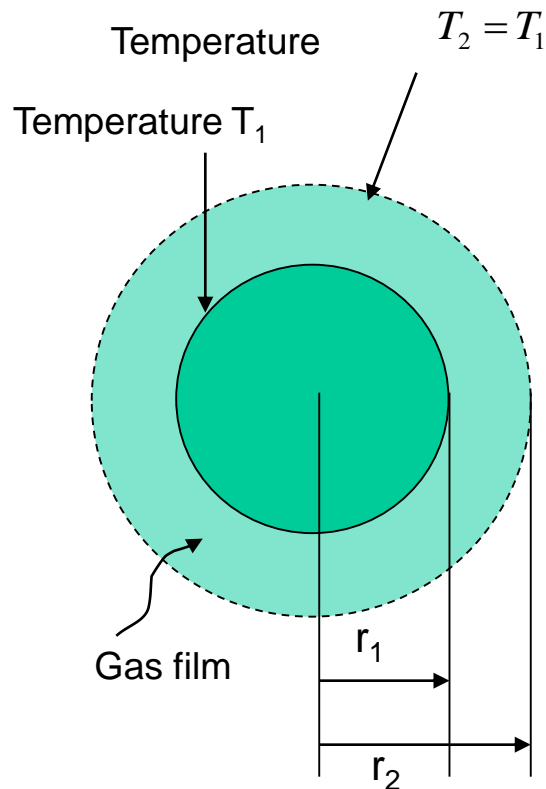
$$\frac{\rho_{A,L}}{M_A} \frac{dz}{dt} = \frac{C \mathcal{D}_{AB}}{z} \frac{y_{A1} - y_{A2}}{y_{B,ln}} \quad \text{at } t = 0, \quad z = z_0$$

$$\text{at } t = t, \quad z = z_t$$

$$t = \frac{\rho_{A,L} y_{B,ln} / M_A}{C \mathcal{D}_{AB} (y_{A1} - y_{A2})} \left(\frac{z_t^2 - z_0^2}{2} \right)$$

$$\mathcal{D}_{AB} = \frac{\rho_{A,L} y_{B,ln} / M_A}{C (y_{A1} - y_{A2})} t \left(\frac{z_t^2 - z_0^2}{2} \right)$$

Diffusion through a Isothermal Spherical Film



$$\frac{d}{dr} (r^2 N_{A,r}) = 0$$

$$N_{A,r} = -C \mathcal{D}_{AB} \frac{dx_A}{dr} + x_A (N_{A,r} + N_{B,r})$$

$$N_{B,r} = 0 \quad \text{Since B is insoluble in liquid A}$$

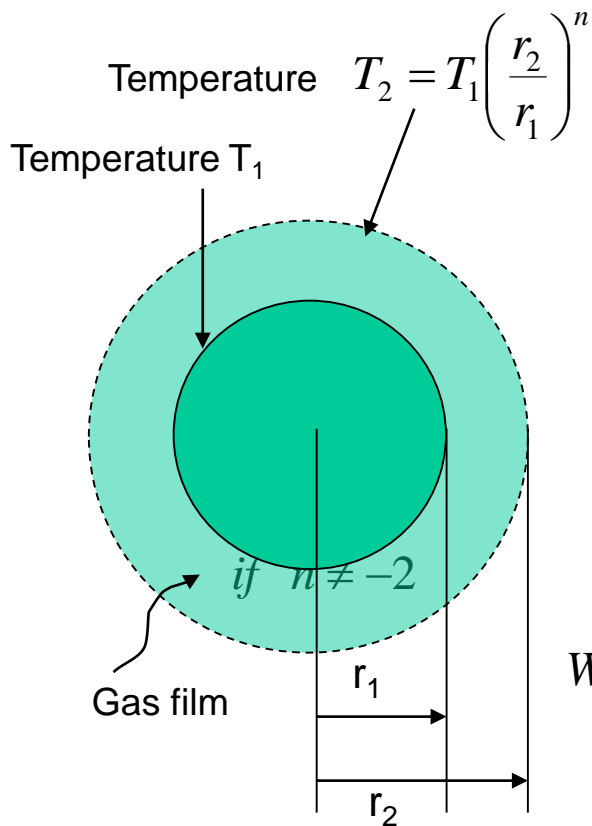
$$\frac{d}{dr} \left(r^2 \frac{C \mathcal{D}_{AB}}{1 - x_A} \frac{dx_A}{dr} \right) = 0$$

for constant temperature $C \mathcal{D}_{AB}$ is constant

$$\frac{1 - x_A}{1 - x_{A1}} = \left(\frac{1 - x_{A2}}{1 - x_{A1}} \right)^{\frac{(1/r_1) - (1/r)}{(1/r_1) - (1/r_2)}}$$

$$W_A = 4\pi r_1^2 N_{A,r} \Big|_{r=r_1} = \frac{4\pi C \mathcal{D}_{AB}}{(1/r_1) - (1/r_2)} \ln \left(\frac{1 - x_{A2}}{1 - x_{A1}} \right)$$

Diffusion through a Nonisothermal Spherical Film



$$\frac{\mathcal{D}_{AB}}{\mathcal{D}_{AB,1}} = \left(\frac{r}{r_1} \right)^{3n/2}$$

$$\frac{d}{dr} \left(r^2 \frac{C \mathcal{D}_{AB}}{1 - x_A} \frac{dx_A}{dr} \right) = 0$$

$$\frac{d}{dr} \left(r^2 \frac{P \mathcal{D}_{AB,1} / RT_1 \left(\frac{r}{r_1} \right)^{3n/2}}{1 - x_A} \frac{dx_A}{dr} \right) = 0$$

$$W_A = 4\pi r_1^2 N_{A,r} \Big|_{r=r_1} = \frac{4\pi (P \mathcal{D}_{AB,1} / RT) [1 + (n/2)]}{\left[(1/r_1)^{1+(n/2)} - (1/r_2)^{1+(n/2)} \right] r_1^{n/2}} \ln \left(\frac{1 - x_{A2}}{1 - x_{A1}} \right)$$

Diffusion with Heterogeneous Chemical Reaction

Solid catalyzed dimerization of $\text{CH}_3\text{CH}=\text{CH}_2$



$$N_{B,z} = -\frac{1}{2}N_{A,z}$$

$$N_{A,z} = -\frac{C\mathcal{D}_{AB}}{1-\frac{1}{2}x_A} \frac{dx_A}{dz}$$

$$\frac{d}{dz} \left(\frac{1}{1-\frac{1}{2}x_A} \frac{dx_A}{dz} \right) = 0$$

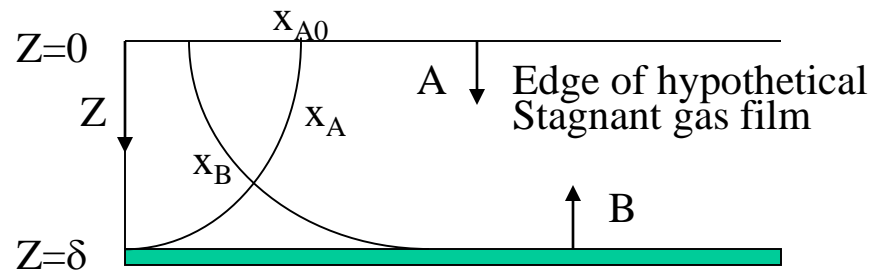
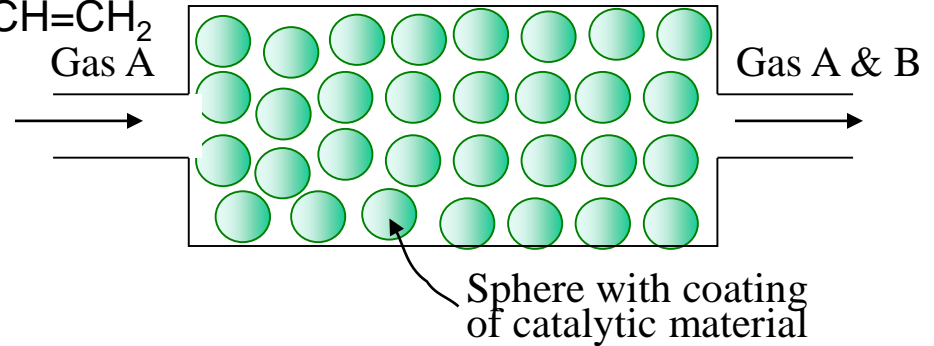
$$-2\ln\left(1-\frac{1}{2}x_A\right) = C_1z + C_2 = -(2\ln K_1)z - (2\ln K_2)$$

$$\text{at } z = 0, \quad x_A = x_{A0}$$

$$\text{at } z = \delta, \quad x_A = 0$$

Irreversible and instantaneous rxn

$$\left(1-\frac{1}{2}x_A\right) = \left(1-\frac{1}{2}x_{A0}\right)^{1-(z/\delta)}$$



Catalytic surface

$$N_{A,z} = \frac{2C\mathcal{D}_{AB}}{\delta} \ln \left(\frac{1}{1-\frac{1}{2}x_{A0}} \right)$$

Diffusion with Slow Heterogeneous Chemical Reaction



$$N_{B,z} = -\frac{1}{2}N_{A,z} \qquad N_{A,z} = -\frac{C\mathcal{D}_{AB}}{1-\frac{1}{2}x_A} \frac{dx_A}{dz}$$

$$\frac{d}{dz} \left(\frac{1}{1-\frac{1}{2}x_A} \frac{dx_A}{dz} \right) = 0 \qquad -2\ln\left(1-\frac{1}{2}x_A\right) = C_1z + C_2$$

$$\text{at } z = 0, \quad x_A = x_{A0}$$

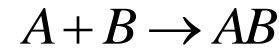
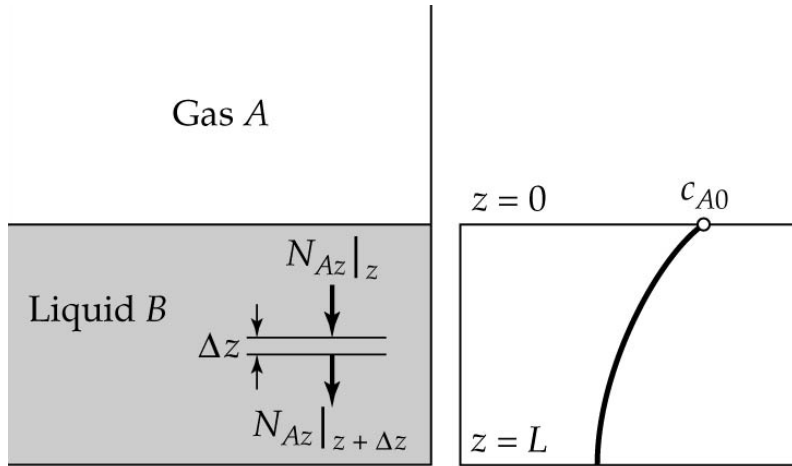
$$\text{at } z = \delta, \quad x_A = \frac{N_{A,z}}{k_1C} \left(N_{A,z} = k_1C_A \right) \quad \text{assume pseudo 1st order rxn}$$

$$\left(1-\frac{1}{2}x_A\right) = \left(1-\frac{1}{2}\frac{N_{Az}}{k_1C}\right)^{z/\delta} \left(1-\frac{1}{2}x_{A0}\right)^{1-(z/\delta)}$$

$$N_{A,z} = \frac{2C\mathcal{D}_{AB}/\delta}{1+\mathcal{D}_{AB}/k_1\delta} \ln\left(\frac{1}{1-\frac{1}{2}x_{A0}}\right) \quad (k_1 \text{ large})$$

$Da = k_1\delta/\mathcal{D}_{AB}$ Damkohler No.: the effect of the surface reaction on the overall diffusion reaction process

Diffusion with Homogeneous Chemical Reaction



First order reaction

$$N_{A,z}|_z S - N_{A,z}|_{z+\Delta z} S - k_1 C_A S \Delta z = 0$$

$$\frac{dN_{A,z}}{dz} + k_1 C_A = 0$$

$$N_{A,z} = -\mathcal{D}_{AB} \frac{dC_A}{dz}$$

$$\mathcal{D}_{AB} \frac{d^2 C_A}{dz^2} - k_1 C_A = 0$$

$$\text{at } z = 0, \quad C_A = C_{A0}$$

$$\text{at } z = L, \quad N_{A,z} = 0 \text{ (or } dC_A/dz = 0)$$

$$\Gamma = C_A / C_{A0} \quad \zeta = z / L$$

$$\phi = \sqrt{k_1 L^2 / \mathcal{D}_{AB}} \quad \text{Thiele modulus}$$

$$\frac{d^2 \Gamma}{d\zeta^2} - \phi^2 \Gamma = 0$$

$$\text{at } \zeta = 0, \quad \Gamma = 1$$

$$\text{at } \zeta = 1, \quad d\Gamma/d\zeta = 0$$

$$\Gamma = C_1 \cosh \phi \zeta + C_2 \sinh \phi \zeta$$

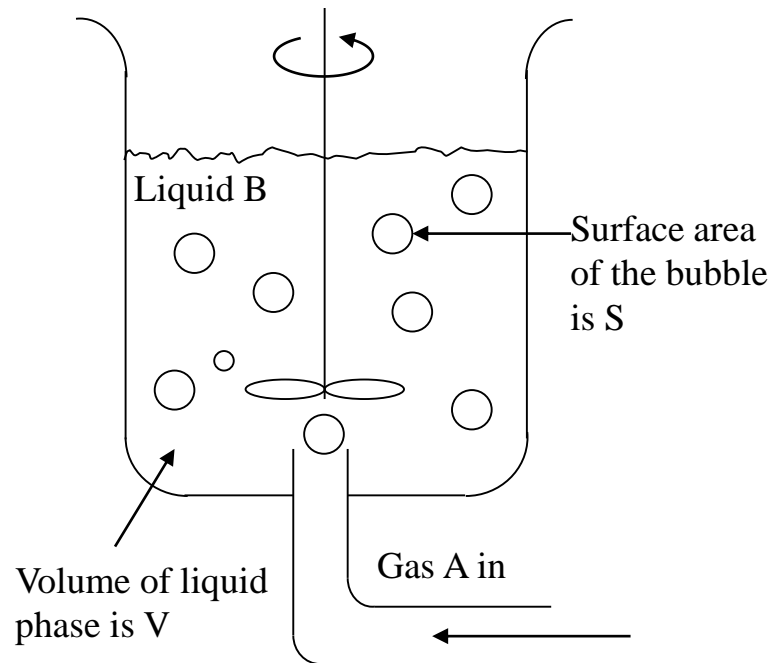
$$\Gamma = \frac{\cosh \phi \cosh \phi \zeta - \sinh \phi \sinh \phi \zeta}{\cosh \phi} = \frac{\cosh[\phi(1-\zeta)]}{\cosh \phi}$$

$$\frac{C_A}{C_{A0}} = \frac{\cosh\left[\sqrt{k_1 L^2 / \mathcal{D}_{AB}} (1 - (z/L))\right]}{\cosh\sqrt{k_1 L^2 / \mathcal{D}_{AB}}}$$

$$\frac{C_{A,avg}}{C_{A0}} = \frac{\int_0^L (C_A / C_{A0}) dz}{\int_0^L dz} = \frac{\tanh \phi}{\phi}$$

$$N_{A,z}\Big|_{z=0} = -\mathcal{D}_{AB} \frac{dC_A}{dz}\Big|_{z=0} = \left(\frac{C_{A0} \mathcal{D}_{AB}}{L}\right) \phi \tanh \phi$$

Gas Absorption with Chemical Reaction in an Agitated Tank



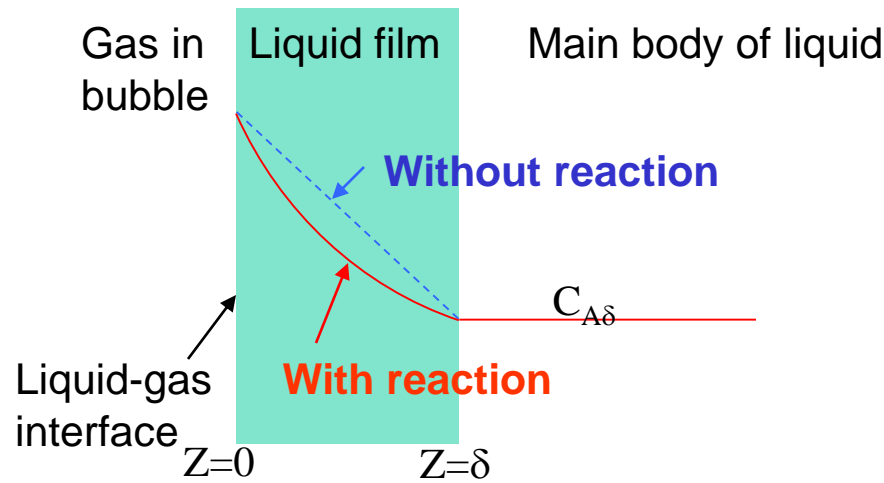
effect of chemical reaction rate on the rate of gas absorption in an agitated tank

Example) The absorption of SO_2 or H_2S in aqueous NaOH solutions

Semiquantitative understanding can be obtained by the analysis of a relatively simple model

Assumptions:

- 1) Each gas bubble is surrounded by a stagnant liquid film of thickness d , which is small relative to the bubble diameter
- 2) A Quasi-steady state concentration profile quickly established in the liquid film after the bubble is formed
- 3) The gas A is only sparingly soluble gas in the liquid, so that we can neglect the convection term.
- 4) The liquid outside the stagnant film is at a concentration $C_{A\delta}$, which changes so slowly with respect to time that it can be considered constant.



$$\mathcal{D}_{AB} \frac{d^2 C_A}{dz^2} - k_1 C_A = 0$$

$$\Gamma = C_1 \cosh \phi \zeta + C_2 \sinh \phi \zeta$$

$$\text{at } z = 0, \quad C_A = C_{A0}$$

$$\text{at } z = \delta, \quad C_A = C_{A\delta}$$

$$\Gamma = C_A / C_{A0} \quad \zeta = z / \delta \quad \phi = \sqrt{k_1 \delta^2 / \mathcal{D}_{AB}}$$

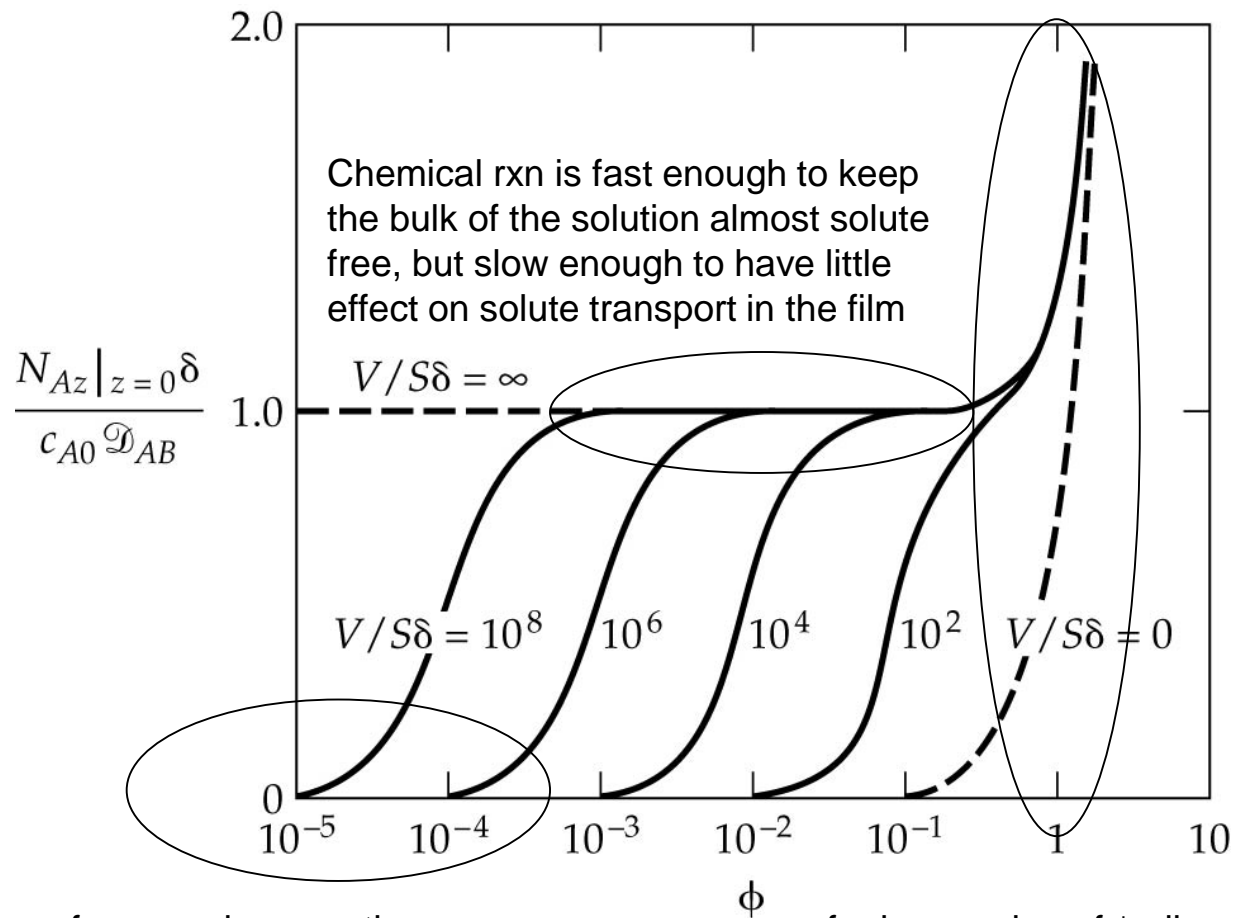
$$\frac{C_A}{C_{A0}} = \frac{\sinh \phi \cosh \phi \zeta + (B - \cosh \phi \sinh \phi \zeta)}{\sinh \phi}$$

$$\text{Assumption (d)} \quad -S \mathcal{D}_{AB} \left. \frac{dC_A}{dz} \right|_{z=\delta} = V k_1 C_{A\delta}$$

$$B = \frac{1}{\cosh \phi + (V/S\delta) \sinh \phi}$$

The total rate of absorption with chemical reaction

$$\tilde{N} = \frac{N_{A,z}|_{z=0} \delta}{C_{A0} \mathcal{D}_{AB}} = \frac{\phi}{\sinh \phi} \left(\cosh \phi - \frac{1}{\cosh \phi + (V/S\delta) \sinh \phi} \right)$$



for very slow reactions,
the liquid is nearly
saturated with dissolved gas

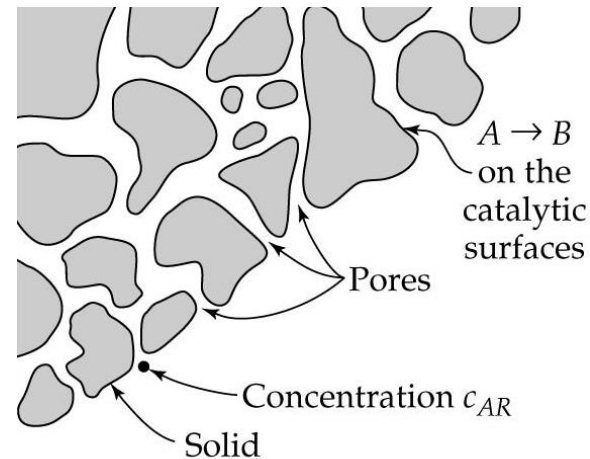
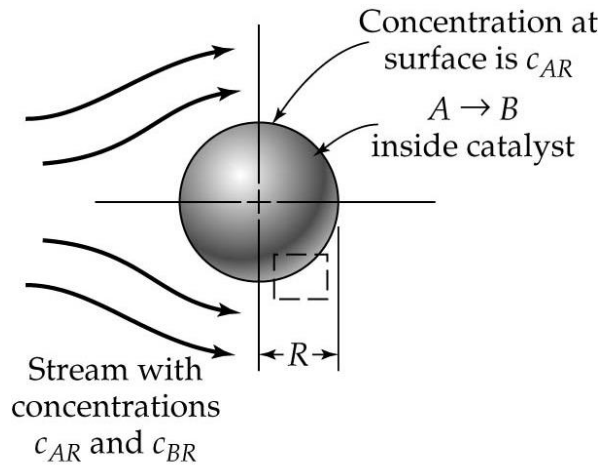
for large value of ϕ , dimensionless surface
mass flux increases rapidly with ϕ and
becomes nearly independent of $V/S\delta$.

Diffusion and Chemical Reaction inside a Porous Catalyst

We make no attempt to describe the diffusion inside the tortuous void passages in the pellet. Instead, we describe the “averaged diffusion” of the reactant ~ **effective diffusivity**

$$N_{A,r}|_r 4\pi r^2 - N_{A,r}|_{r+\Delta r} 4\pi(r + \Delta r)^2 + R_A 4\pi r^2 \Delta r = 0$$

$$\lim_{\Delta r \rightarrow 0} \frac{(r^2 N_{A,r})|_{r+\Delta r} - (r^2 N_{A,r})|_r}{\Delta r} = r^2 R_A \quad \frac{d}{dr}(r^2 N_{A,r}) = r^2 R_A$$



$$N_A = -\mathcal{D}_A \frac{dC_A}{dr}$$

$$\mathcal{D}_A \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_A}{dr} \right) = -R_A$$

effective diffusivity

depends on P, T
and pore structure

First order chemical reaction,

a is the available catalytic surface per unit volume

$$\mathcal{D}_A \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dC_A}{dr} \right) = k_1 a C_A$$

at $r = R$, $C_A = C_{AR}$
at $r = 0$, $C_A = \text{finite}$

$$\frac{C_A}{C_{AR}} = \frac{1}{r} f(r) \qquad \frac{d^2 f}{dr^2} = \left(\frac{k_1 a}{\mathcal{D}_A} \right) f$$

$$\frac{C_A}{C_{AR}} = \frac{C_1}{r} \cosh \sqrt{\frac{k_1 a}{\mathcal{D}_A}} r + \frac{C_2}{r} \sinh \sqrt{\frac{k_1 a}{\mathcal{D}_A}} r$$

$$\frac{C_A}{C_{AR}} = \left(\frac{R}{r} \right) \frac{\sinh \sqrt{k_1 a / \mathcal{D}_A} r}{\sinh \sqrt{k_1 a / \mathcal{D}_A} R}$$

$$W_A = 4\pi R^2 N_{A,R} = -4\pi R^2 \mathcal{D}_A \left. \frac{dC_A}{dr} \right|_{r=R}$$

$$W_A = 4\pi R \mathcal{D}_A C_{AR} \left(1 - \sqrt{\frac{k_1 a}{\mathcal{D}_A}} R \coth \sqrt{\frac{k_1 a}{\mathcal{D}_A}} R \right)$$

If the catalytically active surface were all exposed to the stream, then the species A would not have to diffuse through the pores to a reaction site.

$$W_{AR,0} = \left(\frac{4}{3} \pi R^3 \right) (a) (-k_1 C_{AR})$$

Effective factor $\eta_A = \frac{W_{AR}}{W_{AR,0}} = \frac{3}{\phi^2} (\phi \coth \phi - 1)$

$$\phi = \sqrt{k_1 a / \mathcal{D}_A} \quad \text{Thiele modulus}$$

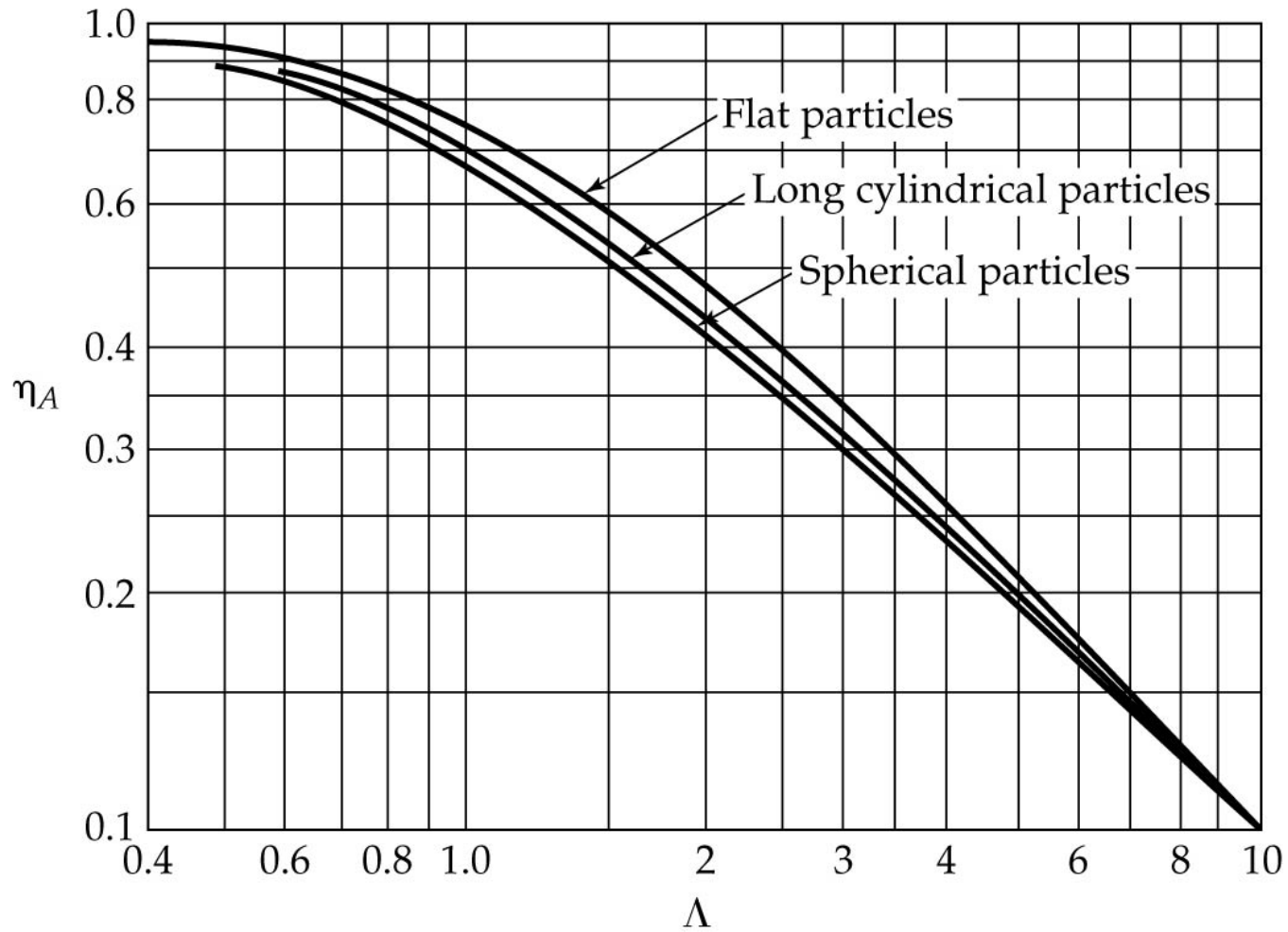
For nonspherical catalyst particles

$$R_{nonsph} = 3 \left(\frac{V_p}{S_p} \right)$$

$$|W_{AR}| \approx V_p a k_1 C_{AR} \eta_A$$

$$\eta_A = \frac{1}{3\Lambda^2} (3\Lambda \coth 3\Lambda - 1)$$

$$\Lambda = \sqrt{k_1 a / \mathcal{D}_A} (V_p / S_p) \quad \text{generalized modulus}$$



Diffusion in a Multi-Component System

Liquid water(species 1) is evaporating into air, regarded as a binary mixture of nitrogen(2) and oxygen(3) at a given T & P.

$$\frac{dN_{\alpha,z}}{dz} = 0 \quad \alpha = 1, 2, 3$$

Maxwell Stefan equation for multicomponent diffusion in gases at low density

$$\nabla x_{\alpha} = -\sum_{\beta=1}^N \frac{x_{\alpha} x_{\beta}}{\mathcal{D}_{\alpha\beta}} (v_{\alpha} - v_{\beta}) = -\sum_{\beta=1}^N \frac{1}{C\mathcal{D}_{\alpha\beta}} (x_{\beta} N_{\alpha} - x_{\alpha} N_{\beta}) \quad \alpha = 1, 2, 3, \dots, N$$

Since species 2 and 3 are not moving, $N_{2,z} = N_{3,z} = 0$

$$\frac{dx_2}{dz} = \frac{N_{1,z}}{C\mathcal{D}_{12}} x_2; \quad \frac{dx_3}{dz} = \frac{N_{1,z}}{C\mathcal{D}_{13}} x_3$$

$$\int_{x_2}^{x_{2L}} \frac{dx_2}{x_2} = \frac{N_{1,z}}{C\mathcal{D}_{12}} \int_z^L dz; \quad \int_{x_3}^{x_{3L}} \frac{dx_3}{x_3} = \frac{N_{1,z}}{C\mathcal{D}_{13}} \int_z^L dz$$

$$\frac{x_2}{x_{2L}} = \exp\left(-\frac{N_{1,z}(L-z)}{C\mathcal{D}_{12}}\right); \quad \frac{x_3}{x_{3L}} = \exp\left(-\frac{N_{1,z}(L-z)}{C\mathcal{D}_{13}}\right)$$

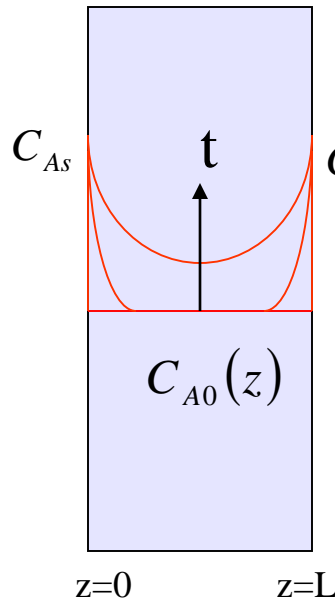
$$x_1 = 1 - x_{2L} \exp\left(-\frac{N_{1,z}(L-z)}{C\mathcal{D}_{12}}\right) - x_{3L} \exp\left(-\frac{N_{1,z}(L-z)}{C\mathcal{D}_{13}}\right)$$

At $z=0$

$$x_{10} = 1 - x_{2L} \exp\left(-\frac{N_{1,z}L}{C\mathcal{D}_{12}}\right) - x_{3L} \exp\left(-\frac{N_{1,z}L}{C\mathcal{D}_{13}}\right)$$

Transient 1-D Diffusion of a Finite Slab

~ negligible surface resistance



$$\frac{\partial C_A}{\partial t} = \mathcal{D}_{AB} \frac{\partial^2 C_A}{\partial z^2}$$

$$C_A = C_{A0}(z) \quad \text{at } t = 0, 0 \leq z \leq L$$

$$C_A = C_{As} \quad \text{at } z = 0, t > 0$$

$$C_A = C_{As} \quad \text{at } z = L, t > 0$$

$$\text{Let } Y = \frac{C_A - C_{As}}{C_{A0} - C_{As}}$$

$$\frac{\partial Y}{\partial t} = \mathcal{D}_{AB} \frac{\partial^2 Y}{\partial z^2}$$

$$Y = 1 \quad \text{at } t = 0, 0 \leq z \leq L$$

$$Y = 0 \quad \text{at } z = 0, t > 0$$

$$Y = 0 \quad \text{at } z = L, t > 0$$

by Separation variables method

$$Y(z, t) = Z(z)G(t)$$

$$Y = \frac{2}{L} \sum_{n=1}^{\infty} \sin\left(\frac{n\pi z}{L}\right) e^{-(n\pi/2)^2 X_D} \int_0^L Y_0(z) \sin\frac{n\pi z}{L} dz \quad X_D = \mathcal{D}_{AB}t / (L/2)^2$$

if $Y_0(z) = Y_0$,

$$\frac{C_A - C_{A_s}}{C_{A_0} - C_{A_s}} = \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi z}{L}\right) e^{-(n\pi/2)^2 X_D} \quad n = 1, 3, 5 \dots$$

$$N_{A,z} = -\mathcal{D}_{AB} \frac{dC_A}{dz} = \frac{4\mathcal{D}_{AB}}{L} (C_{A_s} - C_{A_0}) \sum_{n=1}^{\infty} \cos\left(\frac{n\pi z}{L}\right) e^{-(n\pi/2)^2 X_D} \quad n = 1, 3, 5 \dots$$

Transient Diffusion in a Semi-Infinite Medium

$$\frac{\partial C_A}{\partial t} = \mathcal{D}_{AB} \frac{\partial^2 C_A}{\partial z^2}$$
$$C_A = C_{A0} \quad \text{at } t = 0, \text{ all } z$$
$$C_A = C_{As} \quad \text{at } z = 0, t > 0$$
$$C_A = C_{A0} \quad \text{as } z \rightarrow \infty, t > 0$$

$$\frac{C_A - C_{A0}}{C_{As} - C_{A0}} = f\left(\frac{z}{z_1}, \frac{\alpha t}{z_1^2}\right) = f\left(\frac{\alpha t}{z^2}\right)$$

Let $\eta = z/2\sqrt{\alpha t}$, $Y = (C_A - C_{A0})/(C_{As} - C_{A0}) \sim$ Similarity Solution Technique

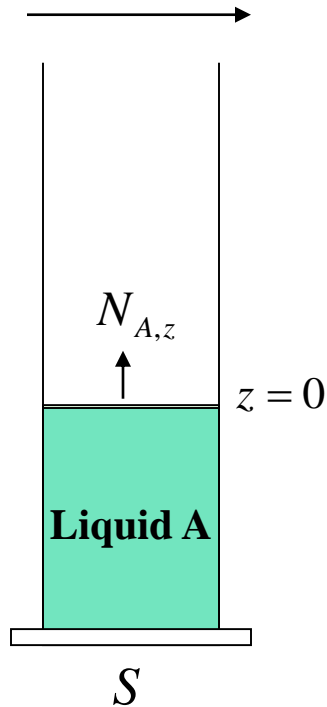
$$\frac{C_A - C_{A0}}{C_{As} - C_{A0}} = 1 - \operatorname{erf}\left(\frac{z}{2\sqrt{\mathcal{D}_{AB}t}}\right) \quad \text{or} \quad \frac{C_{As} - C_A}{C_{As} - C_{A0}} = \operatorname{erf}\left(\frac{z}{2\sqrt{\mathcal{D}_{AB}t}}\right)$$

$$\operatorname{erf}(\phi) = \frac{2}{\sqrt{\pi}} \int_0^\phi e^{-\eta^2} d\eta$$

$$\operatorname{erf}(0) = 0, \operatorname{erf}(\infty) = 1$$

Unsteady State Evaporation of a Liquid

Flowing of gas B



Continuity equation $\frac{\partial V_z}{\partial z} = 0$

$$V_z = V_{z0}(t)$$

In the binary system $V_z = \frac{N_{A,z0} + N_{B,z0}}{C}$

$N_{B,z0} = 0$ Gas B is insoluble in Liquid A

$$V_z = - \frac{D_{AB}}{1 - x_{A0}} \frac{\partial x_A}{\partial z} \Big|_{z=0}$$

$$\frac{\partial x_A}{\partial t} - \left(- \frac{D_{AB}}{1 - x_{A0}} \frac{\partial x_A}{\partial z} \Big|_{z=0} \right) \frac{\partial x_A}{\partial z} = D_{AB} \frac{\partial^2 x_A}{\partial z^2}$$

at $t = 0$, $x_A = 0$

at $z = 0$, $x_A = x_{A0}$

at $z = \infty$, $x_A = 0$

$$x_A/x_{A0} = X, \quad Z = z/\sqrt{4\mathcal{D}_{AB}t}$$

$$\frac{d^2X}{dZ^2} + 2(Z - \varphi)\frac{dX}{dZ} = 0 \quad \begin{array}{l} \text{at } Z = 0, \quad X = 1 \\ \text{at } Z = \infty, \quad X = 0 \end{array}$$

$$\varphi(x_{A0}) = V_z \sqrt{t/\mathcal{D}_{AB}} = -\frac{1}{2} \frac{x_{A0}}{1-x_{A0}} \left. \frac{dX}{dZ} \right|_{Z=0} \quad \begin{array}{l} \text{Dimensionless molar} \\ \text{average velocity} \end{array}$$

$$Y \equiv \frac{dX}{dZ} = C_1 \exp\left[-(Z - \varphi)^2\right]$$

$$X = C_1 \int_0^Z \exp\left[-(\bar{Z} - \varphi)^2\right] d\bar{Z} + C_2$$

$$X(Z) = 1 - \frac{\int_0^Z \exp\left[-(\bar{Z} - \varphi)^2\right] d\bar{Z}}{\int_0^\infty \exp\left[-(\bar{Z} - \varphi)^2\right] d\bar{Z}} = 1 - \frac{\int_{-\varphi}^{Z-\varphi} \exp[-W^2] dW}{\int_{-\varphi}^\infty \exp[-W^2] dW}$$

$$X(Z) = 1 - \frac{\text{erf}(Z - \varphi) + \text{erf}\varphi}{\text{erf}\infty + \text{erf}\varphi} = \frac{1 - \text{erf}(Z - \varphi)}{1 + \text{erf}\varphi}$$

$$\varphi(x_{A0}) = -\frac{1}{2} \frac{x_{A0}}{1-x_{A0}} \frac{dX}{dZ} \Big|_{z=0} \quad \varphi(x_{A0}) = \frac{1}{\sqrt{\pi}} \frac{x_{A0}}{1-x_{A0}} \frac{\operatorname{erf}(-\varphi^2)}{1+\operatorname{erf}\varphi}$$

$$x_{A0} = \frac{1}{1 + \left[\sqrt{\pi} (1 + \operatorname{erf}\varphi) \varphi \exp \varphi^2 \right]^{-1}}$$

Rate of production of vapor from surface of area S

$$\frac{dV_A}{dt} = \frac{N_{A0}S}{C} = S\varphi \sqrt{\frac{\mathcal{D}_{AB}}{t}}$$

V_A : the volume of A evaporation up to time t

$$V_A = S\varphi \sqrt{4\mathcal{D}_{AB}t}$$

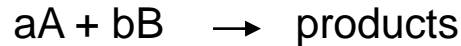
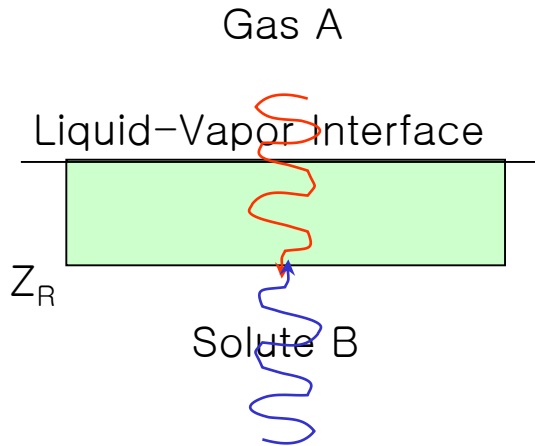
$$\frac{\partial x_A}{\partial t} = \mathcal{D}_{AB} \frac{\partial^2 x_A}{\partial z^2} \quad \Rightarrow \quad V_A^{Fick} = Sx_{A0} \sqrt{\frac{4\mathcal{D}_{AB}t}{\pi}}$$

$$V_A = Sx_{A0} \sqrt{\frac{4\mathcal{D}_{AB}t}{\pi}} \psi \quad \psi = \varphi \sqrt{\pi} / x_{A0}$$

Deviation from the Fick's second law caused
by the nonzero molar average velocity

Gas Absorption with Rapid Reaction

Gas A is absorbed by a stationary liquid solvent S containing solute B



$$\frac{\partial C_A}{\partial t} = \mathcal{D}_{AS} \frac{\partial^2 C_A}{\partial z^2} \quad \text{for } 0 \leq z \leq z_R(t)$$

$$\frac{\partial C_B}{\partial t} = \mathcal{D}_{BS} \frac{\partial^2 C_B}{\partial z^2} \quad \text{for } z_R(t) \leq z < \infty$$

$$\text{at } t = 0, \quad C_B = C_{B\infty} \quad \text{for } z \geq 0$$

$$\text{at } z = 0, \quad C_A = C_{A0}$$

$$\text{at } z = z_R(t), \quad C_A = C_B = 0$$

$$\text{at } z = z_R(t), \quad -\frac{1}{a} \mathcal{D}_{AS} \frac{\partial C_A}{\partial z} = -\frac{1}{b} \mathcal{D}_{BS} \frac{\partial C_B}{\partial z}$$

$$\text{at } z = \infty, \quad C_B = C_{B\infty}$$

$$\frac{C_A}{C_{A0}} = C_1 + C_2 \operatorname{erf} \frac{z}{\sqrt{4D_{AS}t}} \quad \text{for } 0 \leq z \leq z_R(t)$$

$$\frac{C_B}{C_{B\infty}} = C_3 + C_4 \operatorname{erf} \frac{z}{\sqrt{4D_{BS}t}} \quad \text{for } z_R(t) \leq z < \infty$$

$$\frac{C_A}{C_{A0}} = 1 - \frac{\operatorname{erf}\left(z/\sqrt{4D_{AS}t}\right)}{\operatorname{erf}\left(z_R/\sqrt{4D_{AS}t}\right)} \quad \text{for } 0 \leq z \leq z_R(t)$$

$$\frac{C_B}{C_{B\infty}} = 1 - \frac{1 - \operatorname{erf}\left(z/\sqrt{4D_{BS}t}\right)}{1 - \operatorname{erf}\left(z_R/\sqrt{4D_{BS}t}\right)} \quad \text{for } z_R(t) \leq z < \infty$$

from B.C. at $z = \infty$, $C_B = C_{B\infty}$ instead of B.C. at $z = z_R(t)$, $-\frac{1}{a}D_{AS}\frac{\partial C_A}{\partial z} = -\frac{1}{b}D_{BS}\frac{\partial C_B}{\partial z}$

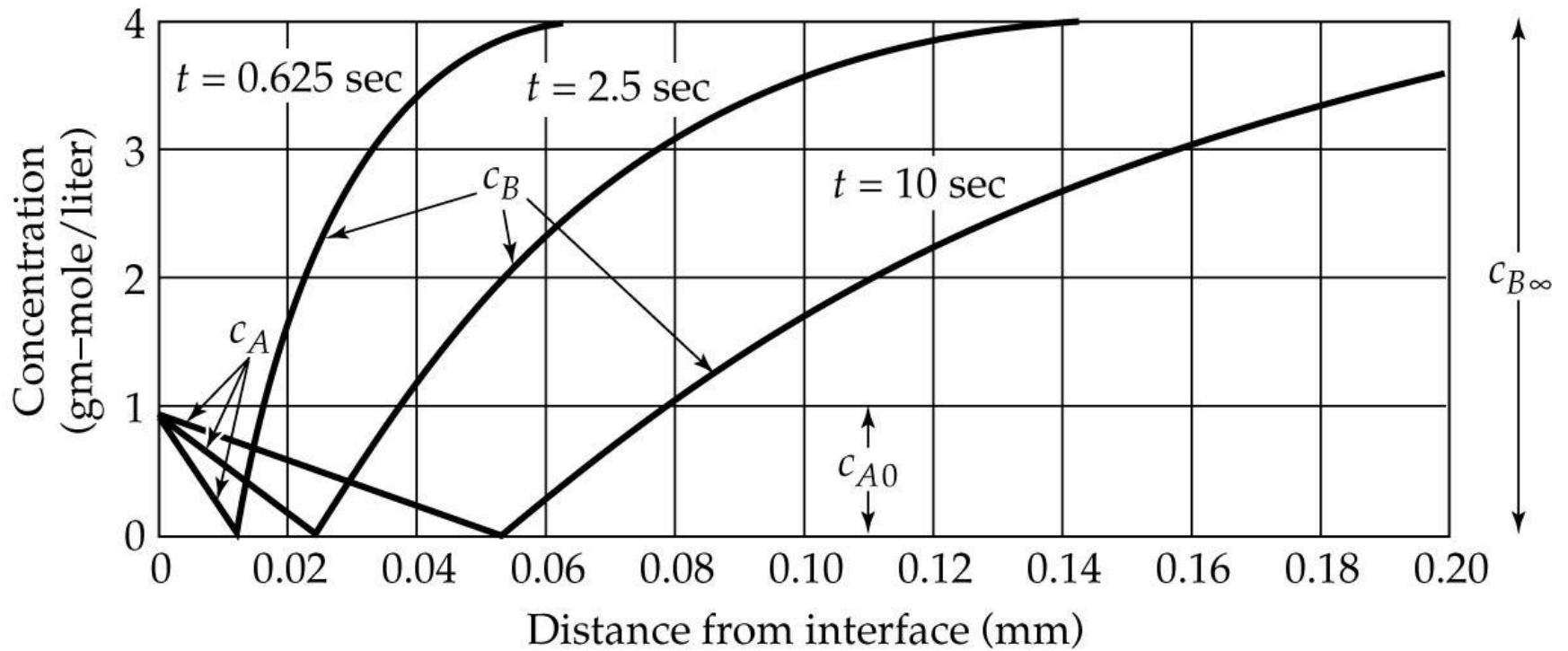
$$1 - \operatorname{erf} \sqrt{\frac{\gamma}{D_{BS}}} = \frac{aC_{B\infty}}{bC_{A0}} \sqrt{\frac{D_{BS}}{D_{AS}}} \operatorname{erf} \sqrt{\frac{\gamma}{D_{AS}}} \exp\left(\frac{\gamma}{D_{AS}} - \frac{\gamma}{D_{BS}}\right)$$

$$\gamma = z_R^2/4t = \text{constant} \quad Z_R \text{ increases as } \sqrt{t}$$

$$N_{A,z0} = -D_{AS} \frac{\partial C_A}{\partial z} \Big|_{z=0} = \frac{C_{A0}}{\operatorname{erf}(\sqrt{\gamma/D_{AS}})} \sqrt{\frac{D_{AS}}{\pi t}}$$

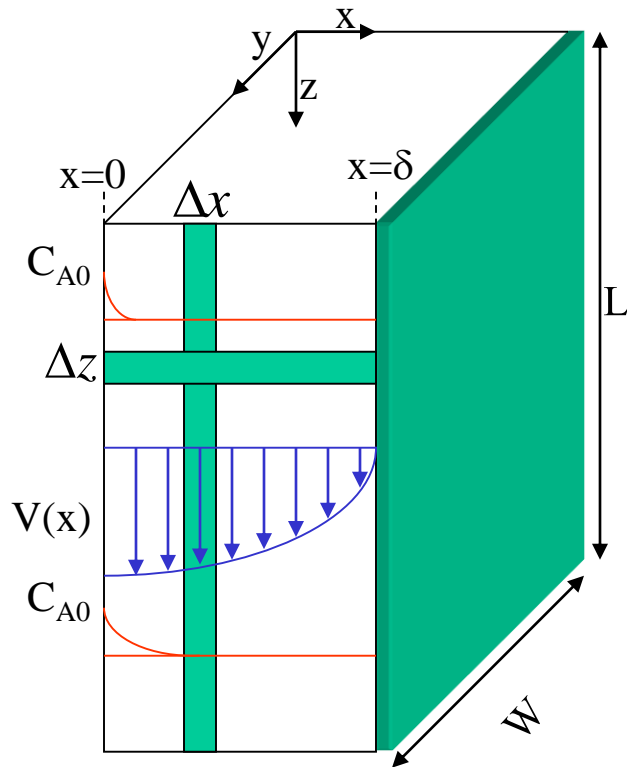
The average rate of absorption up to t

$$N_{A,z0,avg} = \frac{1}{t} \int_0^t N_{A,z0} dt = 2 \frac{C_{A0}}{\operatorname{erf}(\sqrt{\gamma/D_{AS}})} \sqrt{\frac{D_{AS}}{\pi t}}$$



BIRD: *Transport Phenomena, 2e*
 Fig. 20.1-2 W-280

Diffusion into a Falling Liquid Film (Gas Absorption)



$$v_z(x) = v_{max} \left[1 - \left(\frac{x}{\delta} \right)^2 \right]$$

$$N_{A,z}|_z W \Delta x - N_{A,z}|_{z+\Delta z} W \Delta x + N_{A,x}|_x W \Delta z - N_{A,x}|_{x+\Delta x} W \Delta z = 0$$

$$\frac{\partial N_{A,z}}{\partial z} + \frac{\partial N_{A,x}}{\partial x} = 0$$

$$N_{A,z} = -\cancel{D_{AB}} \frac{\partial C_A}{\partial z} + x_A (N_{A,z} + N_{B,z}) \approx C_A v_z(x)$$

$$N_{A,x} = -\cancel{D_{AB}} \frac{\partial C_A}{\partial x} + x_A (N_{A,x} + N_{B,x}) \approx D_{AB} \frac{\partial C_A}{\partial x}$$

$$v_z \frac{\partial C_A}{\partial z} = D_{AB} \frac{\partial^2 C_A}{\partial x^2}$$

$$v_{max} \left[1 - \left(\frac{x}{\delta} \right)^2 \right] \frac{\partial C_A}{\partial z} = \mathcal{D}_{AB} \frac{\partial^2 C_A}{\partial x^2}$$

$$\text{at } z = 0, \quad C_A = 0$$

$$\text{at } x = 0, \quad C_A = C_{A0}$$

$$\text{at } x = \delta, \quad \frac{\partial C_A}{\partial x} = 0$$

The substance A has penetrated only a short distance into the film~penetration model

$$v_{max} \frac{\partial C_A}{\partial z} = \mathcal{D}_{AB} \frac{\partial^2 C_A}{\partial x^2}$$

$$\text{at } z = 0, \quad C_A = 0$$

$$\text{at } x = 0, \quad C_A = C_{A0}$$

$$\text{at } x = \infty, \quad C_A = 0$$

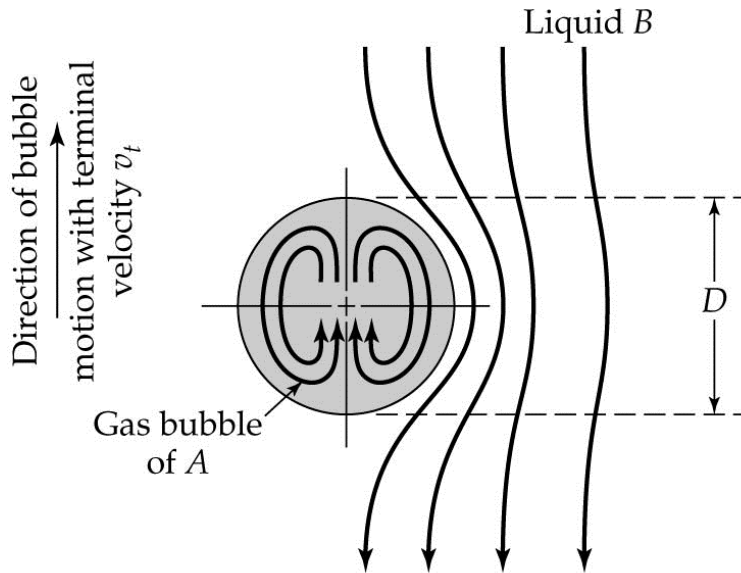
$$\frac{C_A}{C_{A0}} = 1 - \frac{2}{\sqrt{\pi}} \int_0^{x/\sqrt{4\mathcal{D}_{AB}z/v_{max}}} \exp(-\xi^2) d\xi$$

$$\frac{C_A}{C_{A0}} = 1 - \operatorname{erf} \frac{x}{\sqrt{4\mathcal{D}_{AB}z/v_{max}}} = \operatorname{erfc} \frac{x}{\sqrt{4\mathcal{D}_{AB}z/v_{max}}}$$

$$N_{A,x}|_{x=0} = -\mathcal{D}_{AB} \left. \frac{\partial C_A}{\partial x} \right|_{x=0} = C_{A0} \sqrt{\frac{\mathcal{D}_{AB} v_{max}}{\pi z}}$$

$$W_{A0} = \int_0^W \int_0^L N_{A,x}|_{x=0} dz dy = WC_{A0} \sqrt{\frac{\mathcal{D}_{AB} v_{max}}{\pi}} \int_0^L \frac{1}{\sqrt{z}} dz = WC_{A0} \sqrt{\frac{4\mathcal{D}_{AB} v_{max}}{\pi L}}$$

Gas absorption from rising bubbles



Rybczynski-Hadamard circulation

Gas bubbles rising in liquids free surface –active agents undergo a toroidal circulation

$$N_{A,x}|_{x=0} = -D_{AB} \left. \frac{\partial C_A}{\partial x} \right|_{x=0} = \sqrt{\frac{4D_{AB}V_t}{\pi D}} C_{A0}$$

$$t_{\text{exposure}} = \frac{V_t}{D}$$

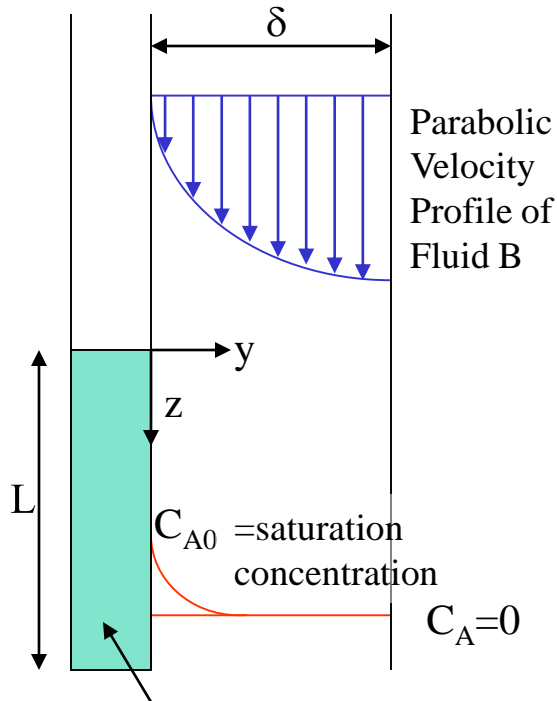
For creeping flow

$$N_{A,x}|_{x=0} = \sqrt{\frac{4D_{AB}V_t}{3\pi D}} C_{A0}$$

Trace of surface-active agents cause a marked decrease in absorption rates from small bubbles
By preventing internal circulation

$$N_{A,x}|_{x=0} \propto D_{AB}^{1/3}$$

Diffusion into a Falling Liquid Film(Solid Dissolution)



Slightly soluble
Wall made of A

$$v_z = \frac{\rho g \delta^2}{2\mu} \left[1 - \left(1 - \frac{y}{\delta} \right)^2 \right] = \frac{\rho g \delta^2}{2\mu} \left[2 \left(\frac{y}{\delta} \right) - \left(\frac{y}{\delta} \right)^2 \right]$$

At end adjacent to the wall $(y/\delta)^2 \ll (y/\delta)$

$$v_z = (\rho g \delta / \mu) y \equiv ay$$

$$ay \frac{\partial C_A}{\partial z} = \mathcal{D}_{AB} \frac{\partial^2 C_A}{\partial y^2} \quad \begin{array}{l} \text{at } z = 0, \quad C_A = 0 \\ \text{at } y = 0, \quad C_A = C_{A0} \\ \text{at } y = \infty, \quad C_A = 0 \end{array}$$

Similarity Solution Technique

$$C_A / C_{A0} = f(\eta), \quad \eta = y(a/9\mathcal{D}_{AB}z)^{1/3}$$

$$\frac{d^2 f}{d\eta^2} + 3\eta^2 \frac{df}{d\eta} = 0 \quad \begin{array}{l} \text{at } \eta = 0, \quad f = 1 \\ \text{at } \eta = \infty, \quad f = 0 \end{array}$$

$$f = C_1 \int_0^\eta \exp\left(-\bar{\eta}^3\right) d\bar{\eta} + C_2$$

$$\frac{C_A}{C_{A0}} = \frac{\int_\eta^\infty \exp\left(-\bar{\eta}^3\right) d\bar{\eta}}{\int_0^\infty \exp\left(-\bar{\eta}^3\right) d\bar{\eta}} = \frac{\int_\eta^\infty \exp\left(-\bar{\eta}^3\right) d\bar{\eta}}{\Gamma\left(\frac{4}{3}\right)}$$

$$N_{A,y}\Big|_{y=0} = -\mathcal{D}_{AB} \frac{\partial C_A}{\partial y}\Big|_{y=0} = -\mathcal{D}_{AB} C_{A0} \left[\frac{d}{d\eta} \left(\frac{C_A}{C_{A0}} \right) \frac{\partial \eta}{\partial y} \right]_{y=0}$$

$$= -\mathcal{D}_{AB} C_{A0} \left[-\frac{\exp(-\eta^3)}{\Gamma\left(\frac{4}{3}\right)} \left(\frac{a}{9\mathcal{D}_{AB}z} \right)^{1/3} \right]_{y=0} = \frac{\mathcal{D}_{AB} C_{A0}}{\Gamma\left(\frac{4}{3}\right)} \left(\frac{a}{9\mathcal{D}_{AB}z} \right)^{1/3}$$

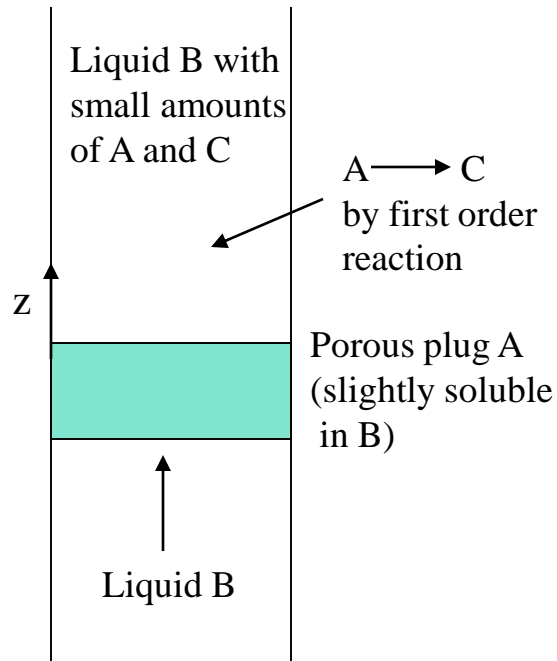
$$\Gamma\left(\frac{4}{3}\right) = 0.8930 \dots$$

$$W_{A0} = \int_0^W \int_0^L N_{A,y}\Big|_{y=0} dz dx = \frac{2\mathcal{D}_{AB} C_{A0} WL}{\Gamma\left(\frac{7}{3}\right)} \left(\frac{a}{9\mathcal{D}_{AB}L} \right)^{1/3}$$

$$\Gamma\left(\frac{7}{3}\right) = \frac{4}{3} \Gamma\left(\frac{4}{3}\right) = 1.1907 \dots$$

$$W_{A0} \propto (\mathcal{D}_{AB} L)^{2/3}$$

Diffusion, Convection and Chemical Reaction



$$v_0 \frac{dC_A}{dz} = \mathcal{D}_{AB} \frac{d^2 C_A}{dz^2} - k_1 C_A$$

$$\text{at } z = 0, \quad C_A = C_{A0}$$

$$\text{at } z = \infty, \quad C_A = 0$$

$$\frac{C_A}{C_{A0}} = \exp \left[- \left(\sqrt{1 + (4k_1 \mathcal{D}_{AB} / v_0^2)} - 1 \right) (v_0 z / 2 \mathcal{D}_{AB}) \right]$$

Analytical Expressions for Mass Transfer Coefficients

Mass Transfer in Falling Film on Plane surfaces

The absorption of a slightly soluble gas into a falling liquid film

$$W_{A0} = \sqrt{\frac{4\mathcal{D}_{AB}v_{\max}}{\pi L}} (WL)(C_{A0} - 0) \equiv k_{c,m}^0 A \Delta C_A$$

$$Sh_m = \frac{k_{c,m}^0 L}{\mathcal{D}_{AB}} = \sqrt{\frac{4Lv_{\max}}{\pi \mathcal{D}_{AB}}} = \sqrt{\frac{4}{\pi} \left(\frac{Lv_{\max}\rho}{\mu} \right) \left(\frac{\mu}{\rho \mathcal{D}_{AB}} \right)} = 1.128 (Re Sc)^{1/2}$$

The dissolution of a slightly soluble solid into a falling liquid film

$$W_{A0} = \frac{2\mathcal{D}_{AB}}{\Gamma\left(\frac{7}{3}\right)} \left(\frac{a}{9\mathcal{D}_{AB}L} \right)^{1/3} (WL)(C_{A0} - 0) = k_{c,m}^0 A \Delta C_A \quad a = \rho g \delta / \mu = 2v_{\max} / \delta$$

$$Sh_m = \frac{k_{c,m}^0 L}{\mathcal{D}_{AB}} = \frac{2}{\Gamma\left(\frac{7}{3}\right)} \sqrt[3]{\frac{(2v_{\max}/\delta)L^2}{9\mathcal{D}_{AB}}} = \frac{1}{\Gamma\left(\frac{7}{3}\right)} \sqrt[3]{\frac{16}{9} \left(\frac{L}{\delta} \right) \left(\frac{Lv_{\max}\rho}{\mu} \right) \left(\frac{\mu}{\rho \mathcal{D}_{AB}} \right)} = 1.07 \sqrt[3]{\left(\frac{L}{\delta} \right)} (Re Sc)^{1/3}$$

Mass Transfer for Flow Around Spheres

The gas absorption from a gas bubble surrounded by liquid in creeping flow

$$N_{A0,avg} = \sqrt{\frac{4}{3\pi} \frac{\mathcal{D}_{AB} v_{\infty}}{D}} (C_A - 0) \equiv k_{cm}^0 \Delta C_A$$

$$Sh_m = \frac{k_{c,m}^0 D}{\mathcal{D}_{AB}} = \sqrt{\frac{4}{3\pi} \frac{D v_{\infty}}{\mathcal{D}_{AB}}} = \sqrt{\frac{4}{3\pi} \left(\frac{D v_{\infty} \rho}{\mu} \right) \left(\frac{\mu}{\rho \mathcal{D}_{AB}} \right)} = 0.6415 (Re Sc)^{1/2}$$

$$Re = 0 \quad Sh_m = 2 \quad Sh_m = 2 + 0.6415 (Re Sc)^{1/2}$$

Creeping flow around a solid sphere with slightly soluble coating

$$N_{A0,avg} = \frac{(3\pi)^{2/3} 2 \mathcal{D}_{AB}}{2^{7/3} \Gamma(\frac{7}{3})} \sqrt[3]{\frac{\mathcal{D}_{AB}^2 v_{\infty}}{D^2}} (C_A - 0) = k_{c,m}^0 \Delta C_A$$

$$Sh_m = \frac{k_{c,m}^0 D}{\mathcal{D}_{AB}} = \frac{(3\pi)^{2/3}}{2^{7/3} \Gamma(\frac{7}{3})} \sqrt[3]{\frac{D v_{\infty}}{\mathcal{D}_{AB}}} = \frac{(3\pi)^{2/3}}{2^{7/3} \Gamma(\frac{7}{3})} \sqrt[3]{\left(\frac{D v_{max} \rho}{\mu} \right) \left(\frac{\mu}{\rho \mathcal{D}_{AB}} \right)} = 0.991 (Re Sc)^{1/3}$$

$$Re = 0 \quad Sh_m = 2 \quad Sh_m = 2 + 0.991 (Re Sc)^{1/3}$$

$$\frac{d}{dr} \left(r^2 \frac{dC}{dr} \right) = 0, \quad C = C_1 \text{ at } r = R, \quad C = C_0 \text{ at } r = \infty$$

$$C = C_1 \frac{R}{r}$$

$$k_c (C_1 - 0) = - D_{AB} \frac{dC}{dr} \Big|_{r=R} = D_{AB} \frac{C_1}{R} \quad \therefore k_c = \frac{D_{AB}}{R}$$

$$Sh = \frac{k_c (2R)}{D_{AB}} = 2$$

Blasius's Solution

Governing Equations

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0$$

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = \nu \frac{\partial^2 v_x}{\partial y^2}$$

$$v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} = \mathcal{D}_{AB} \frac{\partial^2 C_A}{\partial y^2}$$

Boundary Conditions

$$\text{at } y = 0, \quad \frac{v_x}{v_\infty} = \frac{v_y}{v_\infty} = 0, \quad \frac{C_A - C_{As}}{C_{A\infty} - C_{As}} = 0$$

$$\text{as } y \rightarrow \infty, \quad \frac{v_x}{v_\infty} = 1, \quad \frac{C_A - C_{As}}{C_{A\infty} - C_{As}} = 1$$

if $Sc = \frac{\nu}{\mathcal{D}_{AB}} = 1$ (thermal boundary layer = hydrodynamic boundary layer)

$$f' = 2 \frac{v_x}{v_\infty} = 2 \frac{C_A - C_{As}}{C_{A\infty} - C_{As}}$$

$$\eta = \frac{y}{2} \sqrt{\frac{v_\infty}{\nu x}} = \frac{y}{2x} \sqrt{\frac{v_\infty x}{\nu}} = \frac{y}{2x} \sqrt{Re_{,x}}$$

$$\left. \frac{df}{d\eta} \right|_{\eta=0} = f''(0) = \left. \frac{d[2(v_x/v_\infty)]}{d[(y/2x)\sqrt{\text{Re}_x}]} \right|_{\eta=0} = \left. \frac{d[2(C_A - C_{As})/(C_{A\infty} - C_{As})]}{d[(y/2x)\sqrt{\text{Re}_x}]} \right|_{\eta=0} = 1.328$$

$$\left. \frac{dC_A}{dy} \right|_{y=0} = (C_{A\infty} - C_{As}) \left[\frac{0.332}{x} \text{Re}_x^{1/2} \right]$$

$$N_{Ay} = k_c (C_{As} - C_{A\infty}) = -\mathcal{D}_{AB} \left. \frac{\partial C_A}{\partial y} \right|_{y=0}$$

$$k_c = -\frac{\mathcal{D}_{AB}}{(C_{As} - C_{A\infty})} \left. \frac{\partial C_A}{\partial y} \right|_{y=0} = \frac{0.332 \mathcal{D}_{AB}}{x} \text{Re}_x^{1/2}$$

$$Nu_{AB} = \frac{k_c x}{\mathcal{D}_{AB}} = 0.332 \text{Re}_x^{1/2}$$

- Pohlhausen

$$\frac{\delta}{\delta_M} = Sc^{1/3}$$

$$Nu_{AB,x} = 0.332 \text{Re}_x^{1/2} Sc^{1/3}$$

if $x < x_0$, $C_A = C_{A\infty}$ and $x \geq x_0$, $C_A = C_{As}$

$$Nu_{AB} = \frac{0.332}{\sqrt[3]{1 - (x_0/x)^{3/4}}} \text{Re}_x^{1/2} Sc^{1/3}$$

Mean Nusselt Number

$$\left. \frac{\partial C_A}{\partial y} \right|_{y=0} = (C_{A\infty} - C_{As}) \left[\frac{0.332}{x} Re_{,x}^{1/2} Sc^{1/3} \right]$$

$$\frac{k_c x}{\mathcal{D}_{AB}} = Nu_{x,AB} = 0.332 Re_{,x}^{1/2} Sc^{1/3}$$

$$W_A = \bar{k}_c A (C_{As} - C_{A\infty}) = \int_A k_c (C_{As} - C_{A\infty}) dA$$

$$= \bar{k}_c WL (C_{As} - C_{A\infty}) = (C_{As} - C_{A\infty}) \int_A \frac{0.332 \mathcal{D}_{AB} Re_{,x}^{1/2} Sc^{1/3} dA}{x}$$

$$\frac{\bar{k}_c L}{\mathcal{D}_{AB}} = 0.664 Re_{,L}^{1/2} Sc^{1/3}$$

Mass, Energy and Momentum Transfer Analogy

At steady state

$$\left. \frac{d}{dy} \left(\frac{v_x}{v_\infty} \right) \right|_{y=0} = \left. \frac{d}{dy} \left(\frac{C_A - C_{A,s}}{C_{A,\infty} - C_{A,s}} \right) \right|_{y=0}$$

$$\text{if } Sc = \frac{v}{\mathcal{D}_{AB}} = 1 \quad v \left. \frac{d}{dy} \left(\frac{v_x}{v_\infty} \right) \right|_{y=0} = \mathcal{D}_{AB} \left. \frac{d}{dy} \left(\frac{C_A - C_{A,s}}{C_{A,\infty} - C_{A,s}} \right) \right|_{y=0}$$

$$N_{A,y} = k_c (C_{A,s} - C_{A,\infty}) = -\mathcal{D}_{AB} \left. \frac{\partial (C_A - C_{A,s})}{\partial y} \right|_{y=0}$$

$$k_c = \left. \frac{\mu}{\rho v_\infty} \frac{dv_x}{dy} \right|_{y=0} \quad C_f = \frac{\tau_w}{\rho v_\infty^2 / 2} = \left. \frac{2\mu}{\rho v_\infty^2} \frac{dv_x}{dy} \right|_{\eta=0}$$

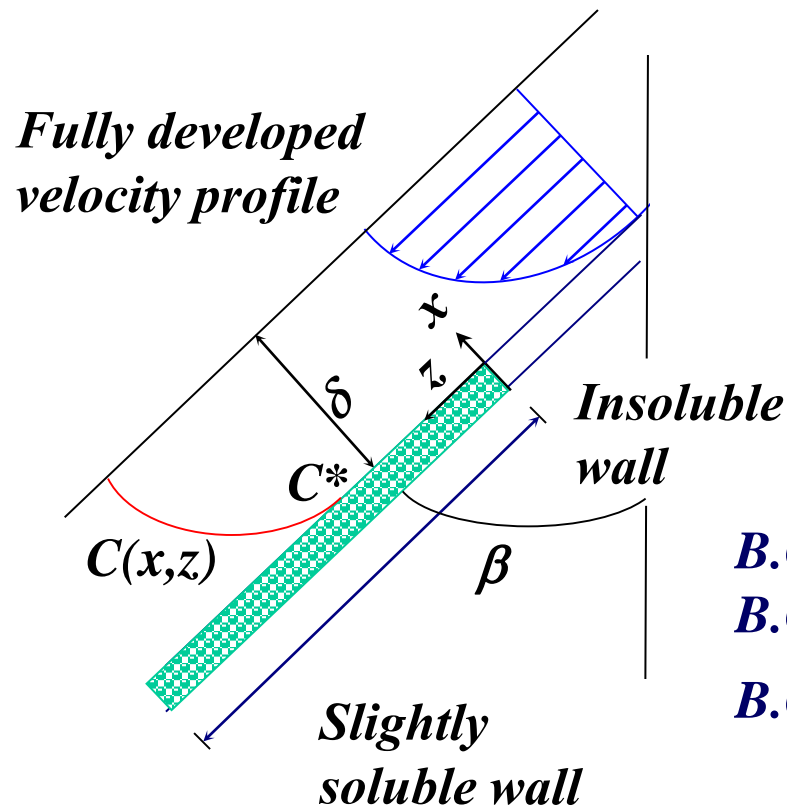
$$\frac{k_c}{v_\infty} = \frac{C_f}{2} \quad \frac{h}{\rho v_\infty C_p} = \frac{C_f}{2}$$

Reynolds Analogy (1) $Sc=1$, and (2) no form drag ~ only skin drag

Mass Transfer to Non-Newtonian Fluids

Mass Transfer to Non-Newtonian Fluids

Mass Transfer to a Power-Law Fluid Flowing on an Inclined Plate



fully developed flow
incompressible power-law fluid,
mass transfer rate is small
no chemical reaction
the solid surface consist of
a soluble material of length L

$$D_A \frac{\partial^2 c}{\partial x^2} = V_z(x) \frac{\partial c}{\partial z}$$

- B.C. 1* *at $z = 0$, $c = c_o$*
- B.C. 2* *at $x = 0$, $c = c^*$ **solubility***
- B.C. 3* *at $x = \delta$, $\frac{\partial c}{\partial x} = 0$*
no mass transfer

The stress distribution in the film

$$\tau_{xz} = \rho g (x - \delta) \cos \beta$$

The mass transfer is confined to a region near the solid surface

$$\tau_{xz} \approx -\rho g \delta \cos \beta$$

$$\text{B.C. 3 at } x = \delta, \quad \frac{\partial c}{\partial x} = 0 \quad \Rightarrow \quad \text{B.C. 3' at } x \rightarrow \infty, \quad c = c_o$$

for power-law fluids

$$m \left| \frac{dV_z}{dx} \right|^n \approx \rho g \delta \cos \beta \quad \text{or} \quad V_z = \left(\frac{\rho g \delta \cos \beta}{m} \right)^{\frac{1}{n}} x$$

the shear rate at the plane surface

$$\dot{\gamma}_w = \left(\frac{\rho g \delta \cos \beta}{m} \right)^{\frac{1}{n}}$$

*Mass Transfer to a Power-Law Fluid
Flowing on an Inclined Plate-2*

$$D_A \frac{\partial^2 c}{\partial x^2} = \dot{\gamma}_w x \frac{\partial c}{\partial z}$$

By using Laplace transform

$$\bar{c}(s) = \int_0^\infty \exp(-sz)(c - c_o) dz$$

$$D_A \frac{\partial^2 \bar{c}(s)}{\partial x^2} = \dot{\gamma}_w x s \bar{c}(s)$$

a form of the Bessel equation

$$c(s) = (c_o^* - c_o) (3^{-\frac{1}{3}}) \Gamma\left(\frac{2}{3}\right) \left(\frac{D_A}{\dot{\gamma}_w s}\right)^{\frac{1}{6}} \sqrt{x} \left[I_{-\frac{1}{3}}(t) - I_{\frac{1}{3}}(t) \right]$$

$$t = \left(\frac{2}{3}\right) \left(\frac{\dot{\gamma}_w s}{D_A}\right)^{\frac{1}{2}} x^{\frac{1}{6}}$$

$I_{-\frac{1}{3}}(t)$, $I_{\frac{1}{3}}(t)$ *the modified Bessel functions of the first kind
of order -1/3 and 1/3, respectively*

*Mass Transfer to a Power-Law Fluid
Flowing on an Inclined Plate-3*

$$\left. \frac{\partial \bar{c}}{\partial x} \right|_{x=0} = -(c^* - c_o) \left(3^{-\frac{1}{6}} \right) \frac{\Gamma\left(\frac{2}{3}\right)}{\Gamma\left(\frac{4}{3}\right)} \left(\frac{\dot{\gamma}_w s}{D_A} \right)^{\frac{1}{3}}$$

$$\left. \frac{\partial c}{\partial x} \right|_{x=0} = -(c^* - c_o) \frac{3^{\frac{1}{3}}}{\Gamma\left(\frac{1}{3}\right)} \left(\frac{\dot{\gamma}_w}{D_A z} \right)^{\frac{1}{3}}$$

the average(over the length L) mass transfer coefficient

$$k_a = \frac{1}{L} \int_0^L \frac{-D_A \left. \frac{\partial c}{\partial x} \right|_{x=0} dz}{(c^* - c_o)} = \frac{3^{\frac{4}{3}} D_A^{\frac{2}{3}}}{2\Gamma\left(\frac{1}{3}\right)} \left(\frac{\dot{\gamma}_w}{L} \right)^{\frac{1}{3}}$$

Mass Transfer to Non-Newtonian Fluids

Mass Transfer to a Power-Law Fluid in Poiseuille Flow

completely analogous to convective heat transfer in Poiseuille flow

$$V_o \frac{y}{R} \frac{\partial c}{\partial z} = D_A \frac{\partial^2 c}{\partial y^2}$$

B.C. 1 at $z = 0$, $c = c_o$ inlet concentration

B.C. 2 at $y = 0$, $c = c^$ solubility*

B.C. 3 at $y = \infty$, $c = c_o$

B.C. 3 is valid only for the case of short contact time for which the mass transfer, or diffusion, proceeds in the vicinity of the wall

Dimensionless variables

$$C = \frac{c^* - c}{c^* - c_o}, \quad \xi = \frac{y}{R}, \quad \zeta = \frac{D_A z}{\langle V \rangle R^2}$$

Mass Transfer to a Power-Law Fluid in Poiseuille Flow-1

The velocity profile for power-law fluids

$$\frac{V_z}{\langle V \rangle} = \frac{V_z}{\frac{Q}{\pi R^2}} = \frac{3 + \frac{1}{n}}{1 + \frac{1}{n}} \left[1 - (1 - \xi)^{1 + \frac{1}{n}} \right]$$

$$\dot{\gamma}_w = - \left(\frac{dV_z}{dy} \right)_{y=0} = - \left(3 + \frac{1}{n} \right) \frac{Q}{\pi R^3} \quad V_o = -\dot{\gamma}_w R = - \left(3 + \frac{1}{n} \right) \frac{Q}{\pi R^2}$$

$$\left(3 + \frac{1}{n} \right) \xi \frac{\partial C}{\partial \zeta} = \frac{\partial^2 C}{\partial \xi^2}$$

- B.C. 1** at $\zeta = 0, C = 1$
B.C. 2 at $\xi = 0, C = 0$
B.C. 3 at $\xi = \infty, C = 1$

Similarity solution technique

$$\theta = \theta(\chi)$$

$$\chi = \xi / \left[\frac{9\zeta}{3 + (1/n)} \right]^{\frac{1}{3}}$$

$$\frac{d^2 C}{d\chi^2} + 3\chi^2 \frac{dC}{d\chi} = 0$$

$$C(0) = 0 \text{ and } C(\infty) = 1$$

$$\theta = \frac{1}{\Gamma\left(\frac{4}{3}\right)} \int_{\chi}^{\infty} e^{-x^3} dx$$

The local mass transfer coefficient

$$-D_A \left. \frac{\partial c}{\partial y} \right|_{y=0} = k_{loc} (c_b - c^*)$$

c_b is the bulk solute concentration in the fluid

For short contact time, $c_b \approx c_o$

local Sherwood number (Nusselt number for mass transfer)

$$Sh_{loc} = \frac{2k_{loc}R}{D_A} = \frac{2R \left(\left. \frac{\partial c}{\partial y} \right|_{y=0} \right)}{(c_o - c^*)} = 2 \left. \frac{\partial C}{\partial \xi} \right|_{\xi=0}$$

$$Sh_{loc} = 2 \left. \frac{\partial C}{\partial \chi} \right|_{\chi=0} \left(\left. \frac{\partial \chi}{\partial \xi} \right) \right) = \frac{2}{\Gamma\left(\frac{4}{3}\right)} \sqrt[3]{\frac{\left(3 + \frac{1}{n}\right) \langle V \rangle R^2}{9D_A z}}$$

average Sherwood number

$$Sh_a = \frac{2k_a R}{D_A} = \frac{1}{L} \int_0^L Sh_{loc} dz = \frac{3}{\Gamma\left(\frac{4}{3}\right)} \sqrt[3]{\frac{\left(3 + \frac{1}{n}\right) \langle V \rangle R^2}{9D_A L}}$$

$$Sh_a = 1.75 \left[\frac{3 + \frac{1}{n}}{4} \right]^{\frac{1}{3}} Gz^{\frac{1}{3}} \quad Gz = \frac{\pi R^2 \langle V \rangle}{D_A L}$$

$$Gz = \frac{\pi R^2 \langle V \rangle}{D_A L} = \frac{\pi}{2} \left(\frac{2R \langle V \rangle \rho}{\eta} \right) \left(\frac{\eta}{\rho D_A} \right) \left(\frac{R}{L} \right) = \frac{\pi}{2} Re Sc \left(\frac{R}{L} \right)$$

Shear thinning(as n decreases) enhances the mass transfer rate

Concentration Distributions in Turbulent Flows

$$v_x = \bar{v}_x(x, y, z) + v'_x(x, y, z, t) \quad C_A = \bar{C}_A(x, y, z) + C'_A(x, y, z, t)$$

$$\frac{\partial C_A}{\partial t} + \underline{v} \cdot \nabla C_A = D_{AB} \nabla^2 C_A - k_n C_A^n$$

$$\frac{\partial \bar{C}_A}{\partial t} + \bar{\underline{v}} \cdot \nabla \bar{C}_A = \mathcal{D}_{AB} \nabla^2 \bar{C}_A + \overline{\underline{v}' \cdot \nabla C'_A} - \begin{cases} k_1 \bar{C}_A \\ k_2 (\bar{C}_A^2 + \overline{C'^2_A}) \end{cases}$$

$$\bar{\underline{J}}_A^{(t)} = \overline{\underline{v}' C'_A}$$

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \bar{\underline{v}} = 0$$

$$\rho \frac{D\bar{\underline{v}}}{Dt} = -\nabla \bar{p} + \nabla \cdot \left(\bar{\underline{\tau}}^{(v)} + \bar{\underline{\tau}}^{(t)} \right) + \rho g$$

$$\frac{D\bar{C}_A}{Dt} = -\left(\nabla \cdot \left(\bar{\underline{J}}_A^{(v)} + \bar{\underline{J}}_A^{(t)} \right) \right) - \begin{cases} k_1 \bar{C}_A \\ k_2 (\bar{C}_A^2 + \overline{C'^2_A}) \end{cases}$$

$$\bar{J}_A^{(t)} = -\mathcal{D}_{AB}^{(t)} \frac{d\bar{C}_A}{dy}$$

Turbulent Prandtl Number

$$Sc^{(t)} = \frac{\nu^{(t)}}{\mathcal{D}_{AB}^{(t)}} = 1$$

Prandtl's mixing length \sim normal to the direction of bulk flow

in the y direction

$$\bar{J}_A^{(t)} = -\overline{v'_y \cdot C'_A} = -l^2 \left| \frac{d\bar{v}_x}{dy} \right| \frac{d\bar{C}_A}{dy}$$

TRANSFER COEFFICIENTS IN ONE PHASE

the rates of mass transfer across phase boundaries to the relevant concentration differences, mainly for binary systems

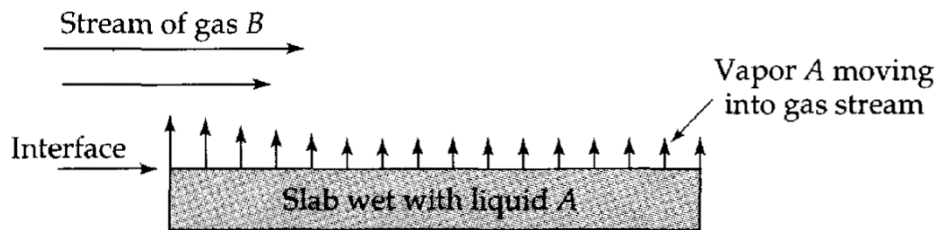


Fig. 22.1-1. Example of mass transfer across a plane boundary: 포화 평판의 건조

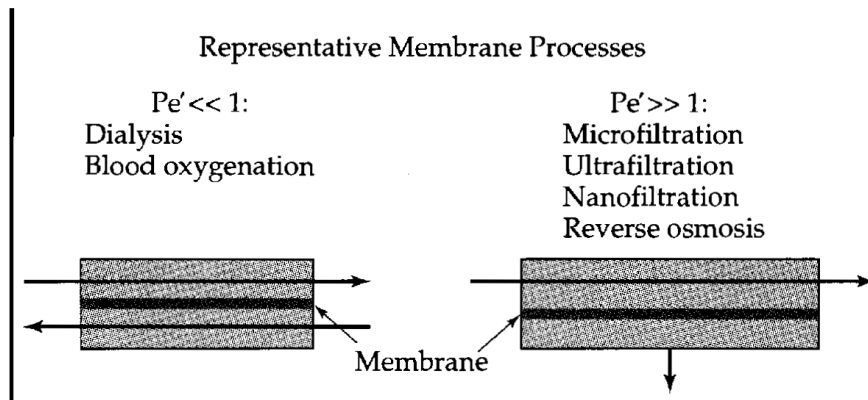
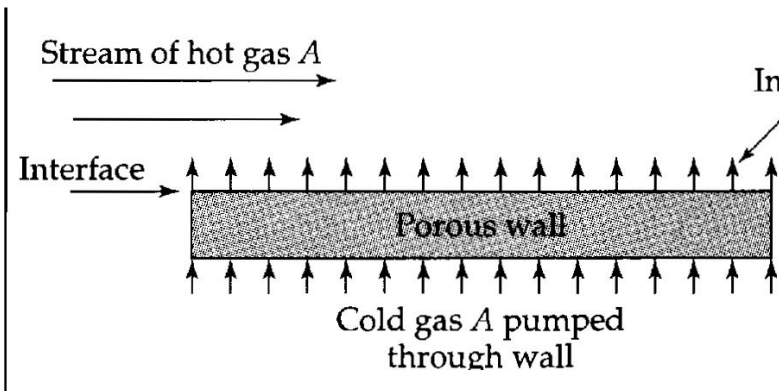


Fig. 22.1-2. Two rather typical kinds of membrane separators, classified here according to a Peclet number, or the flow through the membrane. The heavy line represents the membrane, and the arrows represent the flow along or through the membrane.

선택적 투과막

진짜 상 경계를 가짐



유체역학적 물성의 급격한 변화

Fig. 22.1-3. Example of mass transfer through a porous wall: transpiration cooling.

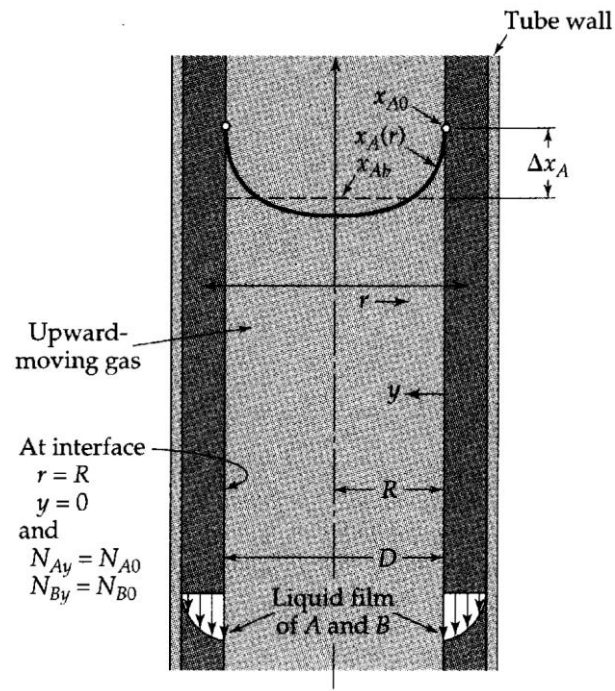


Fig. 22.1-4. Example of a gas-liquid contacting device: the wetted-wall column. Two chemical species A and B are moving from the downward-flowing liquid stream into the upward-flowing gas stream in a cylindrical tube

$$N_{A0} - x_{A0}(N_{A0} + N_{B0}) = -\left(c\mathcal{D}_{AB} \frac{\partial x_A}{\partial y}\right)\Big|_{y=0}$$

$$e_0 - (N_{A0}\bar{H}_{A0} + N_{B0}\bar{H}_{B0}) = -\left(k \frac{\partial T}{\partial y}\right)\Big|_{y=0}$$

$$W_{A0} - x_{A0}(W_{A0} + W_{B0}) = k_{xA}A \Delta x_A$$

$$E_0 - (W_{A0}\bar{H}_{A0} + W_{B0}\bar{H}_{B0}) = hA \Delta T$$

W_{A0} is the number of moles of species A per unit time going through the transfer surface at $y = 0$, and E_0 is the total amount of energy going through the surface

미분 면적에 정의되는 국부 전달계수

$$dW_{A0}/dA = N_{A0} \text{ and } dE_0/dA = e_0$$

$$\mathbf{e} = -k\nabla T + \sum_{\alpha=1}^N \bar{H}_{\alpha} N_{\beta}$$

Partial molar enthalpy

$$N_{A0} - x_{A0}(N_{A0} + N_{B0}) = k_{xA,loc} \Delta x_A$$

$$e_0 - (N_{A0}\bar{H}_{A0} + N_{B0}\bar{H}_{B0}) = h_{loc} \Delta T$$

$$J_{A0}^* = -J_{B0}^*, \quad \Delta x_A = -\Delta x_B \quad \therefore k_{xA,loc} = k_{xB,loc}$$

if the heat of mixing is zero (as in ideal gas mixtures)

$$\bar{H}_A = \tilde{C}_{pA,0}(T_0 - T^\circ) \quad T^\circ: \text{reference temperature}$$

$$N_{A0} - x_{A0}(N_{A0} + N_{B0}) = k_{x,\text{loc}}\Delta x_A$$
$$e_0 - (N_{A0}\tilde{C}_{pA,0} + N_{B0}\tilde{C}_{pB,0})(T_0 - T^\circ) = h_{\text{loc}}\Delta T$$

Partial molar enthalpy

$$\bar{H}_\alpha = \left(\frac{\partial H}{\partial n_\alpha} \right)_{T,P,n_\beta}$$

$$H(kn_1, kn_2, kn_3, \dots) = kH(n_1, n_2, n_3, \dots) \quad \text{Enthalpy} \sim \text{Extensive property}$$

By Euler Theorem

$$H = \sum_\alpha n_\alpha \bar{H}_\alpha$$

Homogeneous of degree 1

$$\bar{H}_A = \tilde{H} - x_B \left(\frac{\partial \tilde{H}}{\partial x_B} \right)_n \quad \bar{H}_B = \tilde{H} + x_A \left(\frac{\partial \tilde{H}}{\partial x_B} \right)_n \quad \tilde{H} = H / (n_A + n_B) = H / n$$

$$\left(\frac{\partial H}{\partial n_A} \right)_{n_B} = \bar{H}_A = \frac{H}{n} - \frac{x_B}{n} \left(\frac{\partial H}{\partial x_B} \right)_n \quad n_A = (1 - x_B)n; \quad n_B = x_B n$$

$$\left(\frac{\partial H}{\partial x_B} \right)_n = \left(\frac{\partial H}{\partial n_A} \right)_{n_B} \left(\frac{\partial n_A}{\partial x_B} \right)_n + \left(\frac{\partial H}{\partial n_B} \right)_{n_A} \left(\frac{\partial n_B}{\partial x_B} \right)_n = \bar{H}_A(-n) + \bar{H}_B(+n)$$

$$H = \sum_\alpha n_\alpha \bar{H}_\alpha = (n_A \bar{H}_A + n_B \bar{H}_B)$$

mass transfer coefficient

$$N_{A0} = k_{x,loc}^0 \Delta x_A$$

"apparent" mass transfer coefficient

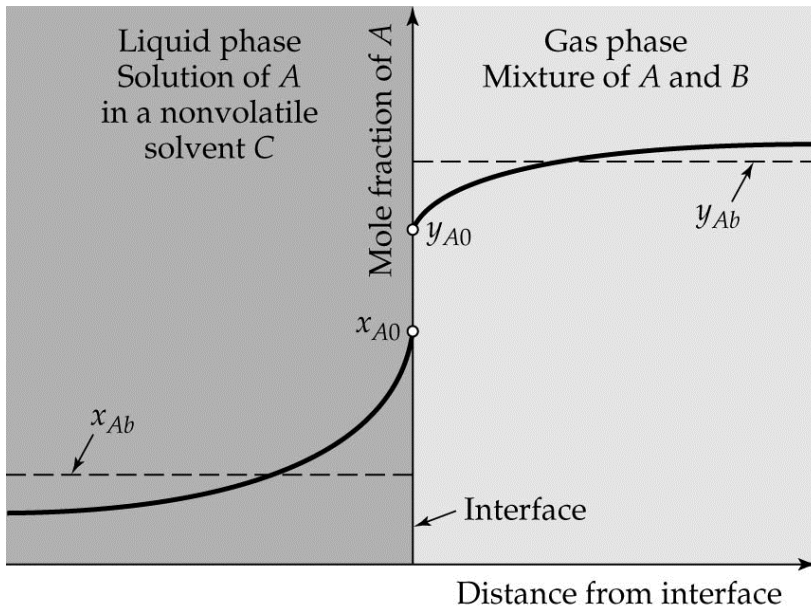
$$k_{x,loc}^0 = \frac{k_{x,loc}}{[1 - x_{A0}(1+r)]}$$

$$\lim_{x_{A0}(1+r) \rightarrow 0} \left\{ \begin{array}{l} k_{x,loc}^0 \\ ck_{c,loc}^0 \\ pk_{p,loc}^0 \\ \rho k_{\rho,loc}^0 \end{array} \right\} = k_{x,loc}$$

The superscript 0 indicates that these quantities are applicable only for small mass-transfer rates and small mole fractions of species A.

TRANSFER COEFFICIENTS IN TWO PHASES

Interphase Mass Transfer



$$N_{A0}|_{gas} = N_{A0}|_{liquid} = N_{A0}$$

$$N_{A0} = k_{y,loc}^0 (y_{Ab} - y_{A0}) = k_{x,loc}^0 (x_{A0} - x_{Ab})$$

Assuming equilibrium across the interface

$$y_{A0} = f(x_{A0}) \quad \text{평형곡선}$$

$$N_{A0} = K_{y,loc}^0 (y_{Ab} - y_{Ae}) = K_{x,loc}^0 (x_{Ae} - x_{Ab})$$

Overall concentration difference

y_{Ae} Gas phase composition in equilibrium with a liquid at composition x_{Ab}

x_{Ae} Liquid phase composition in equilibrium with a gas at composition y_{Ab}

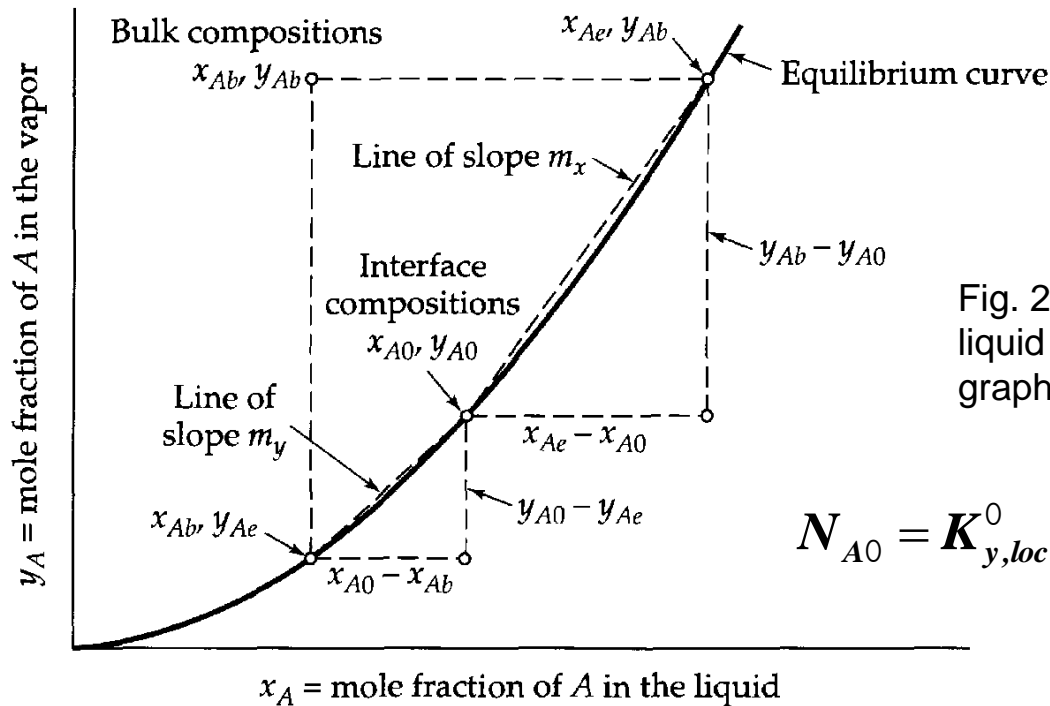


Fig. 22.4-2. Relations among gas- and liquid phase compositions, and the graphical interpretations of m_x , and m_y .

$$N_{A0} = K_{y,loc}^0 (y_{Ab} - y_{Ae}) = K_{x,loc}^0 (x_{Ae} - x_{Ab})$$

$K_{y,loc}^0$

the overall mass transfer coefficient "based on the gas phase"

$K_{x,loc}^0$

the overall mass transfer coefficient "based on the liquid phase"

$$K_{x,loc}^0 (x_{Ae} - x_{Ab}) = k_{x,loc}^0 (x_{A0} - x_{Ab})$$

$$K_{y,loc}^0 (y_{Ab} - y_{Ae}) = k_{y,loc}^0 (y_{Ab} - y_{A0})$$

$$m_x = \frac{y_{Ab} - y_{A0}}{x_{Ae} - x_{A0}}; \quad m_y = \frac{y_{A0} - y_{Ae}}{x_{A0} - x_{Ab}}$$

$$\frac{k_{x,loc}^0}{K_{x,loc}^0} = 1 + \frac{k_{x,loc}^0}{m_x k_{y,loc}^0}; \quad \frac{k_{y,loc}^0}{K_{y,loc}^0} = 1 + \frac{m_y k_{y,loc}^0}{k_{x,loc}^0}$$

If $k_{x,loc}^0 / m k_{y,loc}^0 \ll 1$ the mass-transport resistance of the gas phase has little effect, and it is said that the mass transfer is liquid-phase controlled. In practice, this means that the system design should favor liquid-phase mass transfer.

If $k_{x,loc}^0 / m k_{y,loc}^0 \gg 1$ then the mass transfer is gas-phase controlled. In a practical situation, this means that the system design should favor gas-phase mass transfer.

If $0.1 \ll k_{x,loc}^0 / m k_{y,loc}^0 \ll 10$, roughly, one must be careful to consider the interactions of the two phases in calculating the two-phase transfer coefficients.

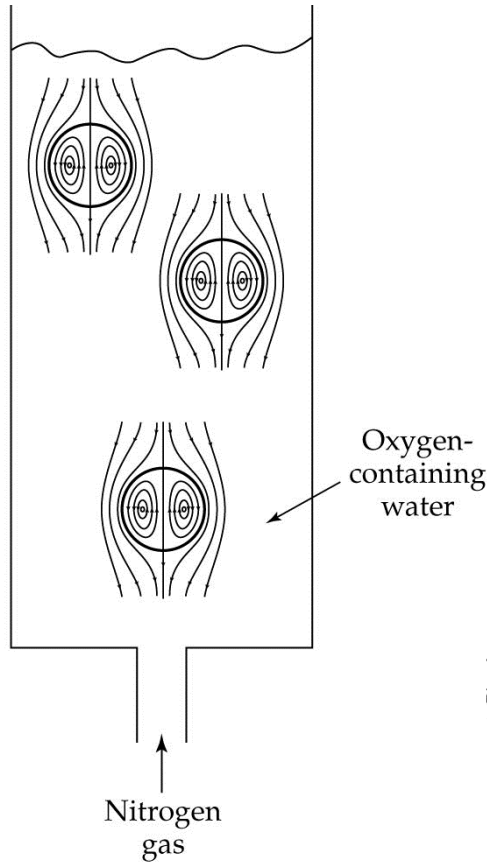
Mean two phase mass transfer coefficient

bulk concentrations in the two adjacent phase do not change significantly over the total mass transfer surface

$$(N_{A0})_m = \frac{1}{S} \int_S K_{x,\text{loc}}^0 (x_{Ae} - x_{Ab}) dS = K_{xm}^0 (x_{Ae} - x_{Ab})$$

$$K_{xm}^0 = \frac{1}{S} \int_S \frac{1}{(1/k_{x,\text{loc}}^0) + (1/m_x k_{y,\text{loc}}^0)} dS$$

$$K_{x,\text{approx}}^0 = \frac{1}{(1/k_{xm}^0) + (1/m_x k_{ym}^0)}$$



Penetration model holds in each phase

$$k_{x,loc}^0 \approx k_{x,loc} = c_l \sqrt{\frac{4D_{AB}}{\pi t_{exp}}}$$

$$k_{y,loc}^0 \approx k_{y,loc} = c_g \sqrt{\frac{4D_{AC}}{\pi t_{exp}}}$$

Total molar concentration in each phase

$$\frac{k_{x,loc}^0}{mk_{y,loc}^0} = \frac{c_l}{c_g} \sqrt{\frac{D_{AB}}{D_{AC}}} \cdot \frac{1}{m} \ll 1$$

Only liquid phase resistance is significant

Absorption or desorption of sparingly soluble gases is almost always liquid phase controlled

an oxygen stripper, in which oxygen(A) from the water(B) diffuses into the nitrogen gas(C) bubbles.

the law of conservation of mass of chemical species α in a multicomponent macroscopic flow system

$$\frac{dm_{\alpha,\text{tot}}}{dt} = -\Delta w_{\alpha} + w_{\alpha,0} + r_{\alpha,\text{tot}} \quad \alpha = 1, 2, 3, \dots, N$$

the instantaneous total mass of α in the system

the mass rate of addition of species α to the system by mass transfer across the bounding surface

the net rate of production of species α by homogeneous and heterogeneous reactions within the system

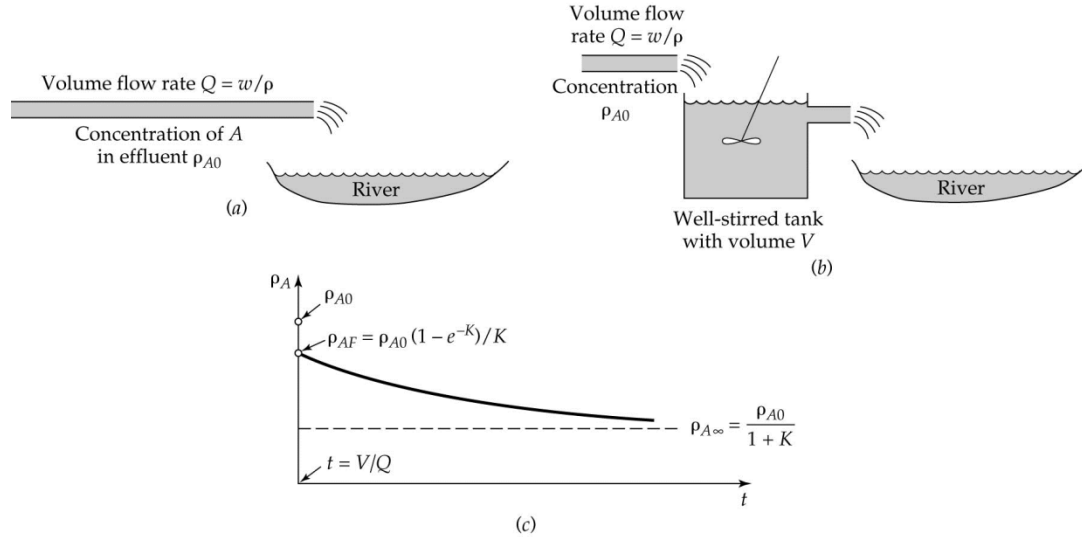
$$\frac{dm_{\text{tot}}}{dt} = -\Delta w + w_0$$

in molar units

$$\frac{dM_{\alpha,\text{tot}}}{dt} = -\Delta W_{\alpha} + W_{\alpha,0} + R_{\alpha,\text{tot}} \quad \alpha = 1, 2, 3, \dots, N$$

$$\frac{dM_{\text{tot}}}{dt} = -\Delta W + W_0 + \sum_{\alpha=1}^N R_{\alpha,\text{tot}}$$

Disposal of an unstable waste product



$$t \leq \rho V / w \quad \frac{d}{dt} m_{A,tot} = w\omega_{A0} - k_1''' m_{A,tot} \quad t = 0 \quad m_{A,tot} = 0$$

$$m_{A,tot} = \frac{w\omega_{A0}}{k_1'''} (1 - \exp(k_1''' t))$$

$$m_{A,tot} = wt\omega_A \quad \frac{\omega_A}{\omega_{A0}} = \frac{1 - \exp(k_1''' t)}{k_1''' t}$$

When the tank is full

$$\frac{\omega_{AF}}{\omega_{A0}} = \frac{1 - e^{-K}}{K} \quad K = k_1''' \rho V / w = k_1''' V / Q$$

$$t \geq \rho V/w \quad \frac{d}{dt}(\rho_A V) = w\omega_{A0} - w\omega_A - k_1''' \rho V$$

$$\frac{d\omega_A}{d\tau} + (1 + K)\omega_A = \omega_{A0}$$

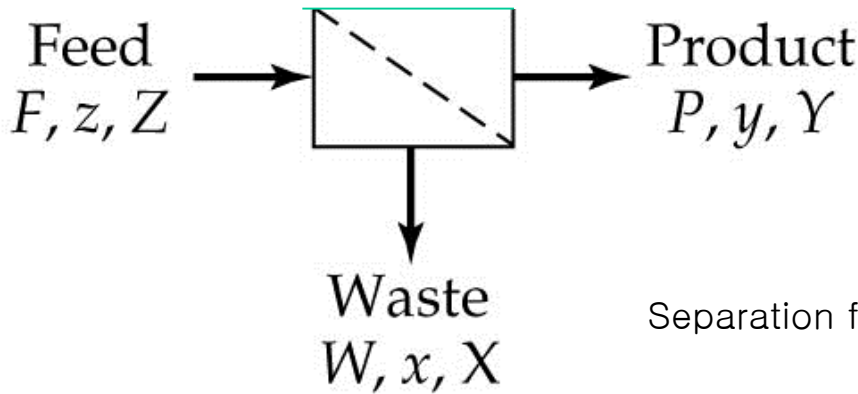
$$\tau = (w/\rho V)t$$

$$\tau = 1 \quad \omega_A = \omega_{AF}$$

$$\frac{\omega_A - [\omega_{A0}/(1 + K)]}{\omega_{AF} - [\omega_{A0}/(1 + K)]} = e^{-(1+K)(\tau-1)}$$

$$\omega_{A\infty} = \frac{\omega_{A0}}{1 + K} = \frac{\omega_{A0}}{1 + (k_1''' \rho V/w)}$$

Binary Splitters



$$zF = yP + xW$$

$$F = P + W$$

Cut $\theta = P/F$

$$z = \theta y + (1 - \theta)x$$

Separation factor α

$$Y = \alpha X$$

Mole ratio $Y = \frac{y}{1-y}, \quad X = \frac{x}{1-x}$

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \quad \text{or} \quad x = \frac{y}{\alpha - (\alpha - 1)y}$$

Gas-liquid Splitters (equilibrium distillation)

α

Relative volatility

Dirac 분리용량(separation capacity) 및 가치함수(value function)

서로 다른 분리공정의 유효성을 비교하기 위한 기준 수립

$$\alpha = \frac{y/(1-y)}{x/(1-x)} = 1 + \frac{y-x}{x(1-y)}$$

약간 농축되는 계 $(\alpha - 1) \ll$

$$y = \frac{x + (\alpha - 1)x}{1 + (\alpha - 1)x} \approx x + (\alpha - 1)x(1 - x)$$

Dirac 분리용량(separation capacity)

$$\Delta = Pv(y) + Wv(x) - Fv(z)$$

Binary Splitters

$$zF = yP + xW$$

$$F = P + W$$

$$\text{Cut } \theta = P/F$$

$$z = \theta y + (1 - \theta)x \quad \text{or} \quad z - x = \theta(y - x)$$

$$\frac{\Delta}{F} = \theta v(y) + (1 - \theta)v(x) - v(z)$$

$$v(y) = v(x) + (y - x)v'(x) + \frac{1}{2}(y - x)^2 v''(x) + \dots$$

$$v(z) = v(x) + (z - x)v'(x) + \frac{1}{2}(z - x)^2 v''(x) + \dots$$

$$\frac{\Delta}{F} = \frac{1}{2}\theta(1 - \theta)(y - x)^2 v''(x)$$

$$y = \frac{x + (\alpha - 1)x}{1 + (\alpha - 1)x} \approx x + (\alpha - 1)x(1 - x) \longrightarrow \frac{\Delta}{F} = \frac{1}{2}\theta(1 - \theta)(\alpha - 1)^2 x^2 (1 - x)^2 v''(x)$$

계의 분리용량은 실질적으로 농도에 무관하다고 가정 $x^2(1 - x)^2 v''(x) = 1$

$$\frac{\Delta}{F} = \frac{1}{2}\theta(1 - \theta)(\alpha - 1)^2$$

$$\frac{d^2 v(x)}{dx^2} = \frac{1}{x^2(1 - x)^2} \longrightarrow v(x) = (2x - 1)\ln \frac{x}{(1 - x)} - 2 + C_1 x + C_2$$

적분 상수를 구하기 위한 조건 선택

$$v\left(\frac{1}{2}\right) = 0, \quad v'\left(\frac{1}{2}\right) = 0$$

$$v(x) = (2x - 1)\ln \frac{x}{(1 - x)}$$

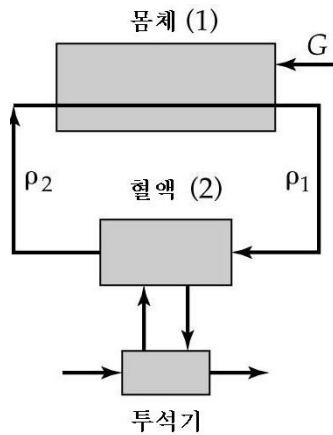
Compartmental Analysis

A complex system is treated as a network of perfect mixers, each constant volume, connected by ducts of negligible volume, with no dispersion occurring in the connecting ducts

$$V_n \frac{d\rho_{\alpha n}}{dt} = \sum_{m=1}^N Q_{mn} (\rho_{\alpha m} - \rho_{\alpha n}) + V_n r_{\alpha n}$$

Q_{mn} The volumetric flow rate of solvent flow from unit m to unit n

Hemodialysis



during dialysis period $V_1 \frac{d\rho_1}{dt} = -Q(\rho_1 - \rho_2) + G$

$$V_1 \frac{d\rho_1}{dt} = G - Q(\rho_1 - \rho_2)$$

$$V_2 \frac{d\rho_2}{dt} = Q(\rho_1 - \rho_2) - D\rho_2$$

Initial condition $t = 0 \quad \rho_1 = \rho_2 = \rho_0$

$$V_2 \frac{d\rho_2}{dt} = Q(\rho_1 - \rho_2) - D\rho_2$$

$$\frac{d^2 \rho_2}{dt^2} + \left(\frac{Q}{V_1} + \frac{Q}{V_2} + \frac{D}{V_2} \right) \frac{d\rho_2}{dt} + \frac{Q}{V_1} \frac{D}{V_2} \rho_2 = \frac{Q}{V_1} \frac{G}{V_2}$$

$$t = 0 \quad \rho_2 = \rho_0 \quad \text{and} \quad \frac{d\rho_2}{dt} = -\frac{D\rho_0}{V_2}$$

For the recovery period


$$\frac{d^2 \rho'_2}{dt'^2} + Q \left(\frac{V_1 + V_2}{V_1 V_2} \right) \frac{d\rho'_2}{dt} = \frac{QG}{V_1 V_2}$$

$$\rho'_{2,cf} = C_3 \exp \left[Q \left(\frac{V_1 + V_2}{V_1 V_2} \right) t' \right] + C_4$$

$$\rho'_{2,pi} = \frac{Gt'}{V_1 + V_2}$$

Initial condition

$$t' = 0 \quad \rho'_2 = \rho_2 \quad \rho'_1 = \rho_1$$


$$\frac{d\rho'_2}{dt} = \frac{d\rho_2}{dt} + \frac{D\rho_2}{V_2}$$

| Quantity | V_1 (liters) | V_2 (liters) | Q (liters per min) | D (liters per min) | G (g/min) | ρ_0 (g per liter) |
|-----------|-------------------|-------------------|-------------------------|-------------------------|----------------|---------------------------|
| Magnitude | 43 | 4.5 | 5.4 | 0.3 | 0.0024 | 0.140 |

during dialysis period $\frac{d^2\rho_2}{dt^2} + (1.3922)\frac{d\rho_2}{dt} + (0.00837)\rho_2 = 6.70 \times 10^{-5}$

I. C.: at time $t = 0$, $\rho_2 = \rho_0$ and $\frac{d\rho_2}{dt} = -0.00933$

$$\rho_{2,ct} = C_1 \exp(0.006043t) + C_2 \exp(1.386t)$$

$$\rho_{2,pt} = 0.0080$$

$$\rho_2 = 0.1258 \exp(0.006043t) + (0.0062 \exp(1.386t) + 0.0080$$

$$\frac{d\rho_2}{dt} = -0.000760 \exp(0.006043t) - 0.0086 \exp(1.386t)$$

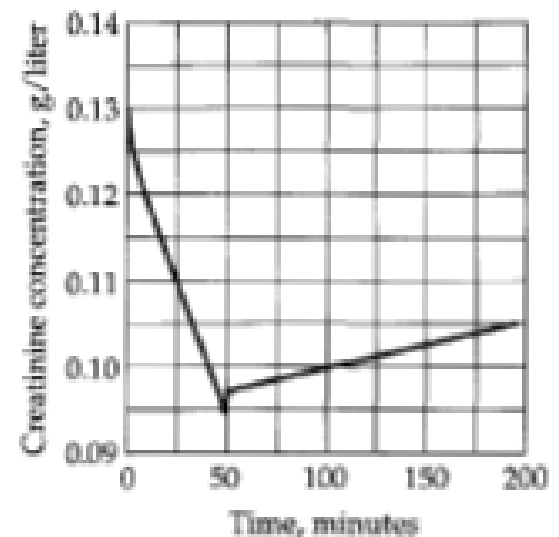
For the recovery period

$$\rho_2' = C_3 \exp(-1.325t') + (5.05 \times 10^{-5})t' + C_4$$

$$\frac{d\rho_2'}{dt'} = -1.325C_3 \exp(-1.325t') + (5.05 \times 10^{-5})$$

$$\text{at } t' = 0, \quad \rho_2(t = 50) = 0.099239 = \rho_2'$$

$$\rho_2' = 0.0972 - 0.00422 \exp(-1.325t') + (5.05 \times 10^{-5})t'$$



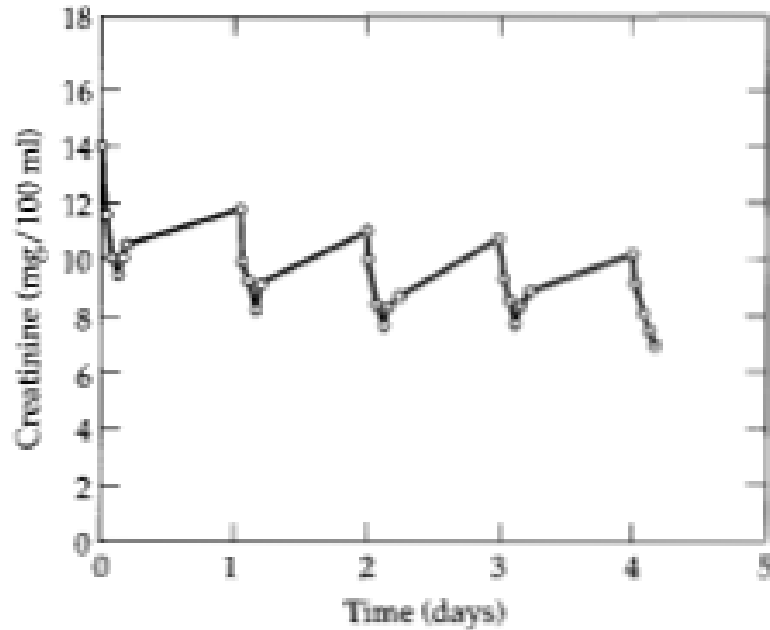


Fig. 23.1-6. Experimental (dots) and simulated creatinine data (solid curve) for a dialysis patient [R. L. Bell, K. Curtiss, and A. L. Babb, *Trans. Amer. Soc. Artificial Internal Organs*, **11**, 183 (1965)].