Lecture 26

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Web Lecture 26
Class Lecture 22

- **Course Information**

  Materials on Ctools

- **Review of 342 Mass Transfer Without Reaction**

  Diffusion and Fick's Law

  Mass Transfer Coefficient

  Drug Delivery Patches

  Robert The Worrier

P14-2$_B$

$$\mathbf{W}_A = \mathbf{J}_A + C_A\mathbf{U}$$

$$\mathbf{U} = \sum y_i \mathbf{U}_i$$

Binary System

$$\mathbf{W}_A = C_A\mathbf{U}_A \text{ and } \mathbf{W}_B = C_B\mathbf{U}_B$$

$$\mathbf{U} = y_A\mathbf{U}_A + y_B\mathbf{U}_B$$

Multiply and divide by

$$\mathbf{U} = \left[\frac{C_A\mathbf{U}_A + C_B\mathbf{U}_B}{C}\right] = \frac{\mathbf{W}_A + \mathbf{W}_B}{C}$$

$$C_A\mathbf{U} = C_A\frac{\mathbf{W}_A + \mathbf{W}_B}{C} = y_A\left[\mathbf{W}_A + \mathbf{W}_B\right]$$

$$\mathbf{W}_A = \mathbf{J}_A + y_A\left(\mathbf{W}_A + \mathbf{W}_B\right)$$

1. For equal molar counter diffusion

$$\mathbf{W}_{\mathrm{A}} = \mathbf{J}_{\mathrm{A}} + y_{\mathrm{A}}\left(\mathbf{W}_{\mathrm{A}} + \mathbf{W}_{\mathrm{B}}\right)$$

$$\mathbf{J}_{\mathrm{A}} = -D_{\mathrm{AB}}\nabla C_{\mathrm{A}}$$

$$\left(\mathbf{W}_{\mathrm{A}} = -\mathbf{W}_{\mathrm{A}}\right)$$

$$\mathbf{W}_{\mathrm{A}} = -D_{\mathrm{AB}}\nabla C_{\mathrm{A}}$$

$$\mathbf{W}_A = \mathbf{J}_A + y_A\left(\mathbf{W}_A + \mathbf{W}_B\right)$$

2. Diffusion through a stagnant film,

3. For dilute concentration

$$\mathbf{W}_A = \mathbf{J}_A + y_A\left(\mathbf{W}_A + \mathbf{W}_B\right)$$

2. Diffusion through a stagnant film, $W_B = 0$

$$\mathbf{J}_\mathbf{A} = -D_{AB}\nabla C_A$$

$$\mathbf{W}_A = -D_{AB}\nabla C_A + y_A\mathbf{W}_A$$

$$\mathbf{W}_A = -\frac{D_{AB}}{1-y_A}\nabla C_A$$

3. For dilute concentration

$$\mathbf{W}_A = \mathbf{J}_A + y_A\left(\mathbf{W}_A + \mathbf{W}_B\right)$$

2. Diffusion through a stagnant film, $W_B = 0$

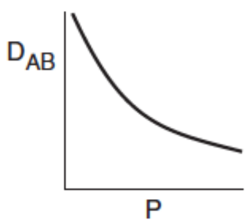
$$\mathbf{W}_A = -D_{AB}\nabla C_A + y_A\mathbf{W}_A$$

$$\mathbf{W}_A = -\frac{D_{AB}}{1-y_A}\nabla C_A$$

3. For dilute concentration

$$y_A << 1$$

$$\mathbf{W}_A = -D_{AB}\nabla C_A$$



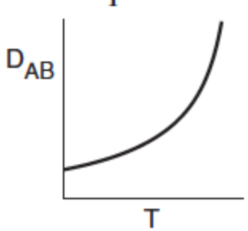


TABLE 14-2. DIFFUSIVITY RELATIONSHIPS FOR GASES, LIQUIDS, AND SOLIDS

	Order of Magnitude		
Phase	cm²/s	m²/s	*Temperature and Pressure Dependences*[a]
Gas			
Bulk	10^{-1}	10^{-5}	$D_{AB}(T_2, P_2) = D_{AB}(T_1, P_1)\dfrac{P_1}{P_2}\left(\dfrac{T_2}{T_1}\right)^{1.75}$
Knudsen	10^{-2}	10^{-6}	$D_A(T_2) = D_A(T_1)\left(\dfrac{T_2}{T_1}\right)^{1/2}$
Liquid	10^{-5}	10^{-9}	$D_{AB}(T_2) = D_{AB}(T_1)\dfrac{\mu_1}{\mu_2}\left(\dfrac{T_2}{T_1}\right)$
Solid	10^{-9}	10^{-13}	$D_{AB}(T_2) = D_{AB}(T_1)\exp\left[\dfrac{E_D}{R}\left(\dfrac{T_2 - T_1}{T_1 T_2}\right)\right]$

[a] μ_1, μ_2, liquid viscosities at temperatures T_1 and T_2, respectively; E_D, diffusion activation energy.

Mass Transfer Coefficient

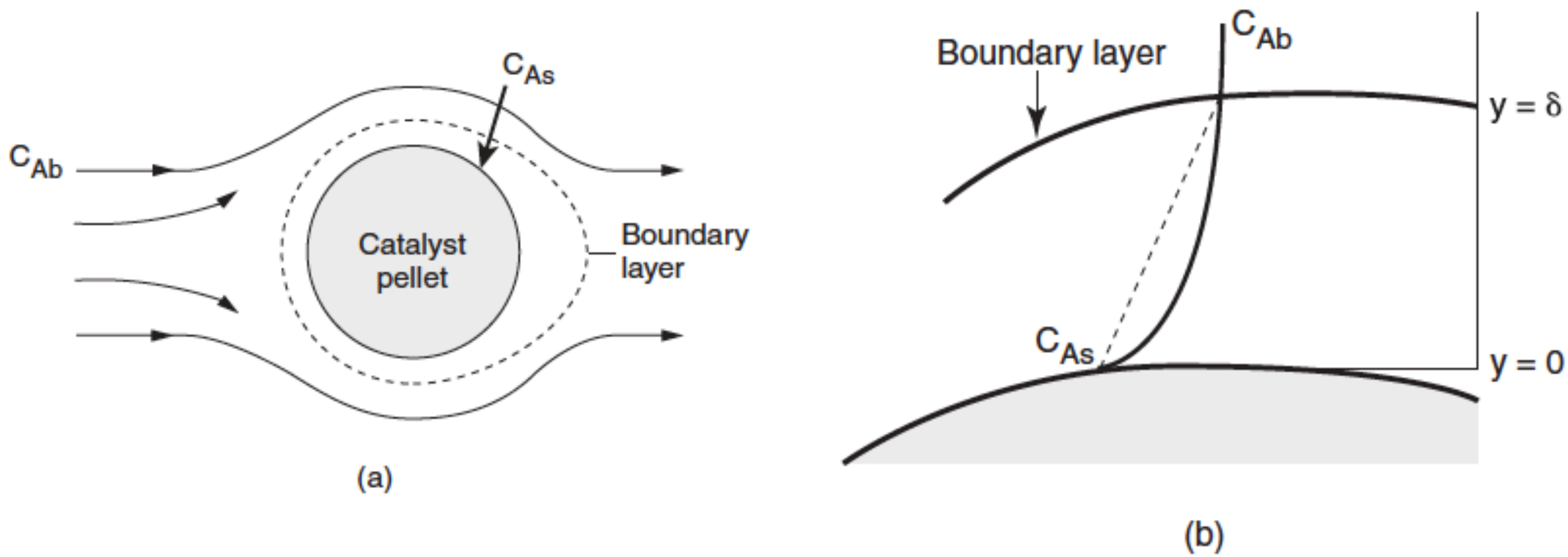
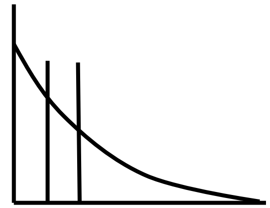


Figure 14-1 Boundary layer around the surface of a catalyst pellet.

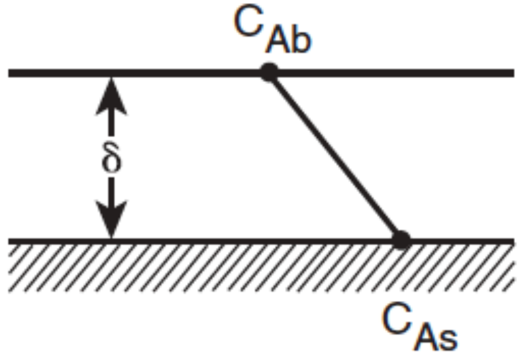


$$W_{Az}A_c\big|_z - W_{Az}A_c\big|_{z+\Delta z} + 0 = 0$$

Divid by $A_c \Delta z$

$$-\left[\frac{W_{Az}\big|_{z+\Delta z} - W_{Az}}{\Delta z}\right] = 0$$

$$\frac{dW_{Az}}{dz} = 0$$

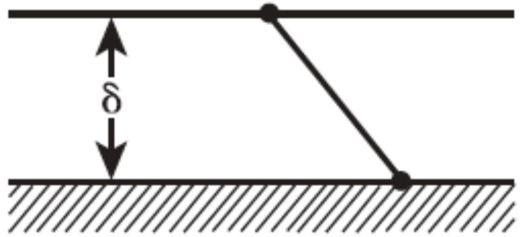


Concentration profile $C_A = C_{As} + (C_{Ab} - C_{As})\frac{z}{\delta}$ (14-25)

Figure 14-2 Concentration profile for EMCD in stagnant film model.

$$W_{Az} = -D_{AB}\frac{dC_A}{dz} = \frac{D_{AB}}{\delta}(C_{A0} - C_{As})$$

$$\boxed{k_c = \frac{D_{AB}}{\delta}} \quad (14\text{-}27)$$



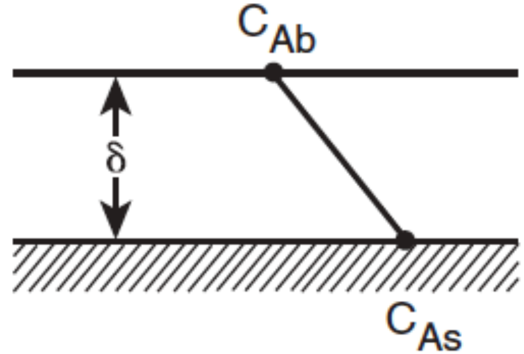
Concentration profile $C_A = C_{As} + \left(C_{Ab} - C_{As}\right)\frac{z}{\delta}$ (14-25)

Figure 14-2 Concentration profile for EMCD in stagnant film model.

$$W_A = -D_{AB}\frac{dC_A}{dz} = \frac{D_{AB}}{\delta}\left(C_{A0} - C_{As}\right)$$

$$\boxed{k_c = \frac{D_{AB}}{\delta}} \quad (14\text{-}27)$$

$$\boxed{W_{Az} = k_c(C_{Ab} - C_{As})} \quad (14\text{-}28)$$



Concentration profile $C_A = C_{As} + (C_{Ab} - C_{As})\frac{z}{\delta}$ (14-25)

Figure 14-2 Concentration profile for EMCD in stagnant film model.

$$W_A = -D_{AB}\frac{dC_A}{dz} = \frac{D_{AB}}{\delta}(C_{A0} - C_{As})$$

$$k_c = \frac{D_{AB}}{\delta} \quad (14\text{-}27)$$

$$W_{Az} = k_c(C_{Ab} - C_{As}) \quad (14\text{-}28)$$

$$W_{Az} = \text{Flux} = \frac{\text{Driving force}}{\text{Resistance}} = \frac{C_{Ab} - C_{As}}{(1/k_c)}$$

$$\mathrm{Sh} = \frac{k_c d_p}{D_{\mathrm{AB}}} = \frac{(\mathrm{m/s})(\mathrm{m})}{\mathrm{m^2/s}} \text{ dimensionless}$$

$$\mathrm{Sc} = \frac{\nu}{D_{\mathrm{AB}}} = \frac{\mathrm{m^2/s}}{\mathrm{m^2/s}} \text{ dimensionless}$$

$$\mathrm{Re} = \frac{\rho D U}{\mu} = \frac{\left(g/m^3\right)(m)(m/s)}{(gm/s)} \text{ dimensionless}$$

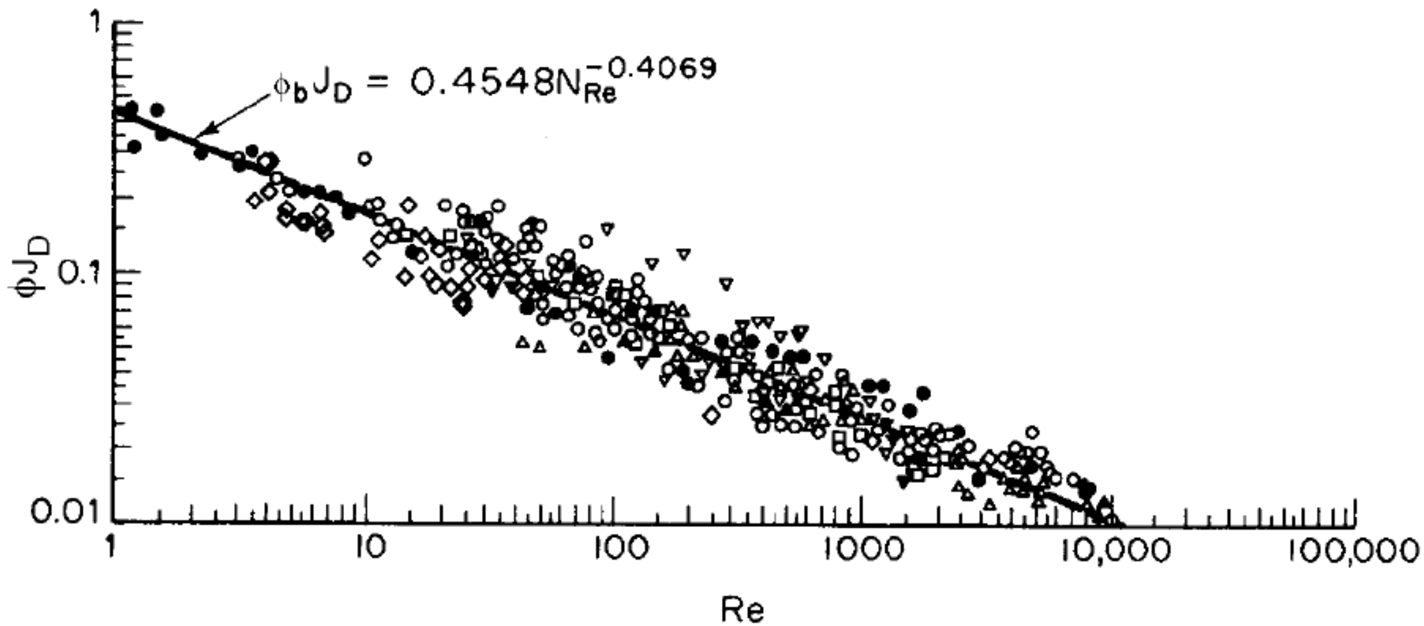
TABLE 14-4. MASS TRANSFER CORRELATIONS

Turbulent flow, mass transfer to pipe wall	$\mathrm{Sh} = .332\,(\mathrm{Re})^{1/2}\,(\mathrm{Sc})^{1/3}$
Mass transfer to a single sphere	$\mathrm{Sh} = 2 + 0.6\,\mathrm{Re}^{1/2}\,\mathrm{Sc}^{1/3}$
Mass transfer in fluidized beds	$\mathrm{Sh} = J_D\,\mathrm{Re}\,\mathrm{Sc}^{1/2}$
	$\phi J_D = \frac{0.765}{\mathrm{Re}^{.82}} + \frac{0.365}{\mathrm{Re}^{0.386}}$
Mass transfer to packed beds	$\mathrm{Sh} = J_D\,\mathrm{Re}\,\mathrm{Sc}^{1/2}$
	$\phi J_D = \underline{0.453}\quad \mathrm{Re}^{0.453}$

$$Sh' = 1.0(Re')^{1/2}Sc^{1/3}$$

$$\left[\frac{k_c d_p}{D_{AB}}\left(\frac{\phi}{1-\phi}\right)\frac{1}{\gamma}\right] = \left[\frac{U d_p \rho}{\mu(1-\phi)\gamma}\right]^{1/2}\left(\frac{\mu}{\rho D_{AB}}\right)^{1/3}$$

$$J_D = \frac{Sh}{Sc^{1/3}\,Re}$$



$$\phi J_D = \frac{0.765}{Re^{0.82}} + \frac{0.365}{Re^{0.386}}$$

$$k_c \propto \left(\frac{D_{AB}^{2/3}}{\nu^{1/6}}\right)\left(\frac{U^{1/2}}{d_p^{1/2}}\right)$$

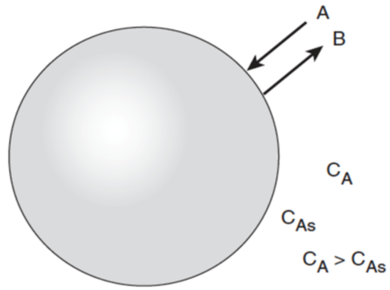


Figure 14-3 Diffusion to, and reaction on, external surface of pellet.

$$-r''_{As} = k_r C_{As}$$

$$W_{ASurface} = -r''_{As}$$

$$W_A = k_C (C_A - C_{As}) = k_r C_{As}$$

We need to eliminate C_{As}.

$$C_{As} = \frac{k_c C_A}{k_r + k_c}$$

and the rate of reaction on the surface becomes

$$\boxed{W_A = -r''_{As} = \frac{k_c k_r C_A}{k_r + k_c}}$$

One will often find the flux to or from the surface as written in terms of an *effective* transport coefficient k_{eff}:

$$W_A = -r''_{As} = k_{\text{eff}} C_A$$

Case 1

$$k_{\text{eff}} = \frac{k_c k_r}{k_c + k_r}$$

$$k_r > k_c$$

$$k_{\text{eff}} = k_c$$

One will often find the flux to or from the surface as written in terms of an *effective* transport coefficient k_{eff}:

where

$$W_A = -r''_{As} = k_{\text{eff}} C_A$$

Case 1

$$k_c = 0.6\left(\frac{D_{AB}}{d_p}\right)\left(\frac{Ud_p}{\nu}\right)^{1/2}\left(\frac{\nu}{D_{AB}}\right)^{1/2}$$

$$k_c \sim (U/d_p)^{1/2}$$

$$-r''_{As} = k_c C_A$$

Case 2

One will often find the flux to or from the surface as written in terms of an *effective* transport coefficient k_{eff}:

$$W_A = -r''_{As} = k_{\text{eff}} C_A$$

where

$$k_{\text{eff}} = \frac{k_c k_r}{k_c + k_r}$$

Case 1

$$k_r > k_c$$

$$k_{\text{eff}} = k_c$$

$$k_c = 0.6\left(\frac{D_{AB}}{d_p}\right)\left(\frac{U d_p}{\nu}\right)^{1/2}\left(\frac{\nu}{D_{AB}}\right)^{1/2}$$

$$k_c \sim (U / d_p)^{1/2}$$

$$-r''_{As} = k_c C_A$$

Case 2

$$k_r < k_c$$

$$W_A = -r''_{As} = \frac{k_r C_A}{1 + k_r / k_c} \approx k_r C_A$$

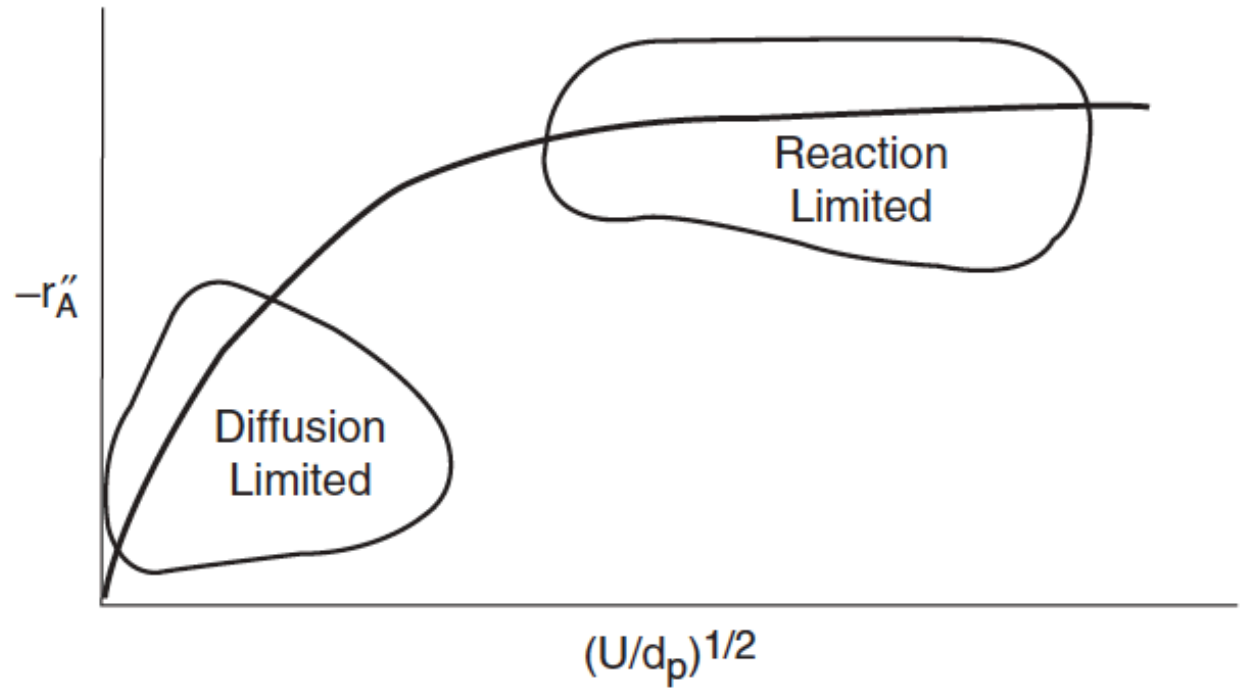
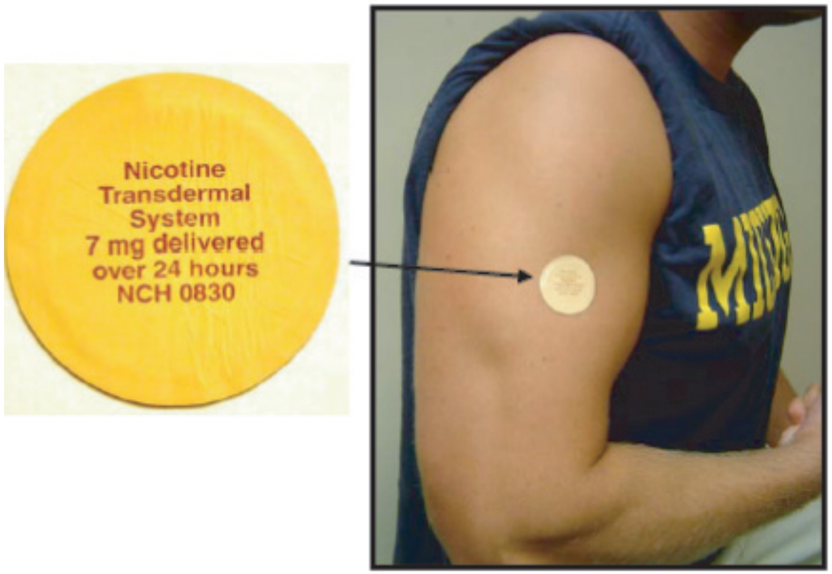
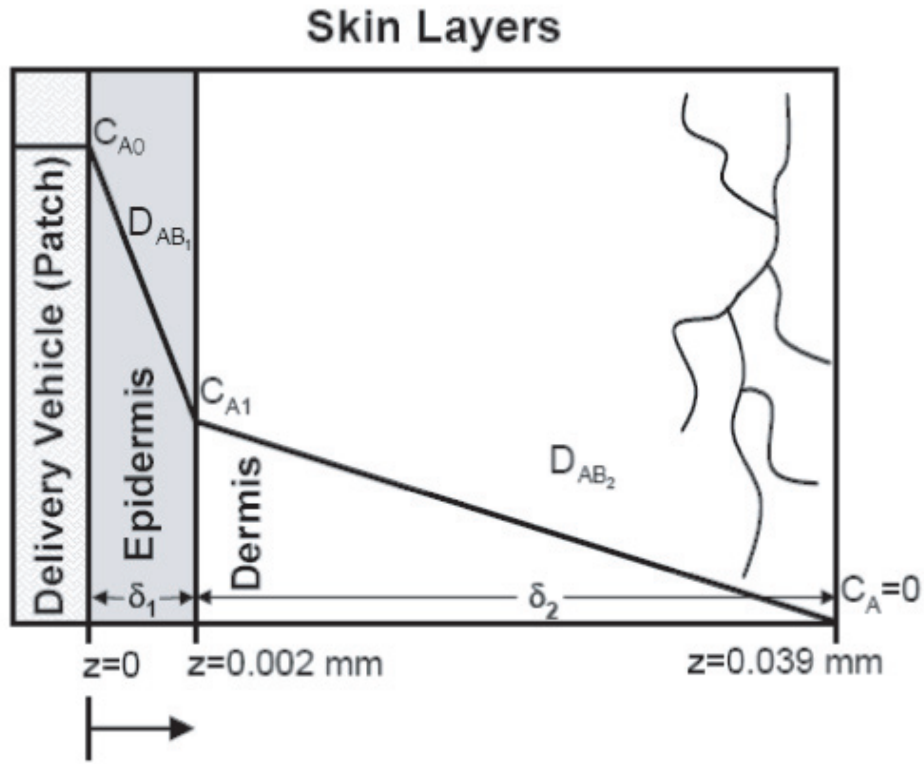


Figure 14-4 Regions of mass transfer–limited and reaction–limited reactions.

Transdermal drug delivery schematic.





$$F_{A(z)} - F_{A(z+\Delta z)} + 0 = 0$$

$$-\frac{AW_{(z+\Delta z)} - AW_{A(z)}}{\Delta z} = 0$$

Step 1. Diffusion of A through the Epidermis film, which is stagnant reduces to

$$\frac{dW_{Az}}{dz} = 0$$

Step 2. Use Fick's law to relate the flux W_{Az} and the concentration gradient

$$W_{A1} = -D_{A1}\frac{dC_A}{dz}$$

Step 3. State the boundary conditions

$$z = 0 \quad C_A = C_{A0}$$

$$z = \delta_1 \quad C_A = C_{A_\delta 1}$$

Step 4. Next substitute for W_{Az} and divide by D_{A1} to obtain

$$\frac{d^2 C_A}{dz^2} = 0$$

Integrating twice

$$C_A = K_1 z + K_2$$

Step 4.

Using the boundary conditions we can eliminate the constants K_1 and K_2 to obtain the concentration profile

$$C_A = K_1 z + K_2$$

$$\frac{C_{A0} - C_A}{C_{A0} - C_A} = \frac{z}{\delta_1}$$

Step 5. Substituting *C*A we obtain the flux in the Epidermis layer

$$W_{A1} = -D_{A1} \frac{dC_A}{dz} = \frac{D_{A1}}{\delta}\left[C_{A0} - C_{A1}\right]$$

Step 6. Carry out a similar analysis for the Dermis layer starting with

$$\frac{d^2C_A}{dz^2} = 0$$

We find

$$z = \delta_1 \quad C_A = C_{A1}$$

Substituting

$$z = \delta_2 \quad C_A = 0$$

Step 7. At the interface between the Epedermis and Dermis layer, i.e., at $z = \delta_1$

$$\frac{C_{A1} - 0}{C_{A1} - 0} = \frac{z}{\delta_2}$$

$$W_{A2} = \frac{D_{A2}}{\delta_2} C_{A1}$$

Substituting

$$W_{A2} = \frac{D_{A2}}{\delta_2} C_{A1}$$

Step 7. At the interface between the Epedermis and Dermis layer, i.e., at $z = \delta_1$

$$W_{A1} = W_{A2} = W_A$$

Equating Equations (E14-1.5) and (E14-1.6)

$$\frac{D_{A1}\left[C_{A0} - C_{A1}\right]}{\delta_1} = \frac{D_{A2}}{\delta_2} C_{A1}$$

Step 7. At the interface between the Epedermis and Dermis layer, i.e., at $z = \delta_1$

$$W_{A1} = W_{A2} = W_A$$

Equating Equations (E14-1.5) and (E14-1.6)

$$\frac{D_{A1}\left[C_{A0} - C_{A1}\right]}{\delta_1} = \frac{D_{A2}}{\delta_2} C_{A1}$$

Solving for C_{A1}

$$C_{A1} = \frac{\dfrac{\dfrac{D_{A1}}{} \dfrac{C_{A0}}{}}{\delta_1}}{\dfrac{D_{A1}}{\delta_1} + \dfrac{D_{A2}}{\delta_2}}$$

Step 7. At the interface between the Epedermis and Dermis layer, i.e., at $z = \delta_1$

$$W_{A1} = W_{A2} = W_A$$

$$W_A = \frac{D_{A2}\, \mathrm{C}_{\mathrm{A1}}}{\delta_2}$$

Substituting for C_{A1} in Equation (E14-1.10)

$$W_A = \frac{C_{A0}}{\dfrac{\delta_2}{D_{A2}} + \dfrac{\delta_1}{D_{A1}}} = \frac{C_{A0}}{R_1 + R_2}$$

$$F_A = A_p W_A = A_p \frac{C_{A0}}{R_1 + R_2} = A_p \frac{C_{A0}}{R}$$

If we consider there is a resistance to the drug release in the patch, R_P, then the total resistance is

$$R_T = R_p + R_1 + R_2$$

$$F_A = A_p W_A = \frac{A_p C_{A0}}{R_T}$$

If the resistance in the dermis layer is neglected

$$\boxed{F_A = A_p \left[\frac{D_{AB_1}}{\delta_1} \right] C_{Ap}}$$

$$\begin{bmatrix}\text{Molar}\\ \text{rate in}\end{bmatrix} - \begin{bmatrix}\text{Molar}\\ \text{rate out}\end{bmatrix} + \begin{bmatrix}\text{Molar rate of}\\ \text{generation}\end{bmatrix} = \begin{bmatrix}\text{Molar rate of}\\ \text{accumulation}\end{bmatrix}$$

$$F_{Az}\big|_{z} - F_{Az}\big|_{z+\Delta z} + r''_A a_c (A_c \Delta z) = 0 \qquad (14\text{-}51)$$

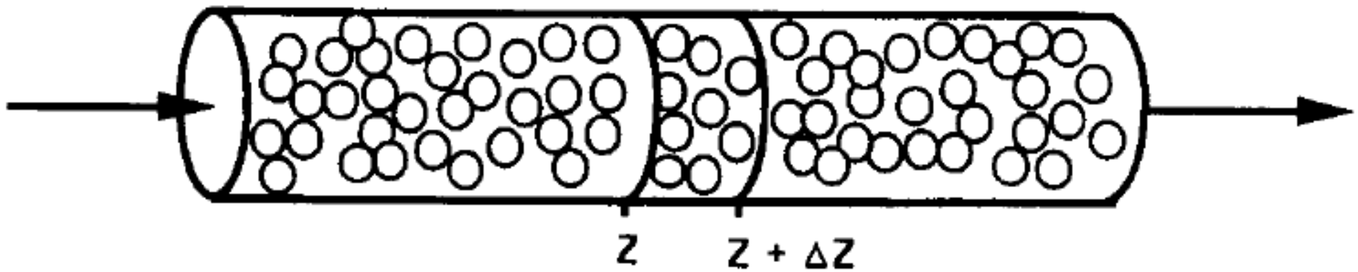


Figure 14-5 Packed-bed reactor.

$$-\frac{1}{A_c}\left(\frac{dF_{Az}}{dz}\right) + r''_A a_c = 0$$

$$-\frac{1}{A_c}\left(\frac{dF_{Az}}{dz}\right)+r_A''a_c=0$$

Neglect

$$F_{Az}=A_cW_{Az}=\left(J_{Az}+B_{Az}\right)A_c$$

$$=B_{Az}A_c=UC_AA_c$$

$$-\frac{UdC_A}{dz}+r_A''a_c=0_c$$

$$\boxed{-U\frac{dC_{\mathrm{A}}}{dz}+r_{\mathrm{A}}''a_c=0}$$

$$-r_A''=W_{Ar}$$

$$-U\frac{dC_A}{dz}-k_c a_c\left(C_A-C_{As}\right)=0$$

$$-U\frac{dC_A}{dz}-k_c a_c C_A=0$$

$$\frac{C_A}{C_{A0}} = \exp-\left(\frac{k_c a_c}{U}\right)z$$

$$-r_A'' = k_c C_A = k_c C_{A0} \exp-\left(\frac{k_c a_c}{U}\right)z$$

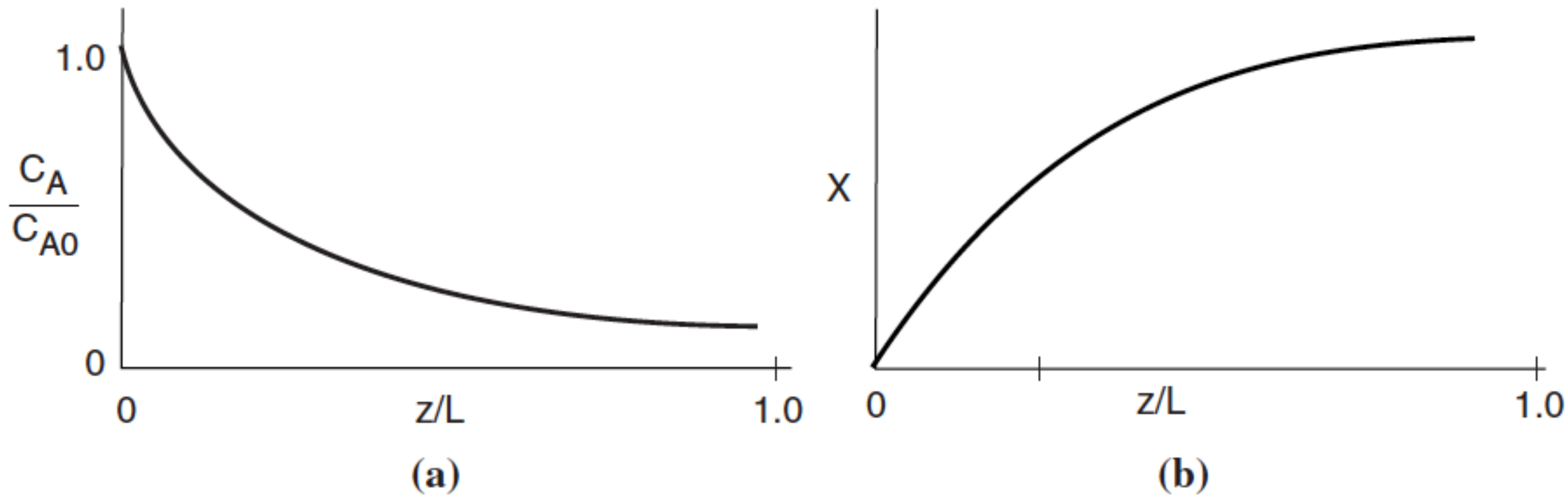


Figure 14-7 Axial concentration (a) and conversion (b) profiles in a packed bed.

$$X = \frac{C_{A0} - C_{AL}}{C_{A0}} = \frac{\mathit{Moles}\ \text{A Reacted}}{\text{Mole A Fed}}$$

$$\ln\frac{1}{1-X} = \frac{k_c a_c}{U} L$$

Robert the Worrier

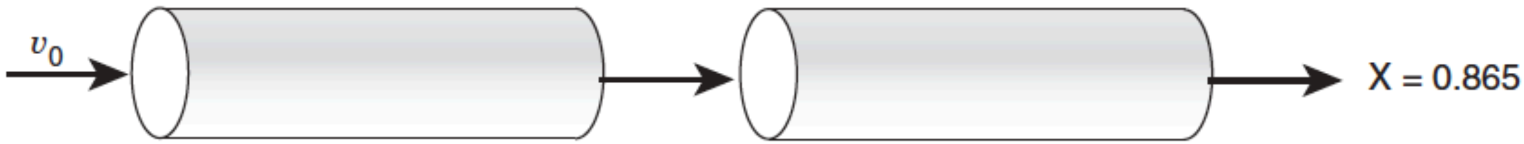


Figure E14-4.1 Series arrangement

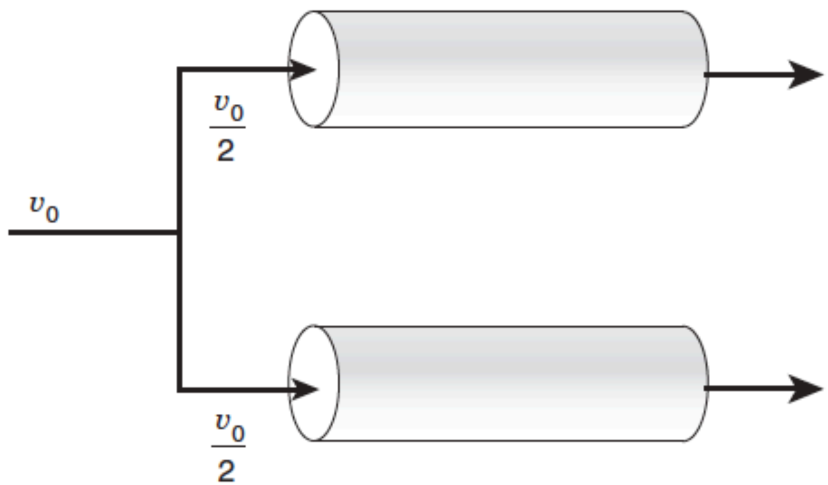


Figure E14-4.2 Parallel arrangement.

$$\ln\frac{1}{1-X} = \frac{k_c a_c}{U} L$$

$$\frac{\ln\frac{1}{1-X_2}}{\ln\frac{1}{1-X_1}} = \frac{k_{c2}}{k_{c1}}\left(\frac{L_2}{L_1}\right)\frac{U_1}{U_2}$$

$$X_1 = 0.865$$

$$X_2 = ?$$

$$\frac{\ln \frac{1}{1-X_2}}{\ln \frac{1}{1-X_1}} = \frac{k_{c2}}{k_{c1}} \left(\frac{L_2}{L_1} \right) \frac{U_1}{U_2}$$

$$X_1 = 0.865$$

$$L_2 = \frac{1}{2} L_1$$

$$U_2 = \frac{1}{2} U_1$$

$$X_1 = 0.865$$

$$X_2 = ?$$

$$k_c \alpha U^{1/2}$$

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{U_2}{U_1}\right)^{1/2}$$

$$\frac{U_1}{U_2}\left(\frac{k_{c2}}{k_{c1}}\right) = \left(\frac{U_1}{U_2}\right)^{1/2}$$

$$\ln\frac{1}{1-X_2} = \left(\ln\frac{1}{1-X_1}\right)\frac{L_2}{L_1}\left(\frac{U_1}{U_2}\right)^{1/2}$$

$$=$$

$$\ln\frac{1}{1-X_2} = \left(\ln\frac{1}{1-X_1}\right)\frac{L_2}{L_1}\left(\frac{U_1}{U_2}\right)^{1/2}$$

$$= \left(\ln\frac{1}{1-0.865}\right)\left[\frac{\frac{1}{2}L_1}{L_1}\left(\frac{U_1}{\frac{1}{2}U_1}\right)^{1/2}\right]$$

$$= 2.00\left(\frac{1}{2}\right)\sqrt{2} = 1.414$$

$$X_2 = 0.76$$

One will often find the flux to or from the surface as written in terms of an *effective* transport coefficient k_{eff}:

$$W_A = -r''_{As} = k_{\text{eff}} C_A$$

where

$$k_{\text{eff}} = \frac{k_c k_r}{k_c + k_r}$$

$$\text{Sh} = \frac{k_c d_p}{D_{AB}} = 2 + 0.6\text{Re}^{1/2}\text{Sc}^{1/3}$$

$$k_c = 0.6\left(\frac{D_{AB}}{d_p}\right)\text{Re}^{1/2}\text{Sc}^{1/3}$$

$$= 0.6\left(\frac{D_{AB}}{d_p}\right)\left(\frac{Ud_p}{\nu}\right)^{1/2}\left(\frac{\nu}{D_{AB}}\right)^{1/3}$$

$$k_c = 0.6 \times \frac{D_{AB}^{2/3}}{\nu^{1/6}} \times \frac{U^{1/2}}{d_p^{1/2}}$$

$$k_c = 0.6 \times (\text{Term 1}) \times (\text{Term 2})$$

$$(U_2/U_1)^{0.5} = 2^{0.5} = 1.41 \text{ or } 41\%$$

$$k_r \ll k_c$$

$$W_A = -r''_{As} = \frac{k_r C_A}{1 + k_r/k_c} \approx k_r C_A$$

$$F_A\Big|_z - F_A\Big|_{z+\Delta z} + r_A A_c \Delta z = 0$$

$$\frac{dF_A}{dz} + r_A A_c = 0$$

$$F_{Az} = A_c W_{Az}$$

$$W_{Az} = -D_{AB}\frac{dC_A}{dz} + C_A U_z$$

$$F_{Az} = W_{Az} A_c = \left[-D_{AB}\frac{dC_A}{dz} + C_A U_z\right] A_c$$

$$\boxed{D_{AB}\frac{d^2 C_A}{dz^2} - U_z \frac{dC_A}{dz} + r_A = 0}$$

Step 4. Next substitute for W_{Az} and divide by D_{A1} to obtain

$$\frac{d^2 C_A}{dz^2} = 0$$

Integrating twice

$$C_A = K_1 z + K_2$$

using the boundary conditions we can eliminate the constants K_1 and K_2 to obtain the concentration profile

$$\frac{C_{A0} - C_A}{C_{A0} - C_A} = \frac{z}{\delta_1}$$

Step 5. Substituting *C*A we obtain the flux in the Epidermis layer

$$W_{A1} = -D_{A1} \frac{dC_A}{dz} = \frac{D_{A1}}{\delta} \left[C_{A0} - C_{A1} \right]$$

TABLE 14-1. TYPES OF BOUNDARY CONDITIONS

1. Specify a concentration at a boundary (e.g., **z** = 0, $C_A = C_{A0}$). For an instantaneous reaction at a boundary, the concentration of the reactants at the boundary is taken to be zero (e.g., $C_{As} = 0$). See Chapter 18 for the more exact and complicated Danckwerts' boundary conditions at **z** = 0 and **z** = L.
2. Specify a flux at a boundary.
   a. No mass transfer to a boundary,

$$W_A = 0 \tag{14-18}$$

   For example, at the wall of a nonreacting pipe. Species A cannot diffuse into the pipe so $W_A = 0$ and then

$$\frac{dC_A}{dr} = 0 \qquad \text{at } r = R \tag{14-19}$$

   That is, because the diffusivity is finite, the only way the flux can be zero is if the concentration gradient is zero.

   b. Set the molar flux to the surface equal to the rate of reaction on the surface,

$$W_A(\text{surface}) = -r''_A(\text{surface}) \tag{14-20}$$

   c. Set the molar flux to the boundary equal to convective transport across a boundary layer,

$$W_A(\text{boundary}) = k_c(C_{Ab} - C_{As}) \tag{14-21}$$

   where k_c is the mass transfer coefficient and C_{As} and C_{Ab} are the surface and bulk concentrations, respectively.
3. Planes of symmetry. When the concentration profile is symmetrical about a plane, the concentration gradient is zero in that plane of symmetry. For example, in the case of radial diffusion in a pipe, at the center of the pipe

$$\frac{dC_A}{dr} = 0 \qquad \text{at } r = 0 \tag{14-22}$$