10.37 Chemical and Biological Reaction Engineering, Spring 2007
Prof. William H. Green
Lecture 17: Mass Transfer Resistances

This lecture covers: External diffusion effects, non-porous packed beds and monoliths, and immobilized cells

Table 1. Homogeneous vs. Heterogeneous Catalysis

Homogeneous	vs.	Heterogeneous Catalysis
acids,bases		immobilized enzymes
radicals		metals
organometallics		solid acids, bases
enzymes		metal oxides, zeolites, clays, silica
better mixing, uniformity		multiphase systems
transport limitations		reuse catalyst easily
		product purity

1. New rate law on surface
2. Model the transport and mixing

$$C_{i(x,y,z)}^{fluid} = \frac{N_i}{Volume}$$

$$\theta_{j(x,y)}^{surface} = \frac{N_j \text{ on surface}}{N \text{ sites on surface}}$$

$$\sum \theta_j + \theta_{vacancy} = 1$$

$$r_i^{fluid} = \sum_{n=1}^{N_{rxn}\,fluid} \underbrace{\nu_{i,n} r_n(\underline{C})}_{\frac{mol}{s \cdot vol}} + \left(\frac{A}{V}\right) \sum_{m=1}^{N_{rxn}\,suface} \underbrace{\nu_{i,m} r_m''(\underline{C},\underline{\theta})}_{\frac{mol}{s \cdot area}}$$

QSSA for surface species: $r_j'' = \sum \nu_{j,m} r_m''(\underline{C},\underline{\theta}) \approx 0$

$\theta_{QSSA} = f(\underline{C}) \leftarrow$ At surface

$$\frac{d\theta_j}{dt} = \cancel{(\text{flows})}^0 + r_j''\left(\frac{area}{N_{sites}}\right) N_{avagadro}$$

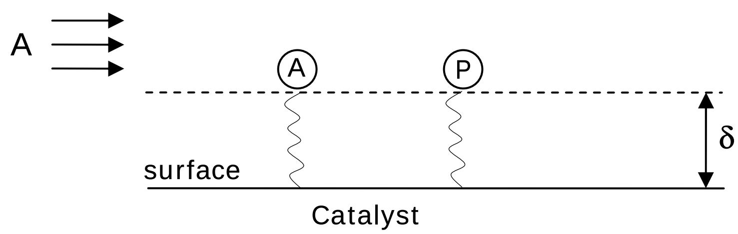

Figure 1. Schematic of boundary layer at catalyst surface for a turbulent, well mixed system where C_A is a function of x.

Flux of A to the surface: $\underline{W_A} = -C_{tot} D \underline{\nabla} y_A + y_A \left(\underline{W_A} + \underline{W_P} \right)$

where y_A is the mole fraction of A

$C_{tot} = const$

$$\underline{W_A} = \overbrace{-D\underline{\nabla}C_A}^{diffusion} + \overbrace{C_A\underline{u}}^{convection}$$

$F_A^{net} = -\oint \underline{W_A} \cdot dn$ ←surface integral

$$F_A = \iiint dxdydz \vec{\nabla} \cdot \underline{W_A}$$

$$\frac{dN_A}{dt} = \iiint dxdydz \left(\pm \vec{\nabla} \underline{W_A} + r_A(x,y,z) \right)$$

$$\boxed{\frac{dC_A}{dt} = \vec{\nabla} \cdot \underline{W_A} + r_A}$$

*See Fogler 11-21

Continuity equation: $\boxed{\frac{dC_A}{dt} = D\nabla^2 C_A - \underline{u} \cdot \underline{\nabla} C_A + r_A(\underline{C})}$

Boundary Condition:

$W_A^{\text{into wall}} = -r_A^{"}$ at surface

1. Steady state
2. Gradients $\frac{dC_A}{dx}$ and $\frac{dC_A}{dy}$ are negligible
3. Velocity u towards the wall = 0
4. No reaction in the fluid

$$0 = D \frac{\partial^2 C_A}{\partial z^2}$$

$$W_A = -r_A^{"}$$

$$-D \left. \frac{dC_A}{dz} \right|_{z=0} = -r_A^{"} \left(\underline{C}_{z=0} \right)$$ (z=0 at the surface)

$$C_A(z) = C_A(z=0) + \left[\frac{C_A^{main} - C_A(z=0)}{\delta} z \right]$$

$$D \left. \frac{dC_A}{dz} \right|_{z=0} = D \frac{C_A^{main} - C_A(z=0)}{\delta} = -r_A^{"} \left(C_{A,z=0} \right)$$

Slow chemistry limit: $C_A(z=0) \approx C_A^{main}$

$r_A^{"} \approx r_A^{"} \left(C_A^{main} \right)$

Fast chemistry limit: $C_A(z=0) \approx 0$

$\frac{D}{\delta} C_A^{main} \approx r_A^{"}$

$\frac{D}{\delta} = k_c$ "mass transfer coefficient"

$Sh = \frac{k_c d_p}{D}$ ←Sherwood number (dimensionless)

For spherical, catalyst particle with diameter d_p:

$Sh = 2 + 0.6\,\mathrm{Re}^{1/2}\,\mathrm{Sc}^{1/3}$

$Sc = \frac{\upsilon}{D}$ $\mathrm{Re} = \frac{u d_p}{\upsilon}$ $\upsilon = \frac{\mu}{\rho}$