LECTURE NINE: Mass Transfer Resistance

This lecture covers: External diffusion effects, non-porous packed beds and monoliths, and immobilized cells AND Gas-liquid reactions in multiphase systems

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

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

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

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

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

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

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

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

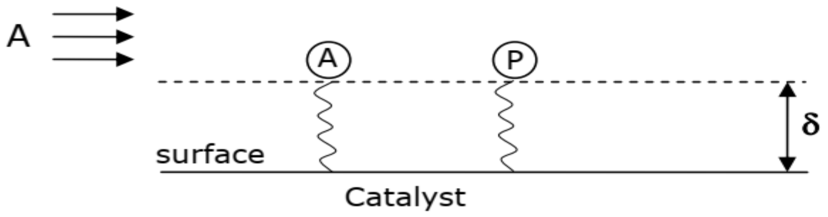

Figure 1. Schematic of boundary layer at catalyst surface for a turbulent, well mixed system where C_A is a function of x.

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

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

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

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

*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 $\underline{u}$ 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:

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

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

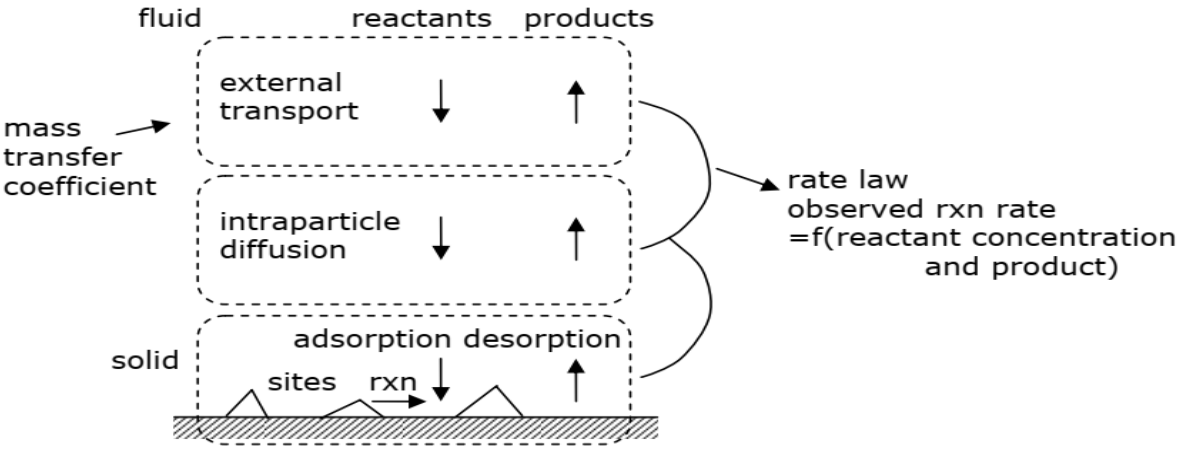

Figure 1. Schematic of surface reaction kinetics.

Analogies:

noncovalent biomolecular interactions	↔	Langmuir adsorption isotherms
Michaelis-Menton enzyme kinetics (Briggs-Haldane, Henri)	↔	Langmuir-Hinshelwood Haugen-Watson kinetics

Logic:

- list rxns
- hypothesize rate-limiting step
- derive rate law
- check for consistency w/ rate data

Single site, unimolecular decomposition

$$A \underset{k_{-A}}{\overset{k_A}{\rightleftarrows}} AS \underset{k_{-S}}{\overset{k_S}{\rightleftarrows}} BS + C \underset{k_{-D}}{\overset{k_D}{\rightleftarrows}} S + B + C$$

product

$S \equiv$ site on catalyst

$r_{A_d} \equiv$ rate of A adsorption

$r_s \equiv$ rate of rxn on surface

$r_D \equiv$ rate of desorption

$$r_{A_d} = k_A P_A C_S - k_{-A} C_{AS}$$

* units partial pressure$_A$ reactive sites $\frac{1}{\text{time}}$ $\frac{\text{sites}}{\text{mass catalyst}}$

often C_S is given as fractional occupancy θ

$$K_A = \frac{k_A}{k_{-A}}$$

$$r_{A_d} = k_A \left(P_A C_S - \frac{C_{AS}}{K_A} \right)$$

Similarly, $r_S = k_S \left(C_{AS} - \frac{P_C C_{BS}}{K_S} \right)$

$$r_D = k_D \left(C_{BS} - \frac{P_B C_S}{K_D} \right) \rightarrow K_B = \frac{1}{K_D} \rightarrow \qquad r_D = k_D \left(C_{BS} - K_B P_B C_S \right)$$

At steady-state, $r_{A_d} = r_S = r_D$ (or else you would accumulate molecules)

For a rate-limiting step i, $\frac{r_i}{k_i} \gg \frac{r_j}{k_j}, \frac{r_l}{k_l}$

Hypothesize, that adsorption is rate-limiting: $\frac{r_A}{k_A} \gg \frac{r_S}{k_S}, \frac{r_D}{k_D} \approx 0$

$$\frac{r_S}{k_S} \approx 0 \Rightarrow C_{AS} - \frac{P_C C_{BS}}{K_S} \Rightarrow C_{AS} \approx \frac{C_{BS} P_C}{K_S}$$

$$\frac{r_D}{k_D} \approx 0 \Rightarrow C_{BS} - K_B P_B C_S \Rightarrow C_{BS} \approx K_B P_B C_S$$

$$\rightarrow \quad C_{AS} \approx \frac{K_B P_B C_S P_C}{K_S}$$

$$\begin{aligned} r_{A_d} &= k_A\left(P_A C_S - \frac{C_{AS}}{K_A}\right) \\ &= k_A\left(P_A C_S - \frac{K_B}{K_S K_A} P_B P_C C_S\right) \\ &= k_A C_S\left(P_A - \frac{K_B}{K_S K_A} P_B P_C\right) \end{aligned}$$

Material balance on C_S (available sites): $C_{S_0} = C_S + C_{AS} + C_{BS}$

$$\begin{aligned} C_{S_0} &= C_S + \frac{K_B}{K_S} P_B P_C C_S + K_B P_B C_S \\ &= C_S\left(1 + \frac{K_B}{K_S} P_B P_C + K_B P_B\right) \end{aligned}$$

Adsorption as rate-limiting step:

$$\boxed{-r_A = \frac{k_A C_{S_0}\left(P_A - \overbrace{\frac{K_B}{K_S K_A} P_B P_C}^{\text{eq. driving force}}\right)}{1 + \frac{K_B}{K_S} P_B P_C + K_B P_B}}$$

equilibrium driving force is 0 at equilibrium!

Surface reaction is rate-limiting:

$$\boxed{-r_A = \frac{k_S C_{S_0} K_A\left(P_A - \frac{P_B P_C}{K_C}\right)}{1 + P_B K_B + P_A K_A}}$$

Desorption is rate-limiting:

$$\boxed{-r_A = \frac{k_D C_{S_0} K_S K_A\left(P_A - \frac{P_B P_C}{K_C}\right)}{P_C + P_A K_A K_S + K_A P_C P_A}}$$

Initial rate expirements, approximate $-r_A = f(P_A)$, $P_B \approx P_C \approx 0$, $K_C = \frac{K_A K_S}{K_B}$.

Adsorption limit:

$$-r_A = k_A C_{S_0} P_{Ao}$$

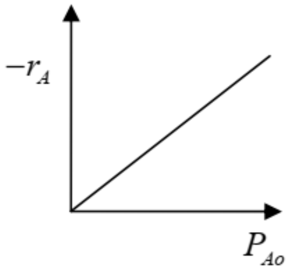

Figure 2. Reaction rate vs. initial partial pressure of A for the absorption limiting case.

Surface reaction limit:

$$-r_A = \frac{k_S C_{S_0} K_A P_{Ao}}{1 + K_A P_{Ao}}$$

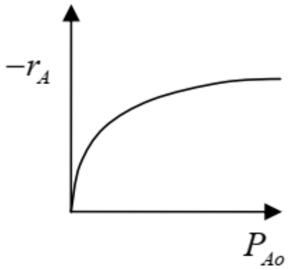

Figure 3. Reaction rate vs. initial partial pressure of A for the surface reaction limiting case.

Desorption limit:

$$-r_A = k_D C_{S_0}$$

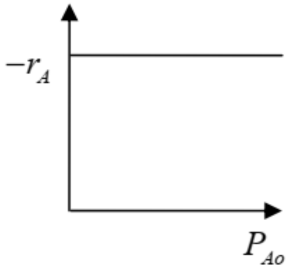

Figure 4. Reaction rate vs. initial partial pressure of A for the desorption limiting case.