10.37 Chemical and Biological Reaction Engineering, Spring 2007
Prof. K. Dane Wittrup

Lecture 18: External Mass-transfer Resistance

This lecture covers: Gas-liquid reactions in multiphase systems

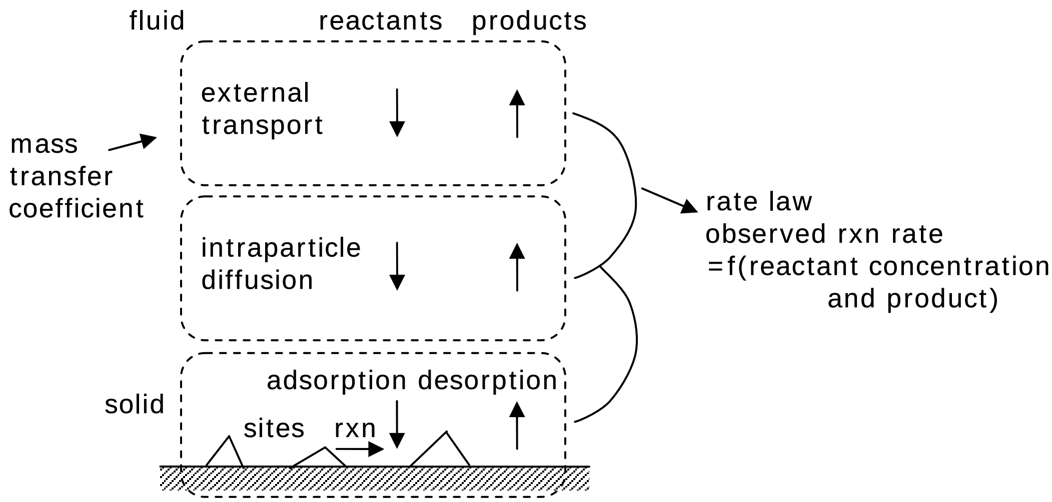

Figure 1. Schematic of surface reaction kinetics.

Analogies:

noncovalent biomolecular interactions	$\leftrightarrow$	Langmuir adsorption isotherms
Michaelis-Menton enzyme kinetics (Briggs-Haldane, Henri)	$\leftrightarrow$	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 $\dfrac{1}{\text{time}}$ $\dfrac{\text{sites}}{\text{mass catalyst}}$

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

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

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

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

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

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

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

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

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

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:

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

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:

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

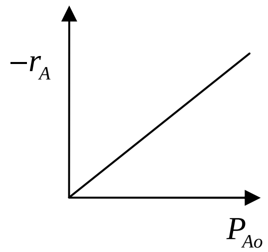

Figure 2. Reaction rate vs. initial partial pressure of A for the absorption limiting case.

Surface reaction limit:

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

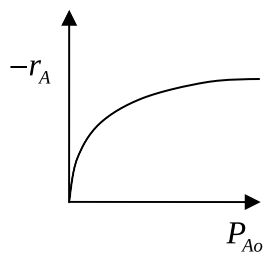

Figure 3. Reaction rate vs. initial partial pressure of A for the surface reaction limiting case.

Desorption limit:

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

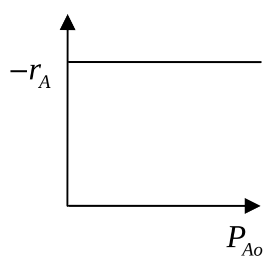

Figure 4. Reaction rate vs. initial partial pressure of A for the desorption limiting case.