10.37 Chemical and Biological Reaction Engineering, Spring 2007
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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 ↔ Langmuir adsorption isotherms
- Michaelis-Menton ↔ Langmuir-Hinshelwood Haugen-Watson
- enzyme kinetics (Briggs-Haldane, Henri) kinetics

Logic:

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

Single site, unimolecular decomposition

$$A \xrightleftharpoons[k_{-4}]{k_4} AS \xrightleftharpoons[k_{-5}]{k_5} BS + C \xrightleftharpoons[k_{-6}]{k_6} S + B + C$$

$S \equiv$ site on catalyst
\[ r_{A_d} \equiv \text{rate of A adsorption} \]
\[ r_s \equiv \text{rate of rxn on surface} \]
\[ r_D \equiv \text{rate of desorption} \]

\[ r_{A_d} = k_A P_s C_s - k_{-A} C_{AS} \]

* units | partial pressure_{A} | reactive sites | time | sites | mass catalyst

often \( C_s \) is given as fractional occupancy \( \theta \)

\[ K_A = \frac{k_A}{k_{-A}} \]
\[ r_{A_d} = k_A \left( P_s C_s - \frac{C_{AS}}{K_A} \right) \]

Similarly, \( r_s = k_S \left( \frac{P_s C_{BS}}{K_S} \right) \)
\[ r_D = k_D \left( C_{BS} - \frac{P_s C_s}{K_D} \right) \rightarrow K_B = \frac{1}{K_D} \rightarrow \]
\[ r_D = k_D \left( C_{BS} - K_B P_s C_s \right) \]

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: \[ \frac{r_s}{k_s} \gg \frac{r_s}{k_D} \approx 0 \]

\[ \frac{r_s}{k_s} \approx 0 \Rightarrow C_{AS} - \frac{P_s C_{BS}}{K_S} \Rightarrow C_{AS} \approx \frac{C_{BS} P_s}{K_S} \]
\[ \frac{r_D}{k_D} \approx 0 \Rightarrow C_{BS} - K_B P_s C_s \Rightarrow C_{BS} \approx K_B P_s C_s \]
\[ \Rightarrow C_{AS} \approx \frac{K_B P_s C_s P_C}{K_S} \]
\[ r_{A_S} = k_A \left( P_A C_S - \frac{C_{AS}}{K_A} \right) \]
\[ = k_A \left( P_A C_S - \frac{K_B}{K_S K_A} P_B P_C C_S \right) \]
\[ = k_A C_S \left( P_A - \frac{K_B}{K_S K_A} P_B P_C \right) \]

Material balance on \( C_S \) (available sites):
\[ C_{S_0} = C_S + \frac{K_B}{K_S} P_B P_C C_S + K_B P_B C_S \]
\[ = C_S \left( 1 + \frac{K_B}{K_S} P_B P_C + K_B P_B \right) \]

Adsorption as rate-limiting step:
\[ -r_A = \frac{k_A C_S}{1 + \frac{K_B}{K_S} P_B P_C + K_B P_B} \]

Surface reaction is rate-limiting:
\[ -r_A = \frac{k_S C_S K_A}{1 + P_B K_B + P_A K_A} \]

Desorption is rate-limiting:
\[ -r_A = \frac{k_D C_S K_S K_A}{P_C + P_A K_A K_S + K_A P_C P_A} \]

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

Adsorption limit:
\[ -r_A = k_A C_{S_0} P_{do} \]
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.