10.37 Chemical and Biological Reaction Engineering, Spring 2007 Prof. William H. Green

Lecture 16: Catalysis

This lecture covers: Inorganic and enzyme catalysis and their properties; kinetics of heterogeneous catalytic reactions; adsorption isotherms, derivation of rate laws; and Langumuir-Hinshelwood kinetics

What initiates the reaction? $A + B \rightarrow$ starts upon mixing

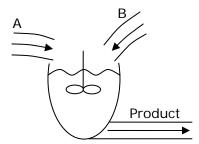


Figure 1. Bi-molecular reaction in a CSTR.

Temperature drastically increases reaction rate.

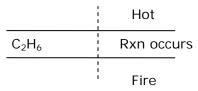


Figure 2. Schematic of tube reactor.

Catalyst dramatically increases reaction rate.

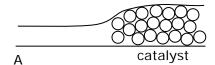


Figure 3. Schematic of packed bed reactor.

Catalyst: Accelerates rate of reaction but is not consumed

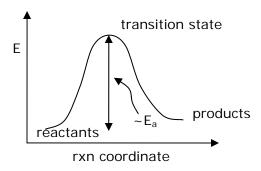


Figure 4. Reaction diagram.

rate constant:

$$k = \frac{k_B T}{h} \exp \left[-\frac{(G_{ts} - G_{reactants})}{RT} \right]$$
$$G = H - TS$$

$$e^{-G/RT} = e^{-H/RT}e^{S/R}$$

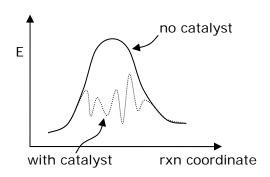


Figure 5. Reaction diagram with and without catalyst.

The reaction forms many intermediates. A catalyst lowers the energy of these intermediates.

Acid/Base catalysis

$$\begin{array}{c} ROR + H_2O \rightarrow 2ROH \\ ROR + H \overset{\oplus}{\underset{k_{-1}}{\rightleftharpoons}} ROR \\ \stackrel{k_1}{\underset{k_{-1}}{\rightleftharpoons}} ROR \\ ROR \overset{k_2}{\underset{\oplus}{\rightarrow}} ROH + R^{\oplus} \\ R^{\oplus} + H_2O \overset{k_3}{\underset{\rightarrow}{\rightarrow}} ROH + H^{\oplus} \end{array}$$

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QSSA
$$ROR_{\oplus}^H$$
, R^{\oplus}

$$O \approx \frac{d \begin{bmatrix} ROR_{\oplus}^H \\ ROR_{\oplus}^T \end{bmatrix}}{dt} = k_1 \begin{bmatrix} H^+ \end{bmatrix} \begin{bmatrix} ROR \end{bmatrix} - (k_{-1} + k_2) \begin{bmatrix} ROR \\ ROR_{\oplus}^T \end{bmatrix}$$

$$\begin{bmatrix} ROR_{\oplus}^H \\ ROR_{\oplus}^T \end{bmatrix}_{QSSA} = \frac{k_1}{k_{-1} + k_2} \begin{bmatrix} H^+ \\ ROR \end{bmatrix} \begin{bmatrix} ROR \end{bmatrix}$$

$$\frac{d \begin{bmatrix} ROH \\ ROH \end{bmatrix}}{dt} = 2k_2 \begin{bmatrix} ROR_{\oplus}^H \\ ROR_{\oplus}^T \end{bmatrix}_{QSSA}$$

$$\frac{d \begin{bmatrix} ROH \\ ROH \end{bmatrix}}{dt} \approx \frac{2k_1k_2}{k_{-1} + k_2} \begin{bmatrix} H^+ \\ ROR \end{bmatrix} \begin{bmatrix} ROR \end{bmatrix} = r$$

$$r_A \sim \begin{bmatrix} A \end{bmatrix}$$

$$[H^+] + \begin{bmatrix} ROR \\ ROR \end{bmatrix} + \begin{bmatrix} R^+ \\ ROR \end{bmatrix} + \begin{bmatrix} N_{H^+ added} \\ V \end{bmatrix} = \begin{bmatrix} H^+ \end{bmatrix}_{added}$$

$$[H^+] \left(1 + \frac{k_1 \begin{bmatrix} ROR \\ k_1 + k_2 \end{bmatrix} + \frac{k_1k_2 \begin{bmatrix} ROR \\ k_3(k_{-1} + k_2) \begin{bmatrix} H_2O \end{bmatrix}}{H_2O} \right) = \begin{bmatrix} H^+ \end{bmatrix}_{added}$$

$$r = \frac{k_{eff} \begin{bmatrix} ROR \end{bmatrix} \begin{bmatrix} H^+ \end{bmatrix}_{added}}{1 + k \begin{bmatrix} ROR \end{bmatrix}}$$

$$r = \frac{k_{eff} \left[ROR\right] \left[H^{+}\right]_{added}}{1 + k \left[ROR\right]}$$

$$r = \frac{k \left[\text{catalyst}\right] \left[A\right]}{1 + k_{A} \left[A\right] + k_{B} \left[B\right] + \dots}$$
 All the things that the catalyst binds to

Langmuir-Hinshelwood: all reagents bind to catalyst, bound forms react

Eley-Rideal: one reagent binds, 2nd reagent reacts with bound form

$$\frac{dN_A}{dt} = Vr_A \qquad f\left([A], [H^+]\right)$$

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$$\frac{dN_A}{dt} = \left(\text{area of metal}\right) r_A'' \qquad \frac{\text{moles}}{\text{area s}}$$
 where $\theta_A = \frac{N_{A\,bound}}{N_{total\,sites}}$ on surface