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

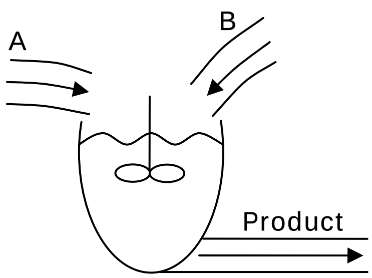

Figure 1. Bi-molecular reaction in a CSTR.

Temperature drastically increases reaction rate.

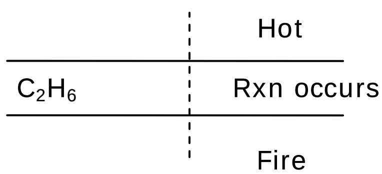

Figure 2. Schematic of tube reactor.

Catalyst dramatically increases reaction rate.

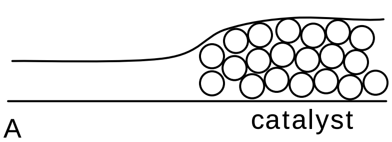

Figure 3. Schematic of packed bed reactor.

Catalyst: Accelerates rate of reaction but is not consumed

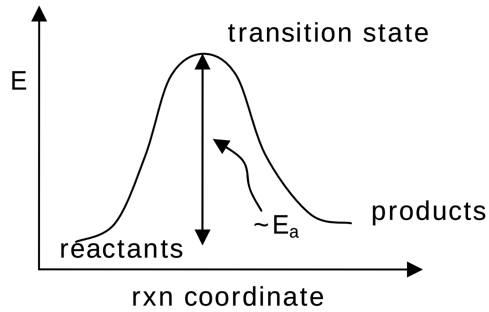

Figure 4. Reaction diagram.

rate constant:

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

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

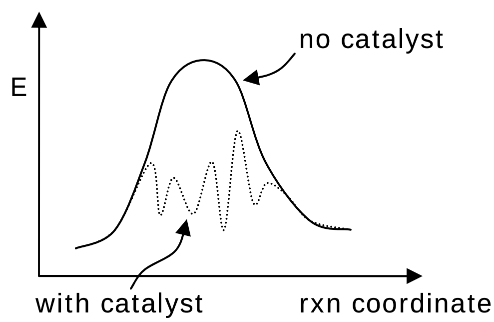

Figure 5. Reaction diagram with and without catalyst.

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

Acid/Base catalysis

$$\boxed{ROR + H_2O \rightarrow 2ROH}$$

$$ROR + H^{\oplus} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\oplus}{\overset{H}{ROR}}$$

$$\underset{\oplus}{\overset{H}{ROR}} \xrightarrow{k_2} ROH + R^{\oplus}$$

$$R^{\oplus} + H_2O \xrightarrow{k_3} ROH + H^{\oplus}$$

QSSA $\quad R\overset{H}{\underset{\oplus}{O}}R$, $R^{\oplus}$

$$O \approx \frac{d\left[R\overset{H}{\underset{\oplus}{O}}R\right]}{dt} = k_1\left[H^+\right]\left[ROR\right] - (k_{-1}+k_2)\left[R\overset{H}{\underset{\oplus}{O}}R\right]$$

$$\left[R\overset{H}{\underset{\oplus}{O}}R\right]_{QSSA} = \frac{k_1}{k_{-1}+k_2}\left[H^+\right]\left[ROR\right]$$

$$\frac{d\left[ROH\right]}{dt} = 2k_2\left[R\overset{H}{\underset{\oplus}{O}}R\right]_{QSSA}$$

$$\frac{d\left[ROH\right]}{dt} \approx \frac{2k_1k_2}{k_{-1}+k_2}\left[H^+\right]\left[ROR\right] = r$$

$r_A \sim \left[A\right]$

$r_A \sim \left[\text{catalyst}\right]$ (where $\sim$ denotes "proportional to")

$$\left[H^+\right] + \left[R\overset{H}{\underset{\oplus}{O}}R\right] + \left[R^+\right] = \frac{N_{H^+\,added}}{V} = \left[H^+\right]_{added}$$

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

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

$$r = \frac{k\left[\text{catalyst}\right]\left[A\right]}{1+k_A\left[A\right]+k_B\left[B\right]+\ldots}$$

All the things that the catalyst binds to

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

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

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

$$\frac{dN_A}{dt} = (\text{area of metal})\, \underbrace{r_A''}_{f(\theta_A)} \leftarrow \frac{\text{moles}}{\text{area s}}$$

where $\theta_A = \dfrac{N_{A\,bound}}{N_{\substack{total\ sites\\ on\ surface}}}$