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CATALYSIS AND CATALYTIC REACTORS

Chapter 10

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Introduction

After this chapter you will be able to

❑ Define a catalyst and its properties

❑ Describe steps in a catalytic reaction

❑ Apply concept of rate limiting step to derive a rate law

❑ Size isothermal reactors for reactions with Langmuir-Hinshelwood kinetics

Catalyst types

☐ Homogeneous catalyst

Propylene + CO + H$_2$ → Isobutylaldehyde (Cobalt catalyst)

❏ Heterogeneous catalyst

Dehydrogenation of cyclohexane to Benzene using Platinum on alumina catalyst

- ▪ Gas – liquid (mass transfer limited)
- ▪ Gas – liquid – solid
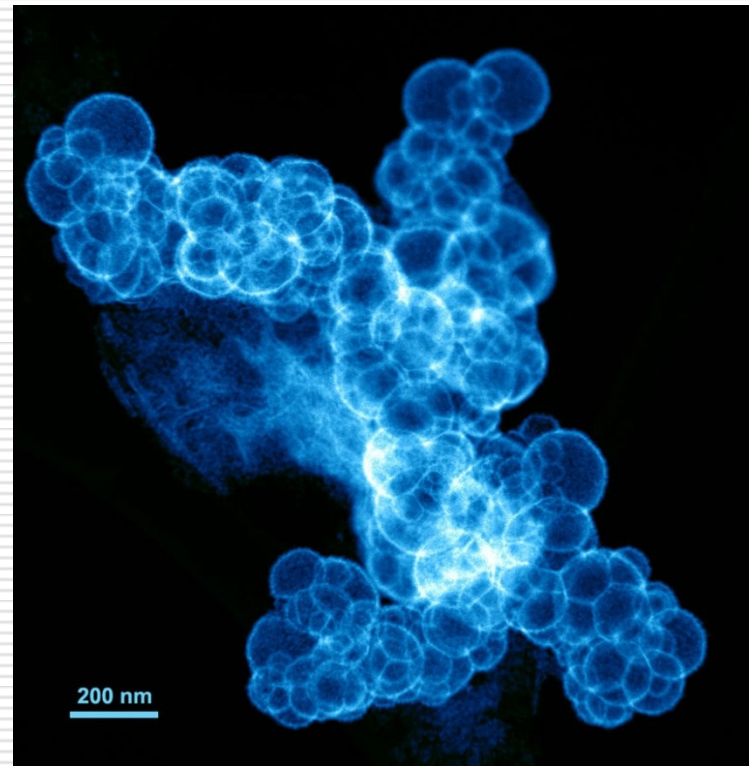
U. S. Football field

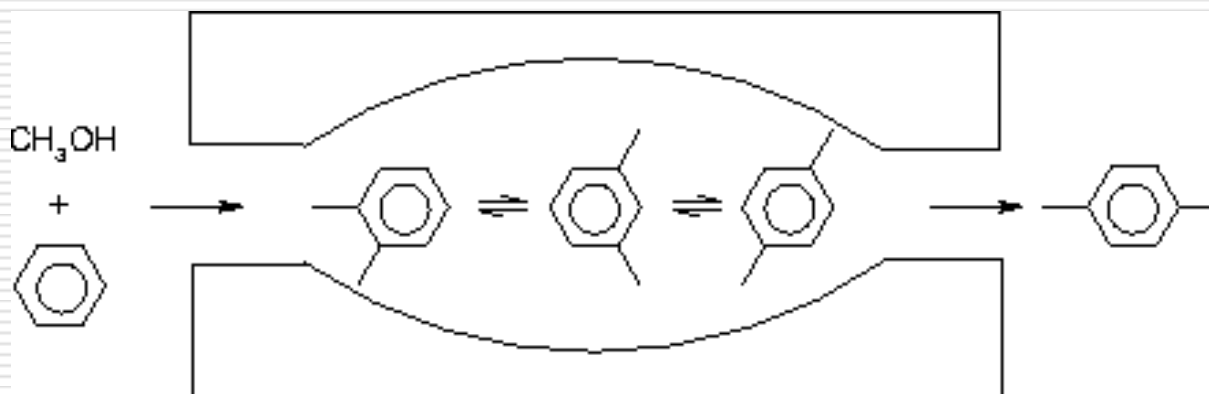10 gms. of catalyst possess more surface area than this football field

Catalyst Terminology
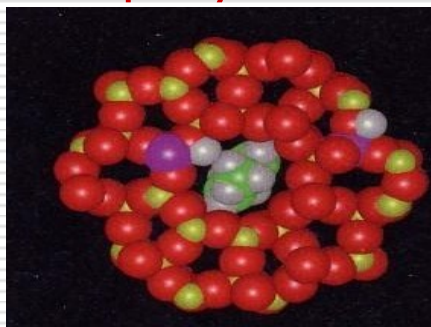
- Porous catalyst

- Molecular sieves

- Monolith catalyst

- Supported / Unsupported catalyst

- Promoters

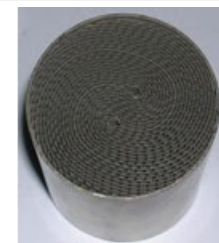- Deactivation

- Active Sites
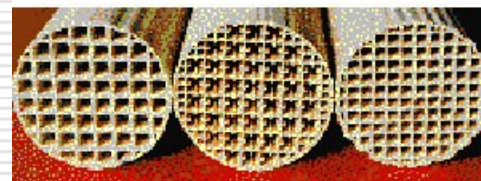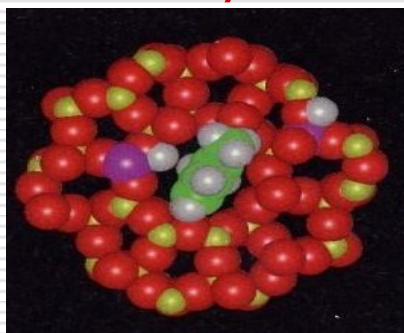

200 nm

The para-Xylene example

p-xylene   m-xylene

Turnover frequency (TOF) / Dispersion

- ☐ Parameter which quantifies the activity of catalyst

- ☐ Number of molecules reacting per active site per second at the conditions of the experiment

- ☐ Fraction of metal atoms deposited that are on the surface (D)

Turnover frequency (TOF) / Dispersion

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

Fischer Tropsch synthesis (0.5% Ru on α - alumina), D = 49%, P = 988 kPa, T = 574 K, f = 0.1607 s^{-1} for methane. What is the rate of formation of methane in mol/s?

Rate in mol/s.g of catalyst
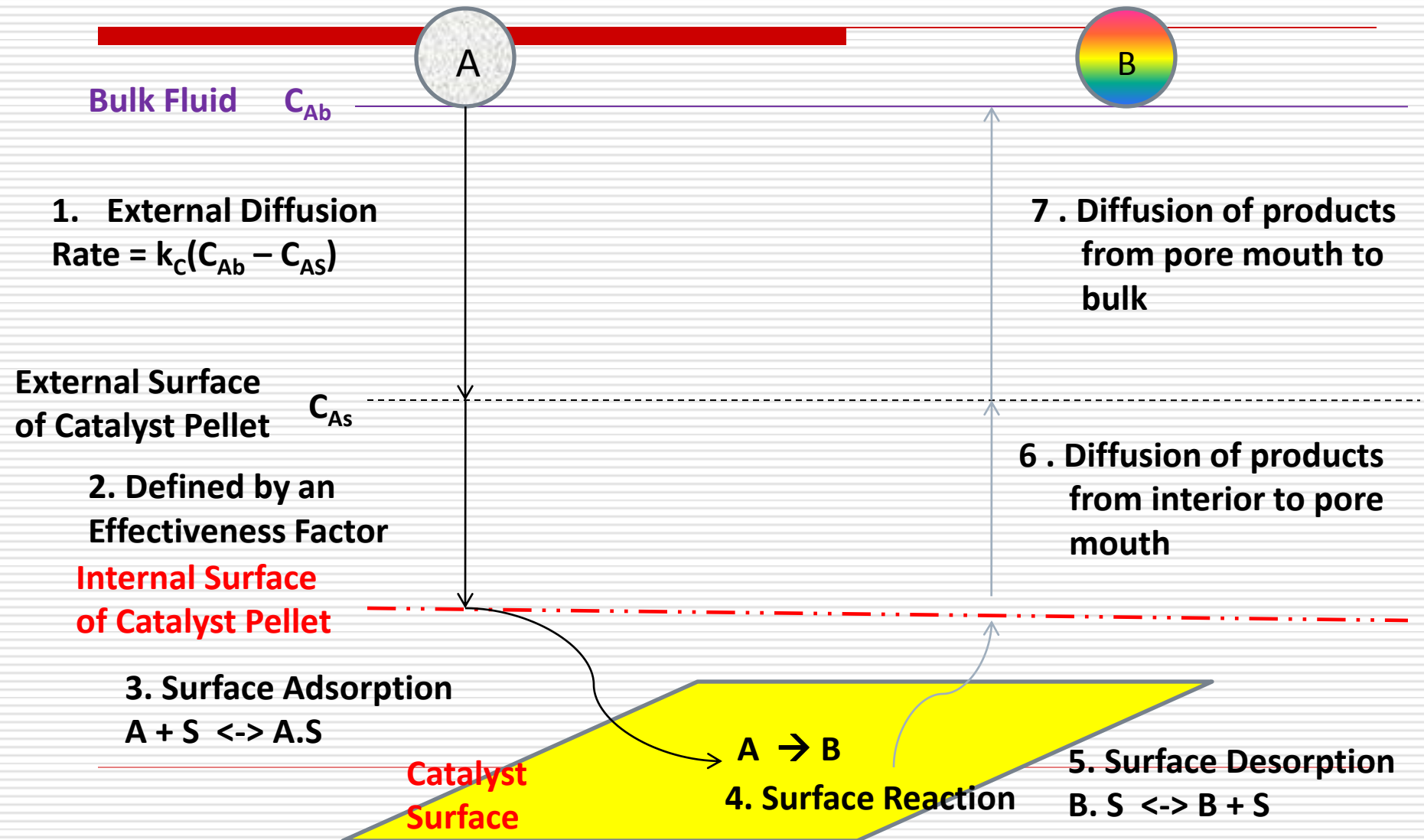
N_{CH4} D (1/MW_{Ru})%Ru/100

Review : Catalytic Reactors – Brief Introduction

Major Steps

Bulk Fluid C_{Ab}

1.   External Diffusion
Rate = $k_C(C_{Ab} - C_{AS})$

7 . Diffusion of products from pore mouth to bulk

External Surface of Catalyst Pellet C_{As}

2. Defined by an Effectiveness Factor

6 . Diffusion of products from interior to pore mouth

Internal Surface of Catalyst Pellet

3. Surface Adsorption
A + S <-> A.S

A → B

Catalyst Surface

4. Surface Reaction

5. Surface Desorption
B. S <-> B + S

A

B

Diffusion from bulk to external surface of catalyst

❑ Rate = $k_c (C_{Ao} - C_{as})$

Where $k_c = D_{AB} / \delta$

turbulent boundary layer

reduced wakes

delayed separation

$-r_A''$

reaction limited

diffusion limited

U1/2
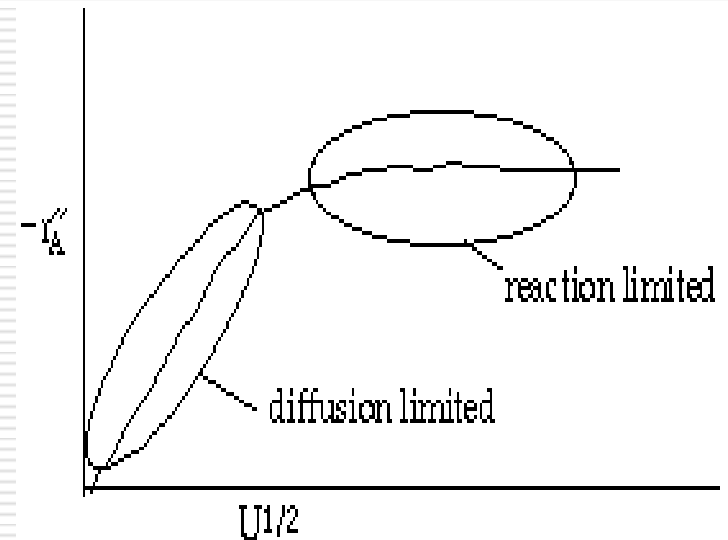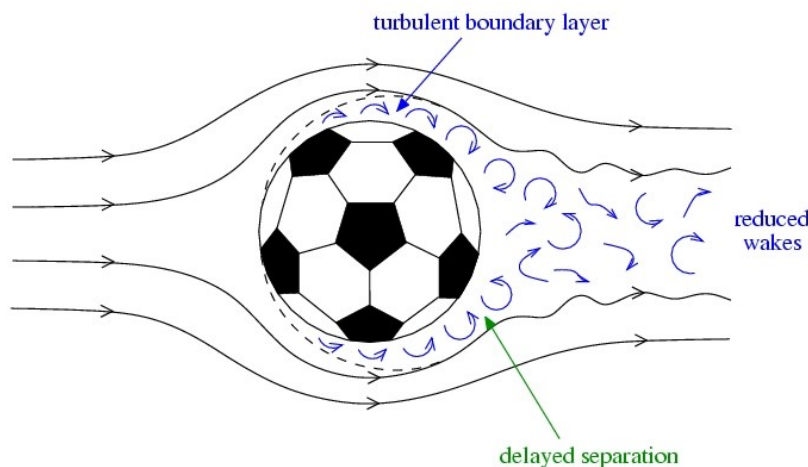
Internal Diffusion
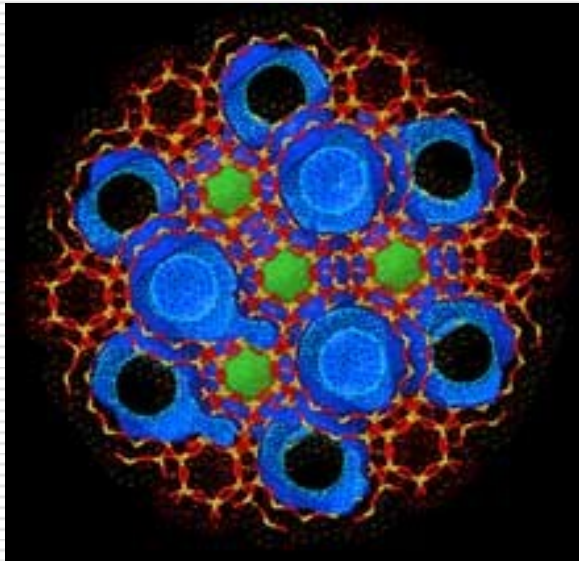
Rate = $k_r C_{as}$

Large particles. More time to diffuse into pellet

Reactant consumes at surface and hence catalyst wastage

As pellet size decreases k_r increases
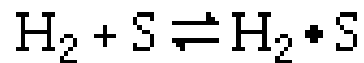
Adsorption

$$H_2 + S \rightleftharpoons H_2 \bullet S$$

$$r_{AD} = 0 = k\left[P_{H_2} C_V - \frac{C_{H_2 \bullet S}}{K_{H_2}} \right]$$ At equilibrium

$$\left. \begin{array}{l} C_{H_2 \bullet S} = K_{H_2}\, P_{H_2}\, C_V \\[1em] C_t = C_V + C_{H_2 \bullet S} \end{array} \right\} \quad C_{H_2 \bullet S} = \frac{K_{H_2} P_{H_2}}{1 + K_{H_2} P_{H_2}} C_t$$

Dissociative Adsorption

$$H_2 + 2S \rightleftharpoons 2H \cdot S$$
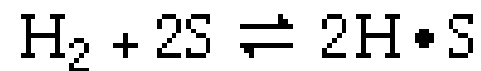
$$r_{AD} = 0 = k\left[P_{H_2}C_V^2 - \frac{C_{H_2 \cdot S}^2}{K_H}\right]$$

At equilibrium

$$C_{H \cdot S} = C_T \frac{\sqrt{P_{H_2}K_H}}{1 + \sqrt{P_{H_2}K_H}}$$

Surface Reaction

Single Site

$$A \bullet S \Leftrightarrow B \bullet S$$

Dual Site

$$A \bullet S + S \Leftrightarrow B \bullet S + S$$

Langmiur-Hinshelwood

A.S + B.S ⇔ C.S + D.S

A.S + B.S' ⇔ C.S' + D.S

Eley-Rideal

A.S + B (g) ⇔ C.S + D(g)
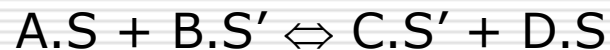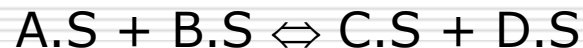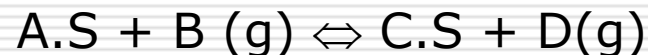
Rate limiting step

☐ The step that needs to be addressed

Assume a sequence of steps (based on some mechanism)

Write rate laws assuming each step to be reversible

Postulate a rate limiting step

Activity of surface uniform

Improvement in Octane number

Catalytic Reaction to Improve the Octane Number of Gasoline from 62 to 90

$$\text{n-pentane} \underset{\text{Pt}}{\overset{-H_2}{\rightleftharpoons}} \text{n-pentene} \underset{Al_2O_3}{\rightleftharpoons} \text{i-pentene} \underset{\text{Pt}}{\overset{+H_2}{\rightleftharpoons}} \text{i-pentane}$$

$$\text{n-pentene} \underset{Al_2O_3}{\rightleftharpoons} \text{i-pentene}$$

$$N \rightleftharpoons I$$
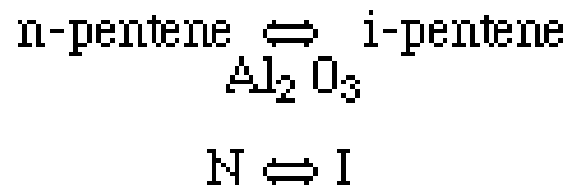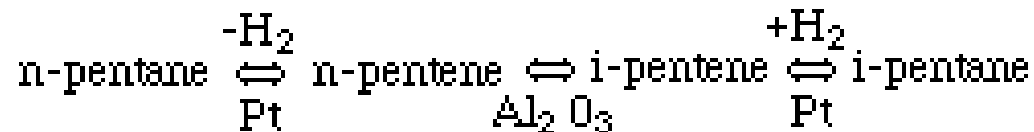
Improvement in Octane number

A $\qquad N + S \Longleftrightarrow N \bullet S \qquad r_{AD} = k_A \left[P_N C_v - \dfrac{C_{N \bullet S}}{K_N} \right]$

SR $\qquad N \bullet S \Longleftrightarrow I \bullet S \qquad r_S = k_S \left[C_{N \bullet S} - \dfrac{C_{I \bullet S}}{K_S} \right]$

D $\qquad I \bullet S \Longleftrightarrow I + S \qquad r_D = k_D \left[C_{I \bullet S} - \dfrac{P_I C_v}{K_{DI}} \right] = k_D \left[C_{I \bullet S} - K_I P_I C_v \right]$

Improvement in Octane number

Assume surface reaction is rate limiting

$$-r_s = k_s\left[C_{NS} - \frac{C_{IS}}{K_s}\right]$$

$$\frac{r_{AD}}{k_A} \cong 0, \quad \therefore C_{N \cdot S} = K_N P_N C_V$$

$$-r_N = k_s\left[K_N P_N - K_I P_I\right]C_V = k_s K_N\left[P_N - \frac{P_I}{K_P}\right]C_V$$

$$\text{where } K_P = \frac{K_S K_N}{K_I}$$

Improvement in Octane number

Site Balance $C_T = C_v + C_{N \cdot S} + C_{I \cdot S}$

Substituting for C_{N-S}, C_{I-S}, and C_V into $C_T = C_V (1 + K_N P_N + K_I P_I)$

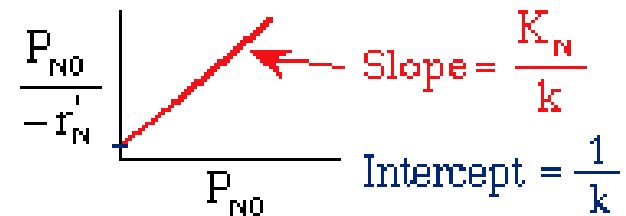$$-r_N' = \frac{k_s K_N C_T \left[P_N - \dfrac{P_I}{K_P} \right]}{1 + K_N P_N + K_I P_I}$$

where K_P is the thermodynamic equilibrium constant for the reactor

Improvement in Octane number
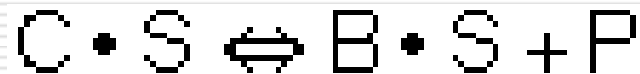
Linearizing the Initial Rate

$$-r_N' = \frac{kP_{N0}}{1+K_N P_{N0}} \Rightarrow \frac{P_{N0}}{-r_N'} = \frac{1}{k} + \frac{K_N}{k} P_{N0}$$

What happens if adsorption is the rate limiting step?
See Section 10.3 of text.

Understanding it better!!!

$$C + S \Leftrightarrow C \cdot S$$

$$C \cdot S \Leftrightarrow B \cdot S + P$$

$$B \cdot S \Leftrightarrow B + S$$

For steady state operation we have

$$-r'_C = r_{AD} = r_S = r_D$$

Understanding it better!!!

For steady state operation we have

$$-r_C^{\prime} = r_{AD} = r_S = r_D$$

$$r_{AD} = k_A P_C \left[C_v - \frac{C_{C \cdot S}}{K_C P_C} \right], \quad k_A = \left(\frac{1}{s \cdot atm} \right) \text{ and } k_A P_C = \left(\frac{1}{s} \right)$$

$$r_S = k_S \left[C_{C \cdot S} - \frac{C_{B \cdot S} P_P}{K_S} \right], \quad k_S = \left(\frac{1}{s} \right)$$

$$r_D = k_D \left[C_{B \cdot S} - \frac{C_v P_B}{K_D} \right], \quad k_D = \left(\frac{1}{s} \right)$$
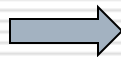
Understanding it better!!!

NOTE: Strictly speaking, We really cannot compare the magnitudes of k_A, k_S, and k_D directly, because k_A has different units than k_S and k_D. Consequently, we must compare the product ($k_A P_C$) with k_S and k_D to determine which reaction step may be limiting. If the surface reaction is limiting, we say $k_A P_C$ and k_D are very large with respect to k_S

$$\frac{r_{AD}}{k_A P_C} \approx 0 = C_v - \frac{C_{C \cdot S}}{K_C P_C}$$

$$\frac{r_D}{k_D} \approx 0 = C_{B \cdot S} - \frac{P_B C_v}{K_D} = C_{B \cdot S} - P_B C_v K_B$$

$$C_{C \cdot S} = K_C P_C C_v$$

$$C_{B \cdot S} = K_B P_B C_v$$

$$\Longrightarrow \qquad r_S = C_v k_S K_C \left[P_C - \frac{K_B P_P P_B}{K_C K_S} \right]$$

Understanding it better!!!

A site balance yields

$$C_t = C_v + C_{C \cdot s} + C_{B \cdot s}$$

$$C_t = \left(1 + K_C P_C + K_B P_B\right) C_v$$

Grouping the equilibrium constants together into one constant, K_P

$$K_P = K_C K_S / K_B$$

$$r_S = \frac{\overbrace{C_t \; k_S \; K_C}^{k}\left[P_C - \dfrac{P_B P_P}{K_P}\right]}{\left(1 + K_C P_C + K_B P_B\right)}$$

$$r_S = \frac{k\left[P_C - \dfrac{P_B P_P}{K_P}\right]}{\left(1 + K_C P_C + K_B P_B\right)}$$

Objective Assessment

➢ Define a catalyst

➢ Understand steps involved in a catalyst reaction

➢ Understand catalyst mechanisms

➢ Develop rate expressions and determine rate limiting steps

I do the very best I know how - the very best I can; and I mean to keep on doing so until the end

Abraham Lincoln