Lecture 17

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Web Lecture 17
Class Lecture 22–Thursday 4/4/2013

Introduction to Catalysts and Catalysis

- Interstage cooling
- Noble Prize 2007
- Catalytic steps

Catalysts and Catalysis

- A ***Catalyst*** is a substance that affects the **rate** of chemical reaction but emerges from the process unchanged.
- ***Catalysis*** is the occurrence, study, and use of catalysts and catalytic processes.

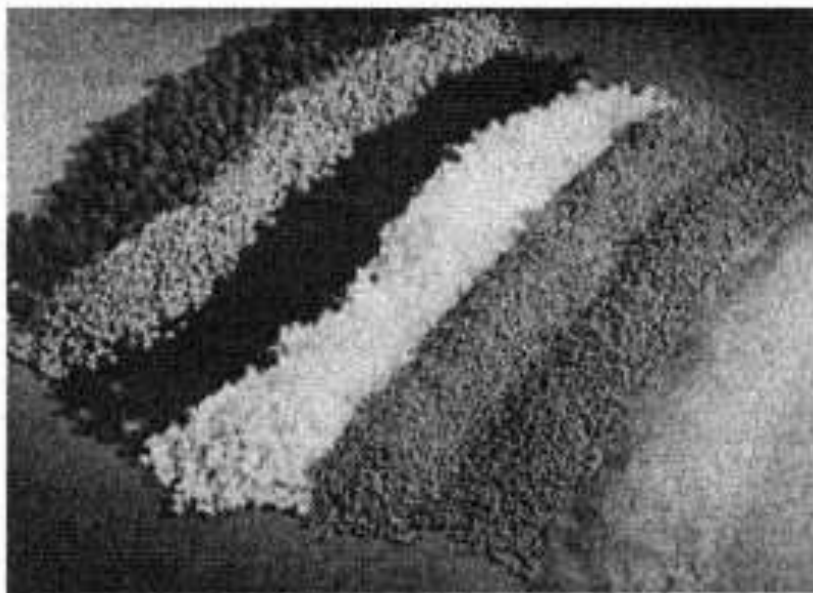Approximately 1/3 of the GNP of materials produced in the U.S. involves a catalytic process.

Catalysts and Catalysis
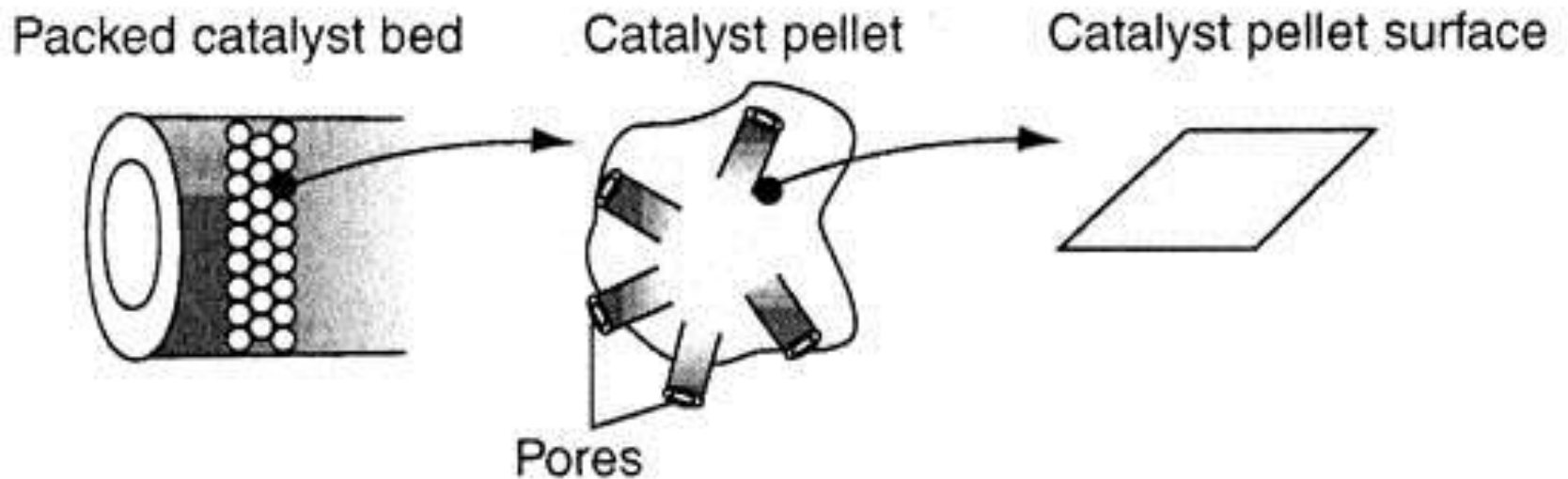
Catalysts affect both selectivity and yield
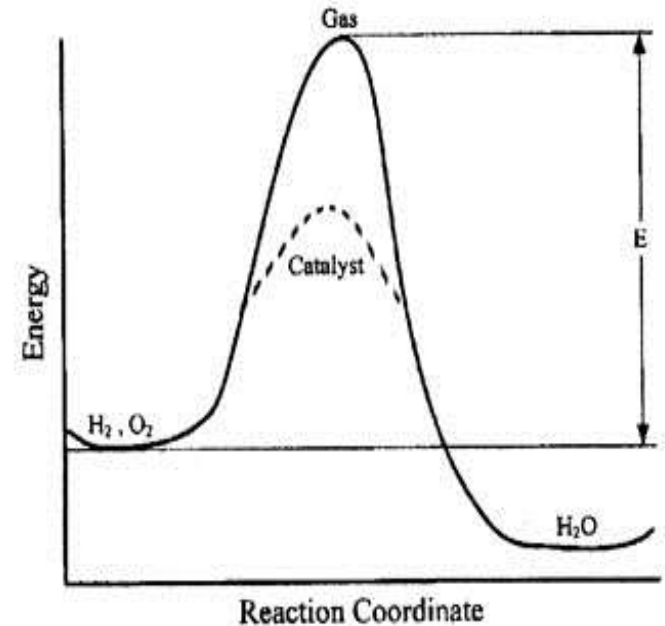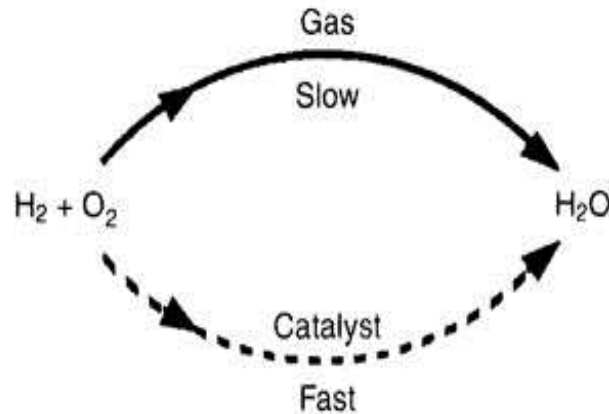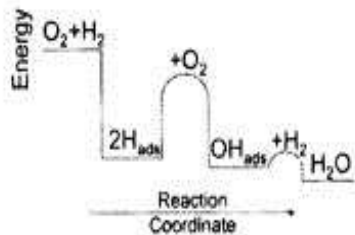
Different reaction paths
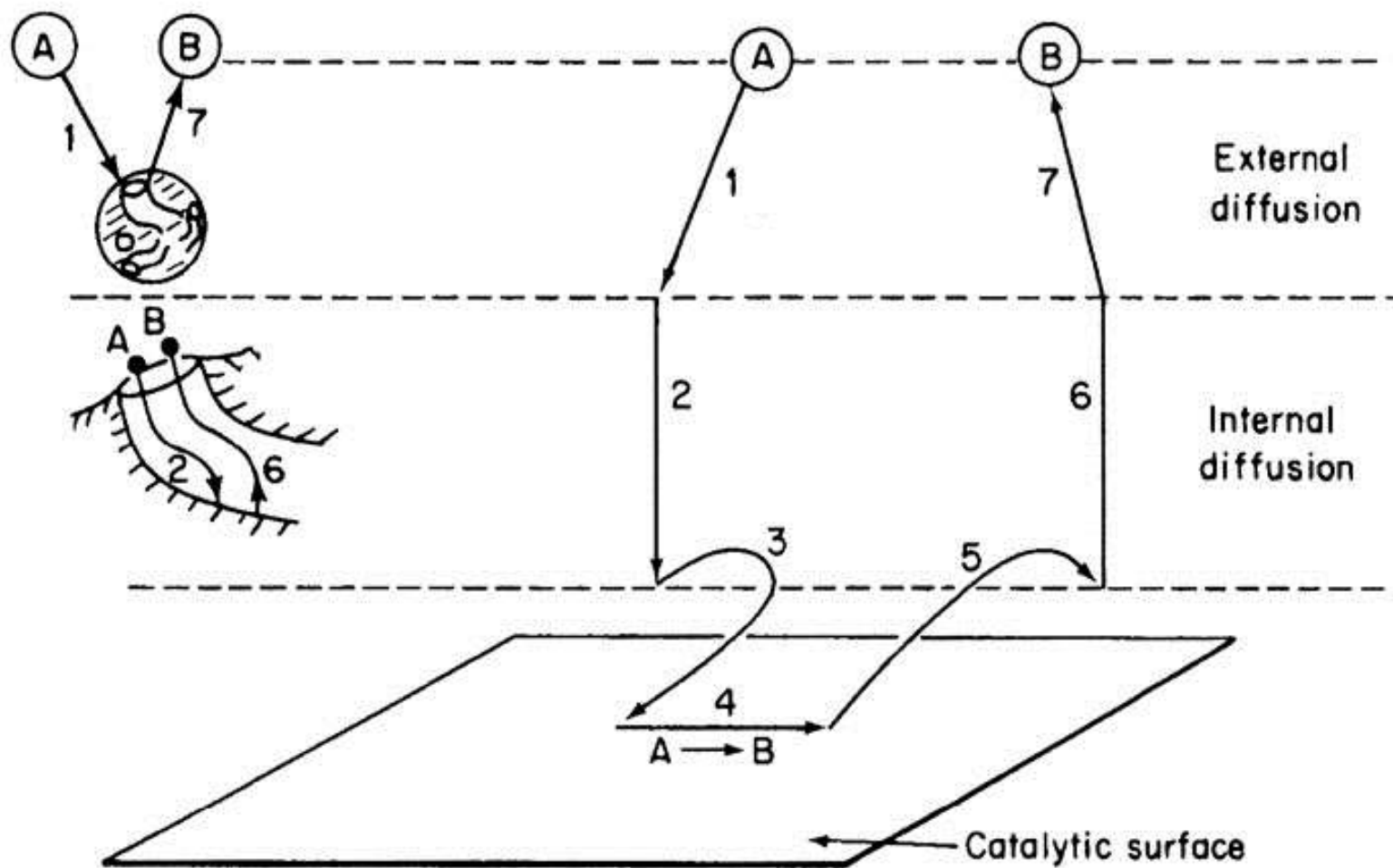
Catalysts and Catalysis

Different shapes and sizes of catalyst.

Catalysts and Catalysis

Catalytic packed-bed reactor, schematic.

Steps in a Catalytic Reaction

External diffusion

Internal diffusion

A → B

Catalytic surface

Active Sites

- Reactions are not catalyzed over the entire surface but only at certain active sites or centers that result from unsaturated atoms in the surface.

- An *active site* is a point on the surface that can form strong chemical bonds with an adsorbed atom or molecule.

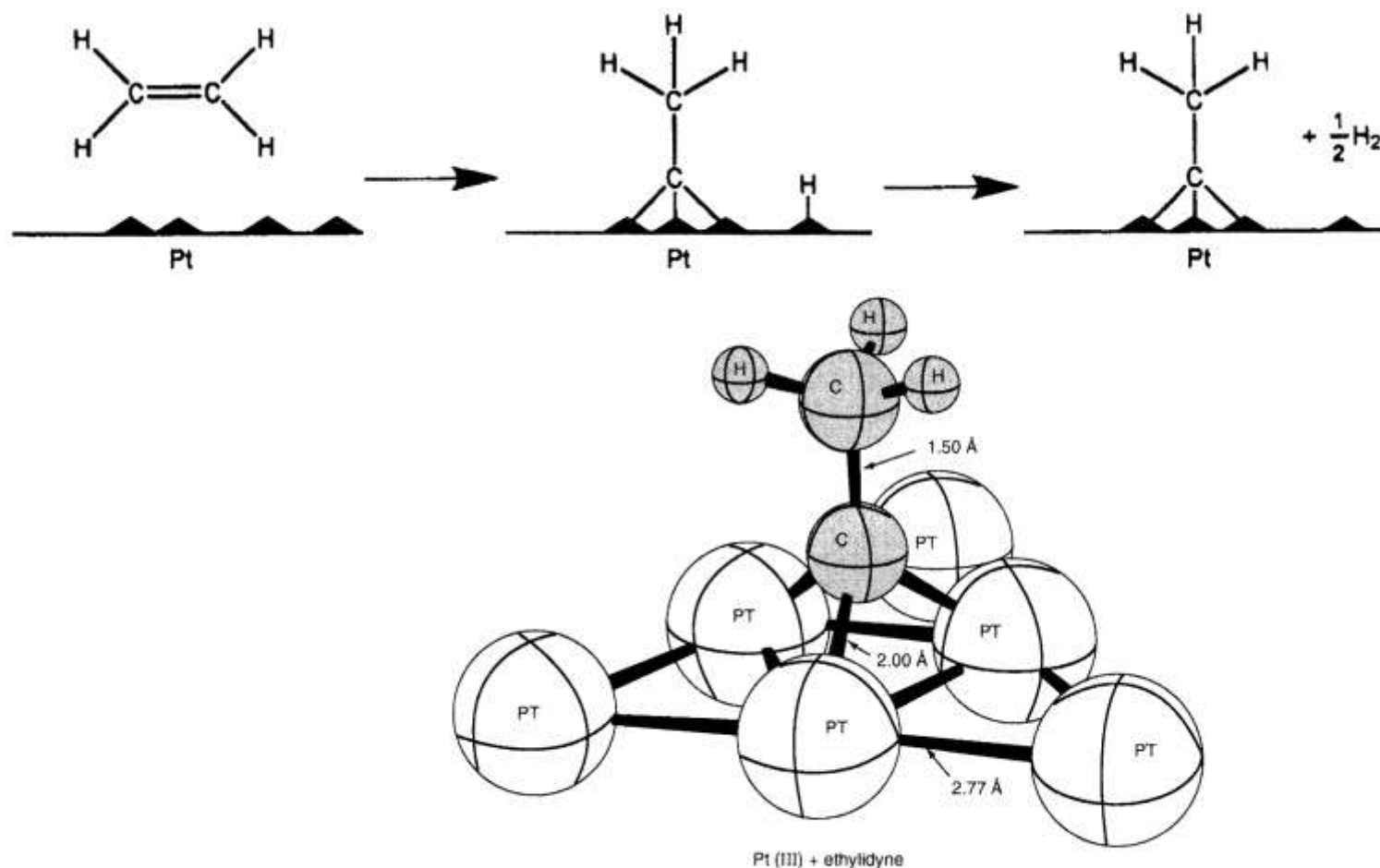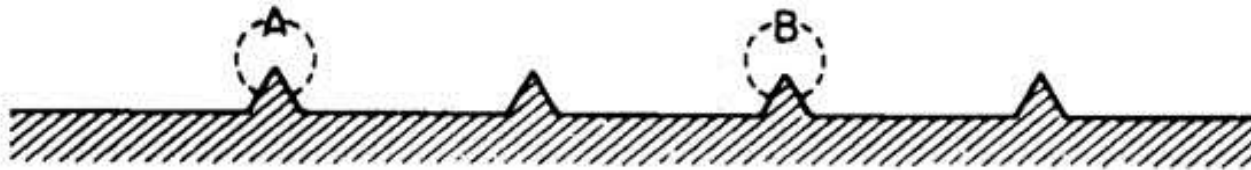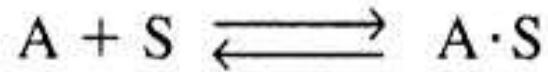# Active Sites – Ethylidyne on Platinum

Figure 10-3 Ethylidyne as chemisorbed on platinum. (Adapted from G. A. Somorjai, *Introduction to Surface Chemistry and Catalysis*, Wiley, New York, 1994.)
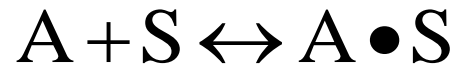
The Adsorption Step

$$A + S \rightleftharpoons A \cdot S$$

Vacant and occupied sites

For the system shown, the total concentration of sites is

$$C_t = C_v + C_{A.S} + C_{B.S}$$

The Adsorption Step

$$A + S \leftrightarrow A \bullet S$$

$$r_{AD} = k_A P_A C_v - k_{-A} C_{A \bullet S} = k_A \left[P_A C_V - C_{A \bullet S} / K_A \right]$$

$$K_A = k_A / k_{-A} \quad [\text{atm}^{-1}]$$

$$@ \text{ equilibrium}: \quad r_{AD} = 0 \qquad C_{AS} = k_A P_A C_V$$

$$r_{AD} / k_A \approx 0 \qquad C_{AS} = k_A P_A C_V$$

$$C_t = C_V + C_{A \bullet S} = C_V + K_A P_A C_V = C_V (1 + K_A P_A)$$

$$C_V = \frac{C_t}{1 + K_A P_A C_V}$$

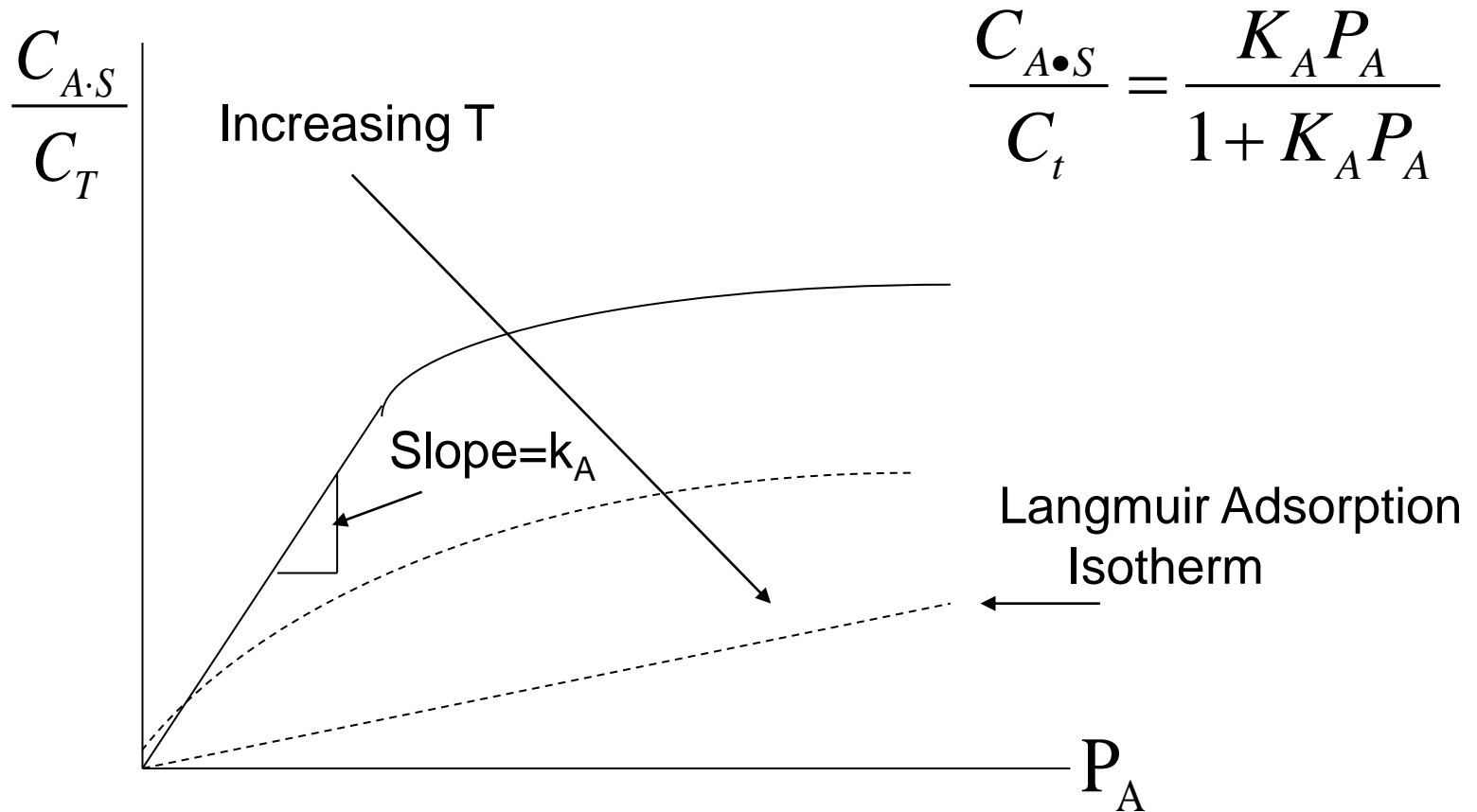# Langmuir Adsorption Isotherm

$$C_V = \frac{C_t}{1 + K_A P_A C_V}$$

$$C_{A \bullet S} = K_A P_A C_V$$

$$C_{A \bullet S} = \frac{K_A P_A}{1 + K_A P_A} C_t$$

$$\frac{C_{A \bullet S}}{C_t} = \frac{K_A P_A}{1 + K_A P_A}$$

Langmuir Adsorption Isotherm

$$\frac{C_{A \cdot S}}{C_t} = \frac{K_A P_A}{1 + K_A P_A}$$

$\dfrac{C_{A \cdot S}}{C_T}$

Increasing T

Slope=k$_A$

Langmuir Adsorption Isotherm

P_A

The Surface Reaction Step

1. *Single site.* The surface reaction may be a single-site mechanism in which only the site on which the reactant is adsorbed is involved in the reaction. For example, an adsorbed molecule of A may isomerize (or perhaps decompose) directly on the site to which it is attached, such as

$$A \cdot S \;\rightleftharpoons\; B \cdot S$$
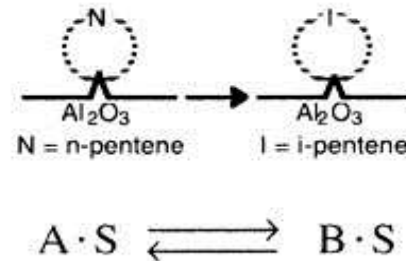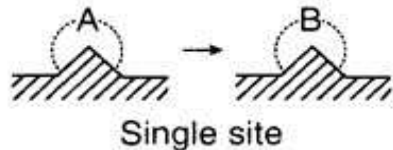
Because in each step the reaction mechanism is elementary, the surface reaction rate law is
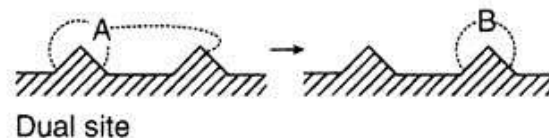
Single Site

$$k_S' = \left(\frac{1}{s}\right)$$

$$r_S = k_S \left(C_{A \cdot S} - \frac{C_{B \cdot S}}{K_S} \right)$$

K_s = (dimensionless)

where K_S is the surface reaction equilibrium constant $K_S = k_S / k_{-S}$

Single site

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The Surface Reaction Step

2. *Dual site.* The surface reaction may be a dual-site mechanism in which the adsorbed reactant interacts with another site (either unoccupied or occupied) to form the product.

Dual site

For example, adsorbed A may react with an adjacent vacant site to yield a vacant site and a site on which the product is adsorbed, such as the dehydration of butanol.
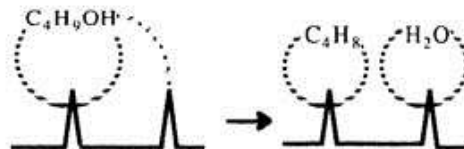
For the generic reaction

$$A \cdot S + S \rightleftharpoons B \cdot S + S$$
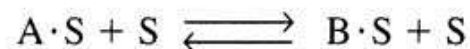
the corresponding surface reaction rate law is

$$r_S = k_S \left(C_{A \cdot S} C_v - \frac{C_{B \cdot S} C_v}{K_S} \right) \qquad (10\text{-}$$

The Surface Reaction Step

Dual Site

$$r_S = \left(\frac{\text{mol}}{\text{gcat} \cdot \text{s}} \right)$$

$$k_S = \left(\frac{\text{gcat}}{\text{mol} \cdot \text{s}} \right)$$
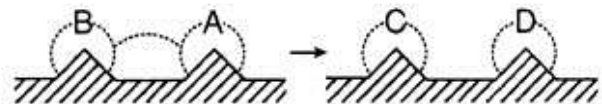
$$K_S = (\text{dimensionless})$$

the corresponding surface reaction rate law is

$$r_S = k_S \left(C_{A \cdot S} C_v - \frac{C_{B \cdot S} C_v}{K_S} \right)$$
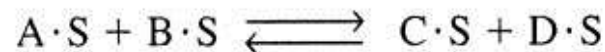
Another example of a dual-site mechanism is the reaction between two adsorbed species, such as the reaction of CO with O

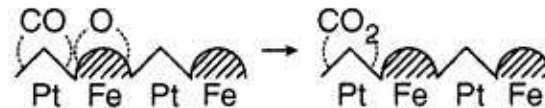
For the generic reaction

Dual site

$$A \cdot S + B \cdot S \rightleftharpoons C \cdot S + D \cdot S$$

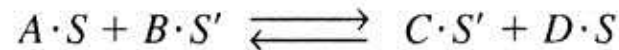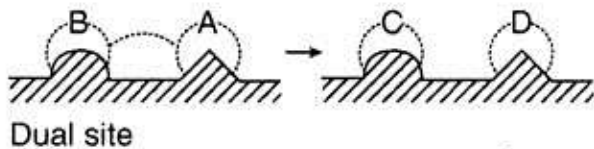the corresponding surface reaction rate law is

$$r_S = k_S \left(C_{A \cdot S} C_{B \cdot S} - \frac{C_{C \cdot S} C_{D \cdot S}}{K_S} \right)$$

The Surface Reaction Step

A third dual-site mechanism is the reaction of two species adsorbed on different types of sites S and S', such as the reaction of CO with O.

For the generic reaction

$$A \cdot S + B \cdot S' \rightleftharpoons C \cdot S' + D \cdot S$$

Dual site

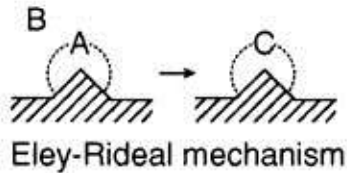the corresponding surface reaction rate law is

$$r_S = k_S \left(C_{A \cdot S} C_{B \cdot S'} - \frac{C_{C \cdot S'} C_{D \cdot S}}{K_S} \right)$$

Langmuir-
Hinshelwood
kinetics

Reactions involving either single- or dual-site mechanisms, which were described earlier are sometimes referred to as following *Langmuir–Hinshelwood kinetics*.

The Surface Reaction Step

3. *Eley–Rideal.* A third mechanism is the reaction between an adsorbed molecule and a molecule in the gas phase, such as the reaction of propylene and benzene

For the generic reaction

$$A \cdot S + B(g) \rightleftharpoons C \cdot S$$
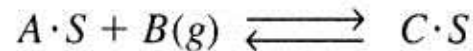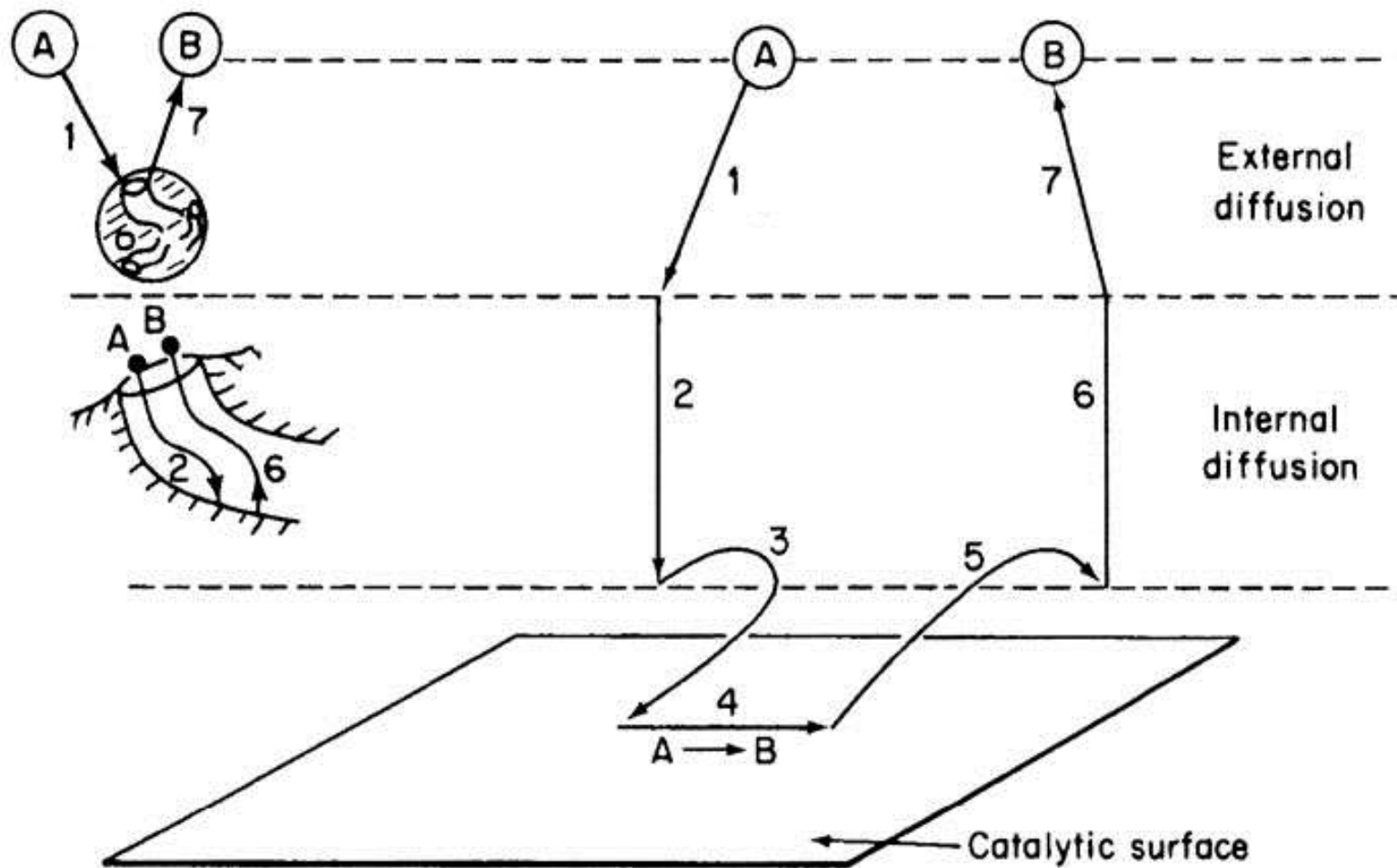
the corresponding surface reaction rate law is

$$r_S = k_S \left(C_{A \cdot S} P_B - \frac{C_{C \cdot S}}{K_S} \right)$$

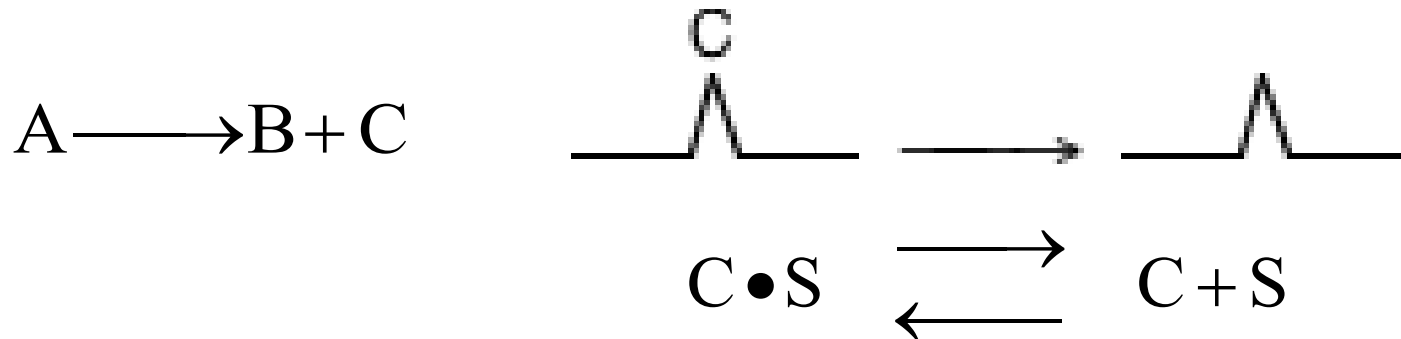This type of mechanism is referred to as an *Eley–Rideal mechanism.*

Eley-Rideal mechanism

$$k_s = \left(\frac{1}{atm \cdot s} \right)$$

$$K_S = \left(\frac{1}{atm} \right)$$

Steps in a Catalytic Reaction

Desorption from the Surface for the Reaction

$$A \longrightarrow B + C$$

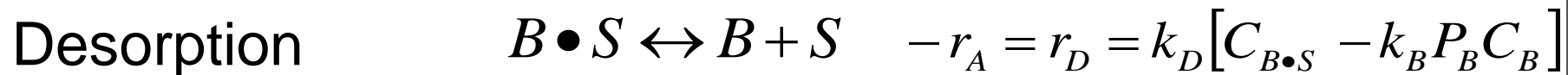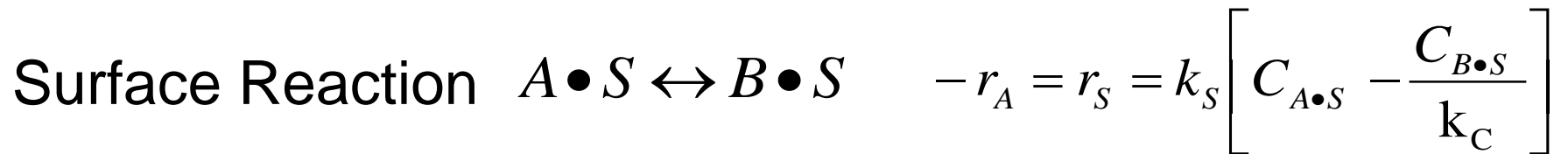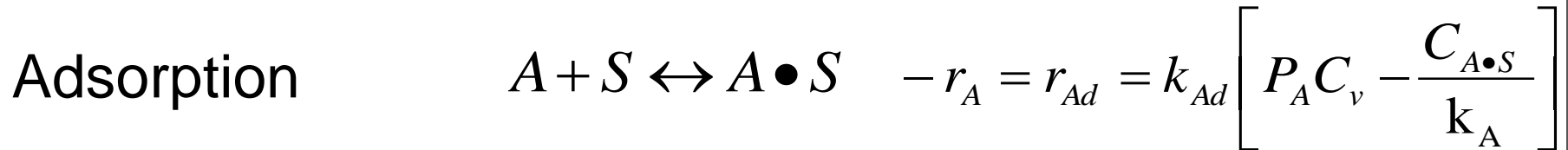$$C \bullet S \rightleftarrows C + S$$

$$r_{DC} = k_D \left[C_{C \bullet S} - \frac{P_C C_{\upsilon}}{K_{DC}} \right] \qquad (10\text{-}20)$$

$$r_{DC} = -r_{ADC}$$
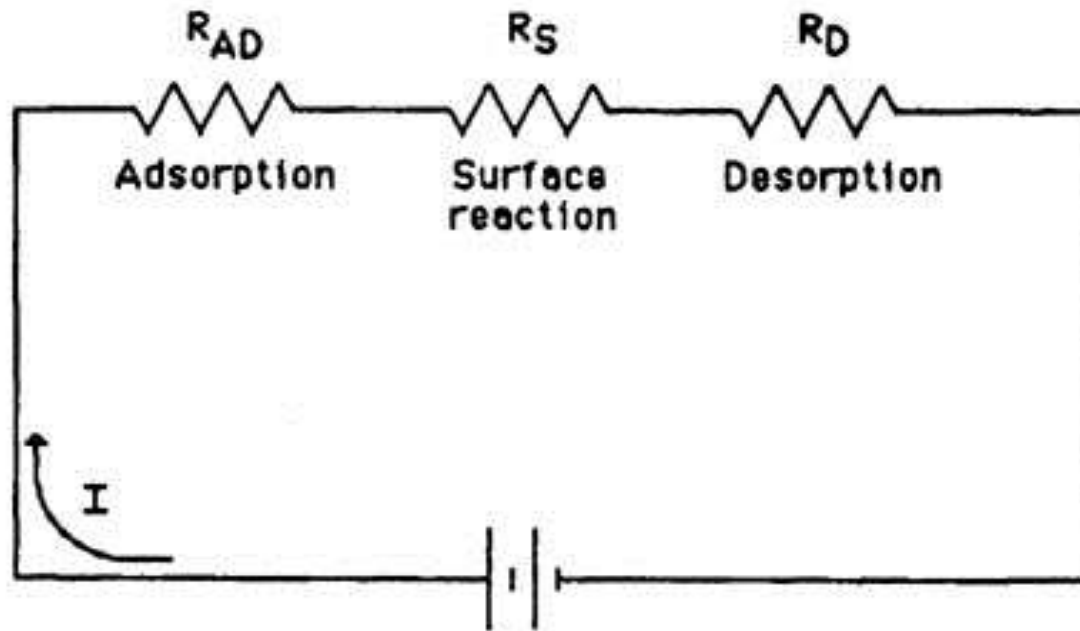
$$K_{DC} = \frac{1}{K_C}$$

$$r_{DC} = k_D \left[C_{C \bullet S} - K_C P_C C_{\upsilon} \right] \qquad (10\text{-}21)$$

Steps in a Single-Site Catalytic Reactor

Adsorption $\qquad A + S \leftrightarrow A \bullet S \qquad -r_A = r_{Ad} = k_{Ad}\left[P_A C_v - \dfrac{C_{A \bullet S}}{\text{k}_A} \right]$

Surface Reaction $\quad A \bullet S \leftrightarrow B \bullet S \qquad -r_A = r_S = k_S\left[C_{A \bullet S} - \dfrac{C_{B \bullet S}}{\text{k}_C} \right]$

Desorption $\qquad B \bullet S \leftrightarrow B + S \qquad -r_A = r_D = k_D\left[C_{B \bullet S} - k_B P_B C_B \right]$
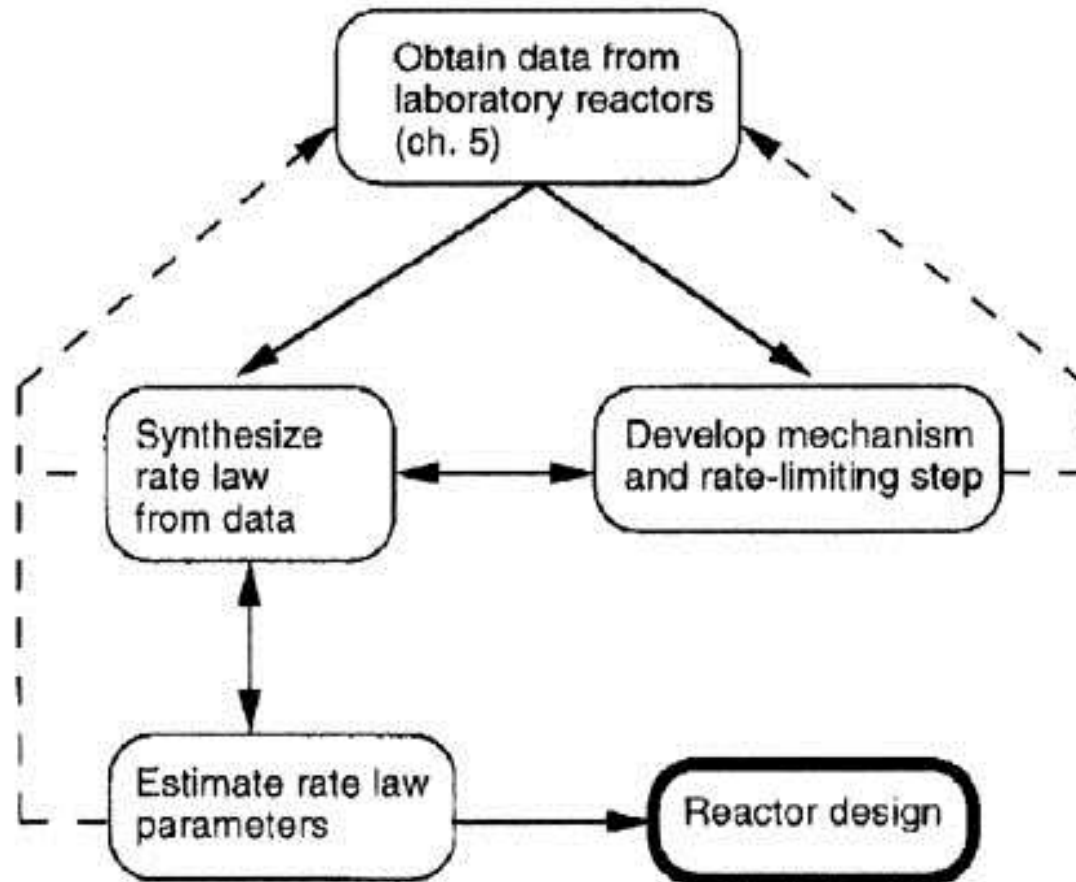
Which step is the **Rate** Limiting Step (RLS)?

The Rate Limiting Step:
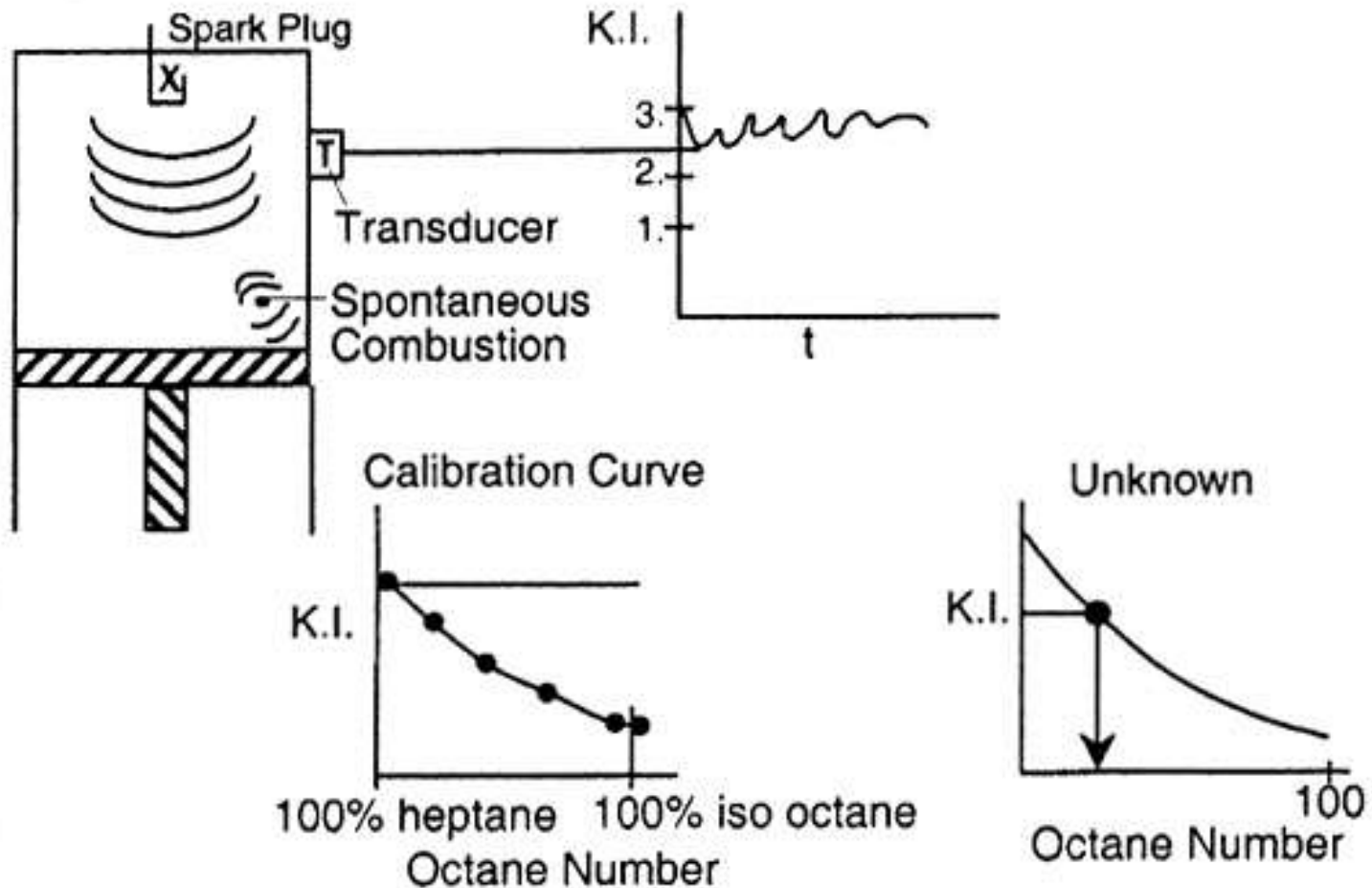# Which step has the largest resistance?

Electrical analog to heterogeneous reactions
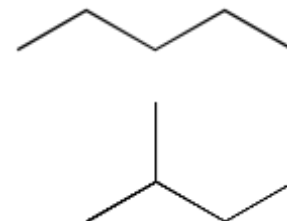
Collecting and Analyzing Data

Collecting information for catalytic reactor design
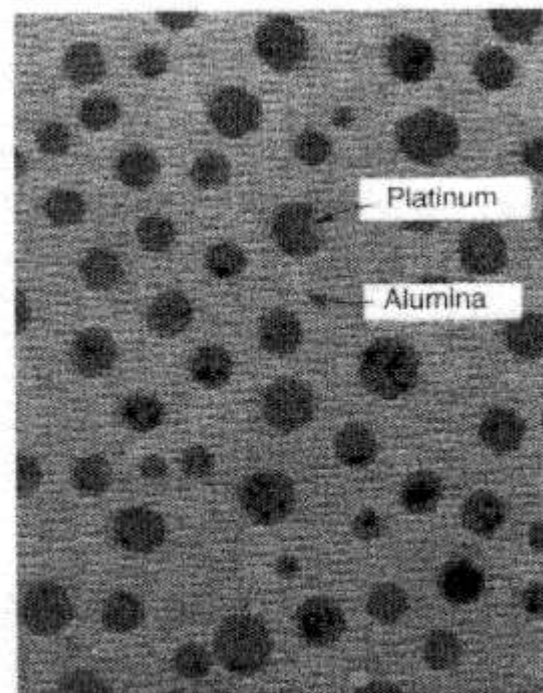
Collecting and Analyzing Data

Catalytic Reformers

- Normal Pentane Octane Number = 62
- Iso-Pentane Octane Number = 95

Gasoline

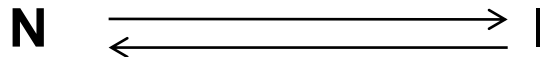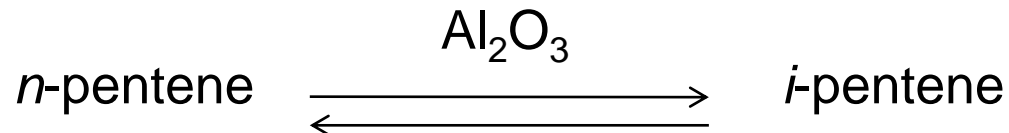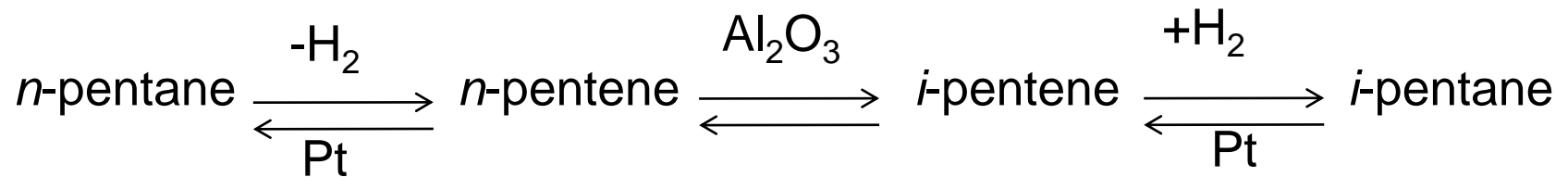|	
C_5	10%
C_6	10%
C_7	20%
C_8	25%
C_9	20%
C_{10}	10%
C_{11-12}	5%

Platinum on alumina. (Figure from R.I. Masel, *Chemical Kinetics and Catalysis*, Wiley, New York, 2001, p 700)

Catalytic Reformers

$$n\text{-pentane} \xrightleftharpoons[\text{Al}_2\text{O}_3]{\text{0.75 wt\% Pt}} i\text{-pentane}$$

$$n\text{-pentane} \xrightleftharpoons[\text{Pt}]{-\text{H}_2} n\text{-pentene} \xrightleftharpoons{\text{Al}_2\text{O}_3} i\text{-pentene} \xrightleftharpoons[\text{Pt}]{+\text{H}_2} i\text{-pentane}$$

$$n\text{-pentene} \xrightleftharpoons{\text{Al}_2\text{O}_3} i\text{-pentene}$$

$$\textbf{N} \rightleftharpoons \textbf{I}$$
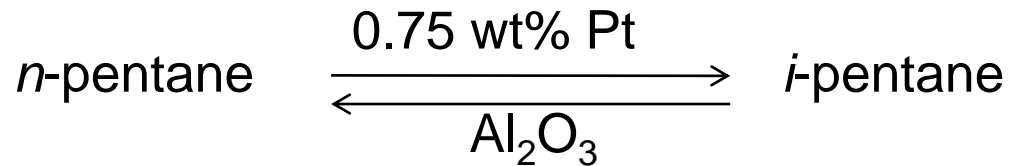
Catalytic Reformers

Isomerization of *n*-pentene (N) to *i*-pentene (I) over alumina

$$N \quad \underset{\longleftarrow}{\overset{Al_2O_3}{\longrightarrow}} \quad I$$
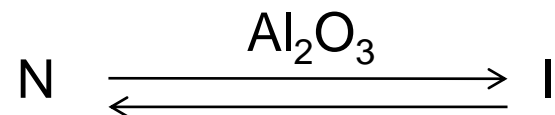
1. *Select a mechanism* (Mechanism Single Site)

Adsorption on Surface: $\qquad N + S \Leftrightarrow N \bullet S$

Surface Reaction: $\qquad N \bullet S \Leftrightarrow I \bullet S$

Desorption: $\qquad I \bullet S \Leftrightarrow I + S$
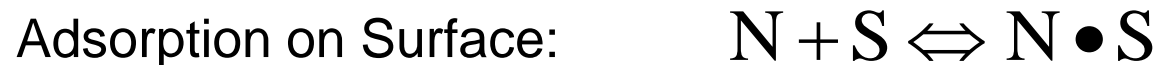
Treat each reaction step as an elementary reaction when writing **rate laws.**

Catalytic Reformers
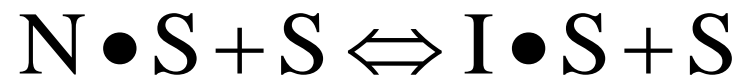
2. *Assume a **rate**-limiting step.*
Choose the surface reaction first, since more than 75% of all heterogenous reactions that are not diffusion-limited are surface-reaction-limited. The **rate law** for the surface reaction step is:

$$N \bullet S + S \Leftrightarrow I \bullet S + S$$

$$-r_N{}' = r_I{}' = r_S = k_S \left(C_{N \bullet S} - \frac{C_{I \bullet S}}{K_S} \right)$$

Catalytic Reformers

3. *Find the expression for the concentrations of the adsorbed species*

$C_{N.S}$ and $C_{I.S}$. Use the other steps that are not limiting to solve for $C_{N.S}$ and $C_{I.S}$. For this reaction:

$$N + S \Leftrightarrow N \bullet S$$

From $\dfrac{r_{AD}}{k_A} \approx 0:$ $\qquad C_{N \bullet S} = P_N K_N C_\upsilon$

$$I \bullet S \Leftrightarrow I + S$$

From $\dfrac{r_D}{k_D} \approx 0:$ $\qquad C_{I \bullet S} = \dfrac{P_I C_\upsilon}{K_D} = K_I P_I C_\upsilon$

Catalytic Reformers

4. *Write a Site Balance.*

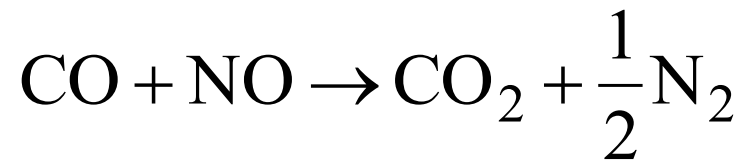$$C_t = C_\upsilon + C_{N \bullet S} + C_{I \bullet S}$$

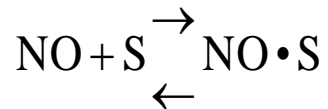5. *Derive the **rate law**.* Combine steps 2, 3 and 4 to arrive at the **rate law** :

$$-r_N' = r_S = \frac{\overbrace{k_s C_t K_N}^{k}\left(P_N - P_I / K_P\right)}{\left(1 + K_N P_N + K_I P_I\right)}$$

$$-r_N' = r_S = \frac{k\left(P_N - P_I / K_P\right)}{\left(1 + K_N P_N + K_I P_I\right)}$$

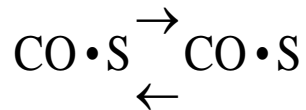# Catalytic Conversion of Exhaust Gas

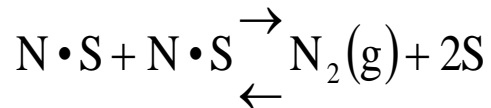|	1994	2004	2008
HC	0.41	0.125	0.10
CO	3.4	3.4	3.4
NO	0.4	0.4	0.14

$$CO + NO \rightarrow CO_2 + \frac{1}{2}N_2$$

Catalytic Conversion of Exhaust Gas

$$NO + S \underset{\leftarrow}{\overset{\rightarrow}{\quad}} NO \cdot S$$

$$r_{ANO} = k_{NO}\left[P_{NO}C_V - \frac{C_{NO \cdot S}}{K_{NO}} \right] \quad C_{NO \cdot S} = K_{NO}P_{NO}C_V$$

$$CO \cdot S \underset{\leftarrow}{\overset{\rightarrow}{\quad}} CO \cdot S$$

$$r_{ACO} = k_{CO}\left[P_{CO}C_V - \frac{C_{CO \cdot S}}{K_{CO}} \right] \quad C_{CO \cdot S} = K_{CO}P_{CO}C_V$$

$$CO \cdot S + NO \cdot S \rightarrow CO_2 + N \cdot S + S \quad r_S = k_S\left[C_{CO \cdot S}C_{NO \cdot S} \right]$$

$$N \cdot S + N \cdot S \underset{\leftarrow}{\overset{\rightarrow}{\quad}} N_2(g) + 2S \qquad r_D = k_D\left[C_{N \cdot S}^2 - K_{N_2}P_{N_2}C_V^2 \right] \quad C_{N \cdot S} = C_V\sqrt{K_N P_{N_2}}$$

Catalytic Conversion of Exhaust Gas

$$r_S = k_S \left[C_{NO \cdot s} C_{CO \cdot s} \right]$$

$$r_S = k_S K_{NO} K_{CO} P_{NO} P_{CO} C_V^2$$

$$C_T = C_V + C_{NO \cdot s} + C_{CO \cdot s} + C_{N \cdot s}$$

$$= C_V + C_V K_{NO} P_{NO} + C_V K_{CO} P_{CO} + C_V \sqrt{K_{N_2} P_{N_2}}$$

Catalytic Conversion of Exhaust Gas

$$C_V = \frac{C_t}{1 + K_{NO}P_{NO} + K_{CO}P_{CO} + \sqrt{K_{N_2}P_{N_2}}}$$

$$-r'_{NO} = r_S = \frac{\overbrace{k_S K_{NO} K_{CO} C_t^2}^{k} P_{NO} P_{CO}}{\left(1 + K_{NO}P_{NO} + K_{CO}P_{CO} + \sqrt{K_{N_2}P_{N_2}}\right)^2}$$
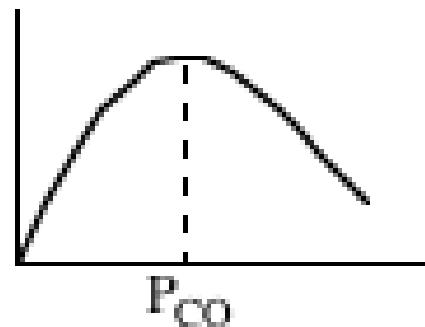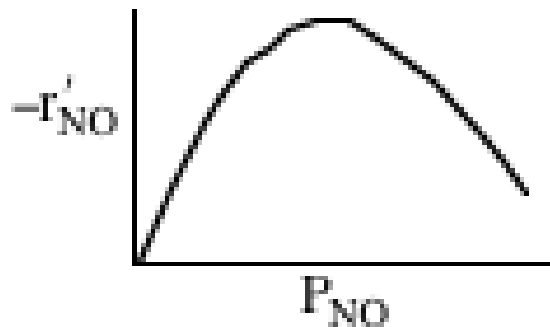
$$-r'_{NO} = \frac{k P_{NO} P_{CO}}{\left(1 + K_{NO}P_{NO} + K_{CO}P_{CO} + \sqrt{K_{N_2}P_{N_2}}\right)^2}$$

Catalytic Conversion of Exhaust Gas

$$-r'_{NO} = \frac{kP_{NO}P_{CO}}{\left(1 + K_{NO}P_{NO} + K_{CO}P_{CO} + \sqrt{K_{N_2}P_{N_2}}\right)^2}$$

Neglect $\sqrt{K_{N_2}P_{N_2}}$

$$-r'_{NO} = \frac{kP_{NO}P_{CO}}{\left(1 + K_{NO}P_{NO} + K_{CO}P_{CO}\right)^2}$$

Catalytic Conversion of Exhaust Gas

$$-r'_{NO} = \frac{kP_{NO}P_{CO}}{\left(1 + K_{NO}P_{NO} + K_{CO}P_{CO}\right)^2}$$

Find optimum partial pressure of CO

$$\frac{d(-r_{NO})}{dP_{CO}} = 0$$

$$P_{CO} = \frac{1 + K_{NO}P_{NO}}{K_{CO}}$$

End of Web Lecture 17