# 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

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

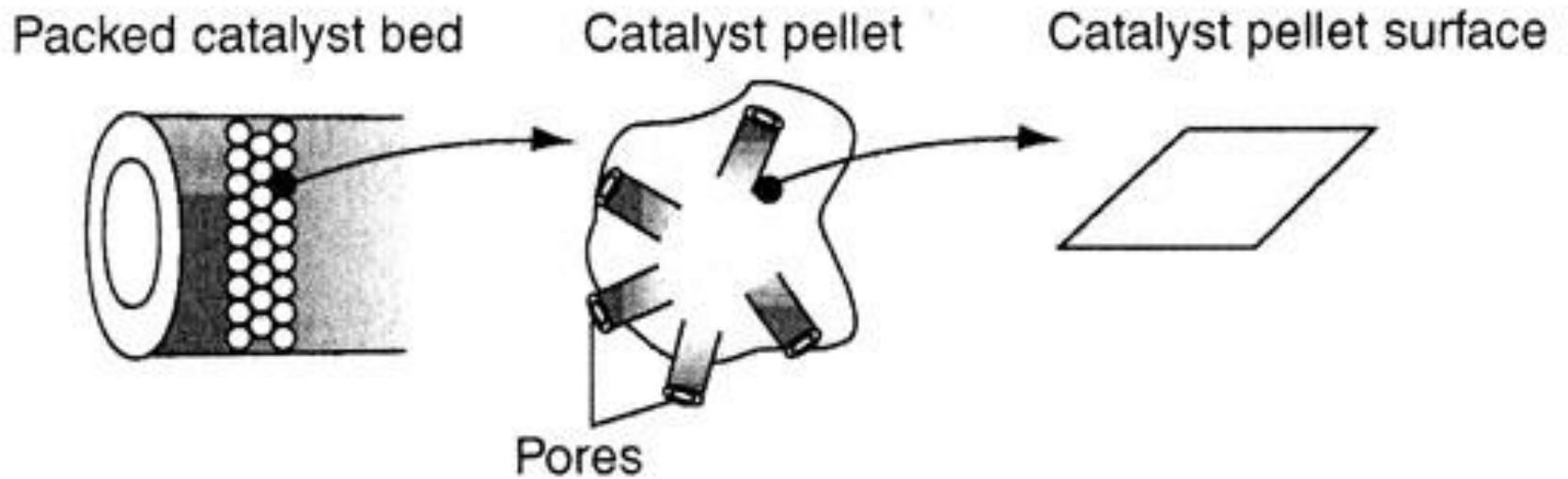Catalysts affect both selectivity and yield
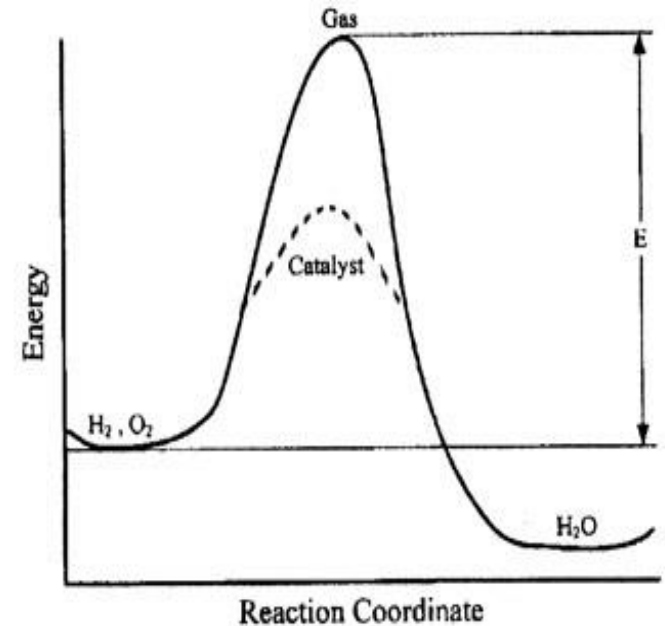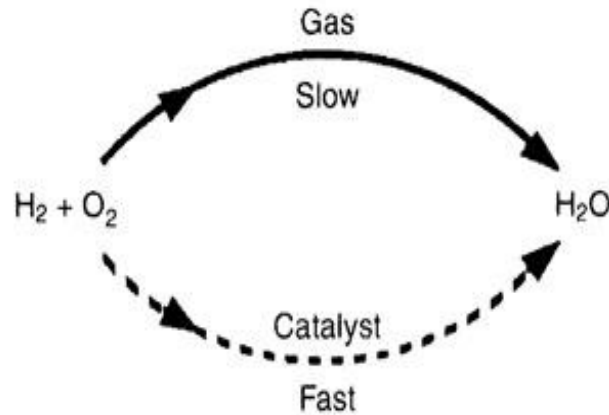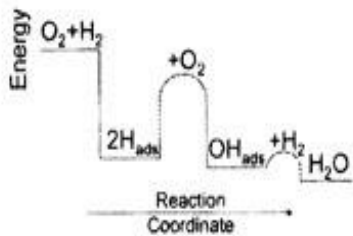


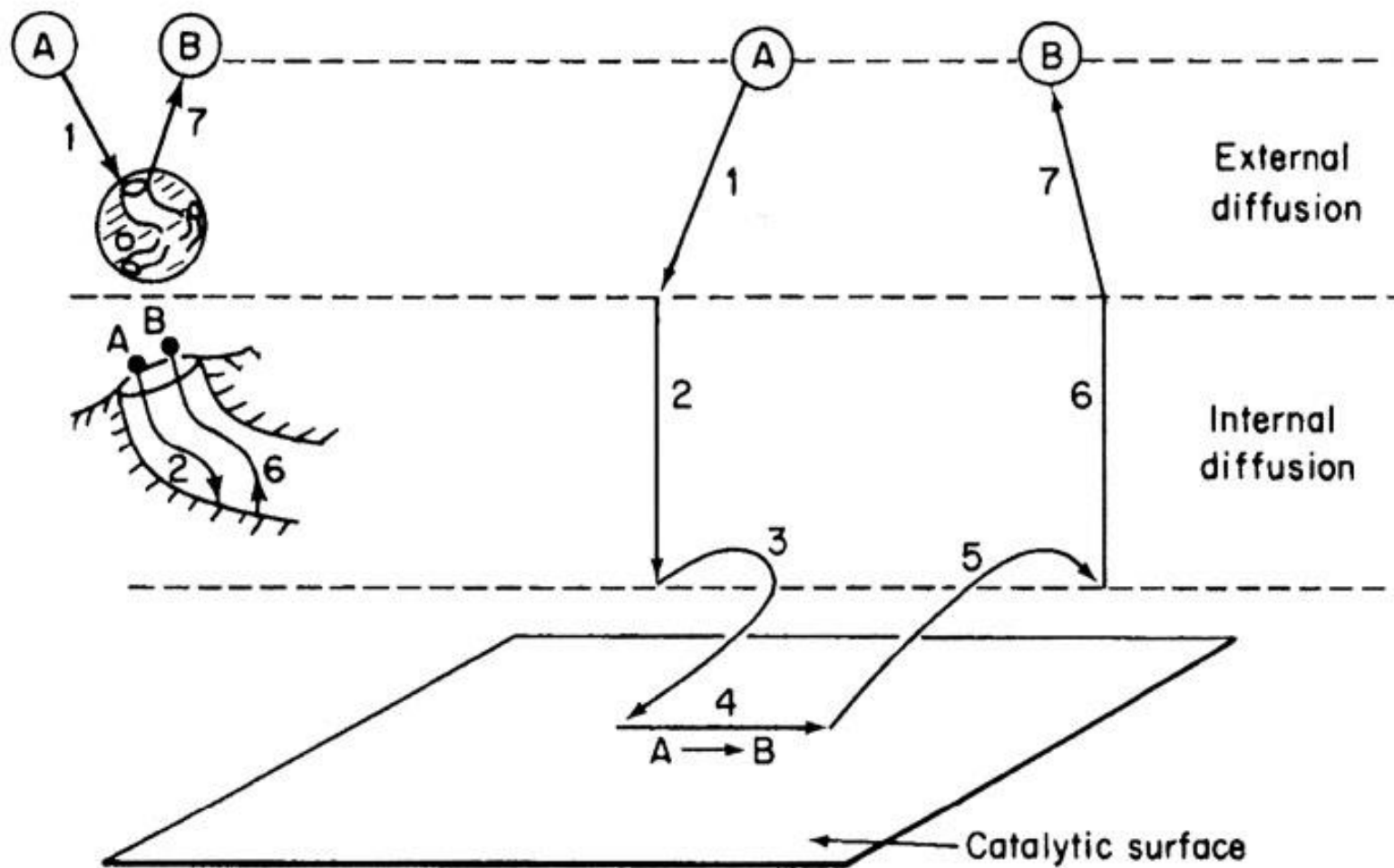Different reaction paths

# Catalysts and Catalysis



Different shapes and sizes of catalyst.

# Catalysts and Catalysis



Catalytic packed-bed reactor, schematic.
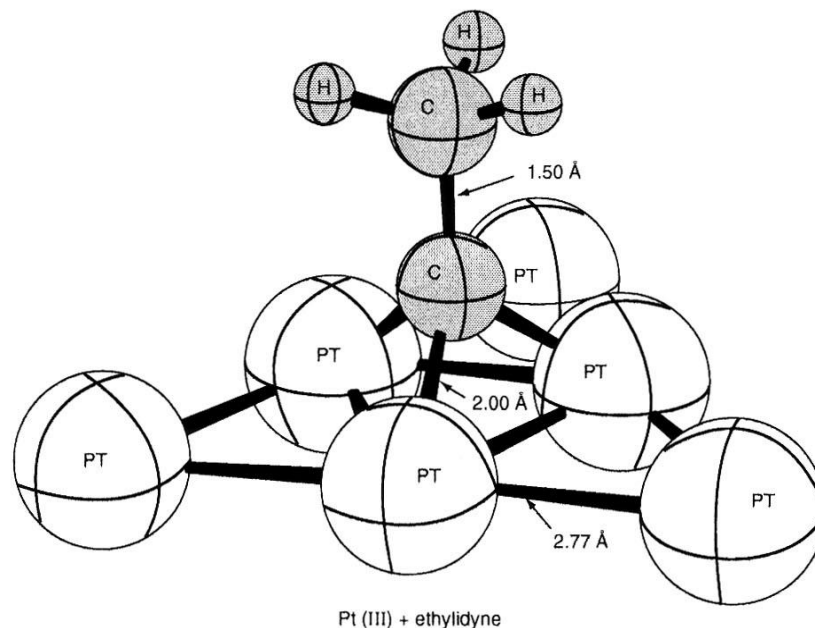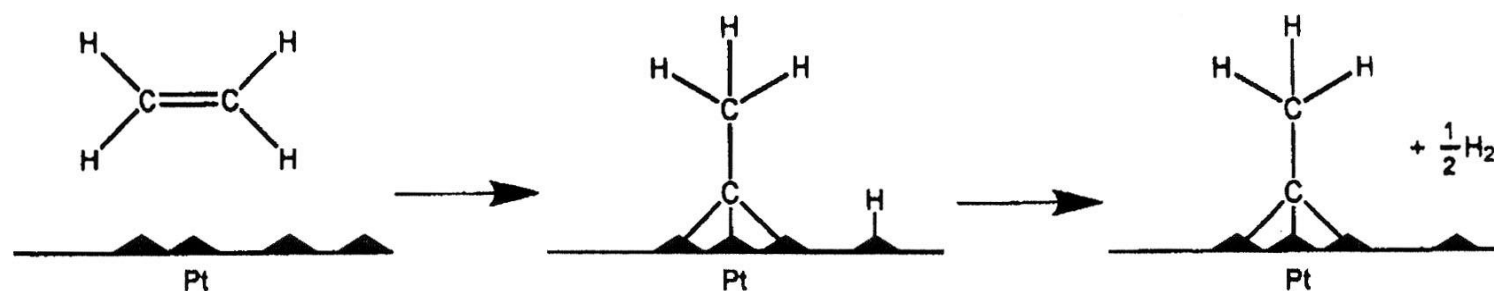
# Steps in a Catalytic Reaction

# 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.
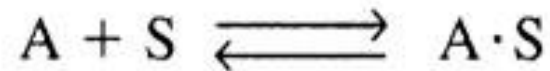
# Active Sites – Ethylidyne on Platinum



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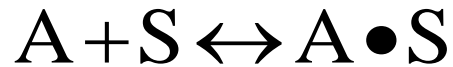
# The Adsorption Step

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

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

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

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

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

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

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

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

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

# 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



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

Increasing T

Slope=$k_A$

Langmuir Adsorption Isotherm

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

$P_A$

# 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



N = n-pentene    I = i-pentene

$$A \cdot S \rightleftharpoons B \cdot S$$
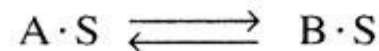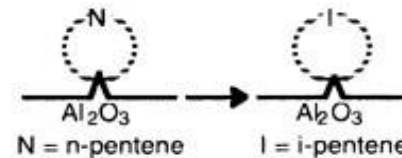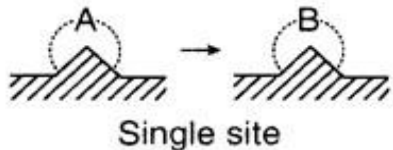


Single site

Because in each step the reaction mechanism is elementary, the surface reaction rate law is

*Single Site*

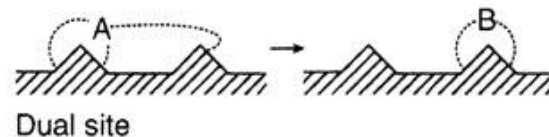$$k_S{}' = \left(\frac{1}{s}\right)$$

$K_s$ = (dimensionless)

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

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

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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.
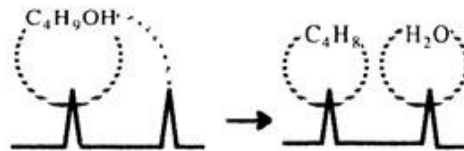


For the generic reaction

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

the corresponding surface reaction rate law is

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

# The Surface Reaction Step

*Dual Site*

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

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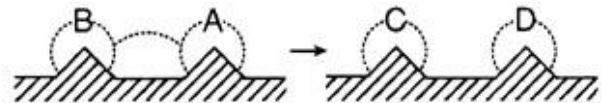
$$K_S = (\text{dimensionless})$$

the corresponding surface reaction rate law is

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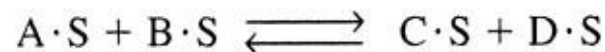
Another example of a dual-site mechanism is the reaction between two adsorbed species, such as the reaction of CO with O



For the generic reaction



Dual site

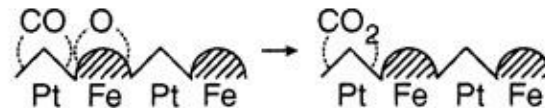$$A \cdot S + B \cdot S \; \rightleftharpoons \; C \cdot S + D \cdot S$$

the corresponding surface reaction rate law is

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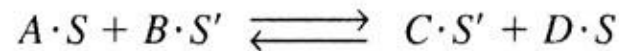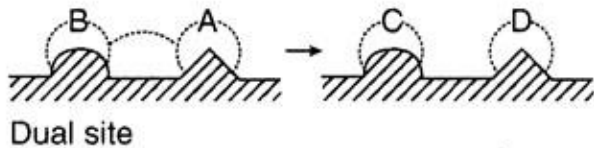
# The Surface Reaction Step

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



Dual site

$$A \cdot S + B \cdot S' \; \rightleftharpoons \; C \cdot S' + D \cdot S$$
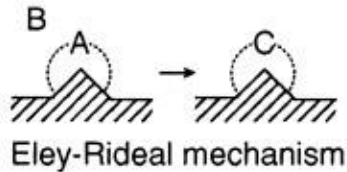
the corresponding surface reaction rate law is

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

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



Eley-Rideal mechanism

For the generic reaction

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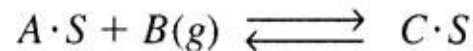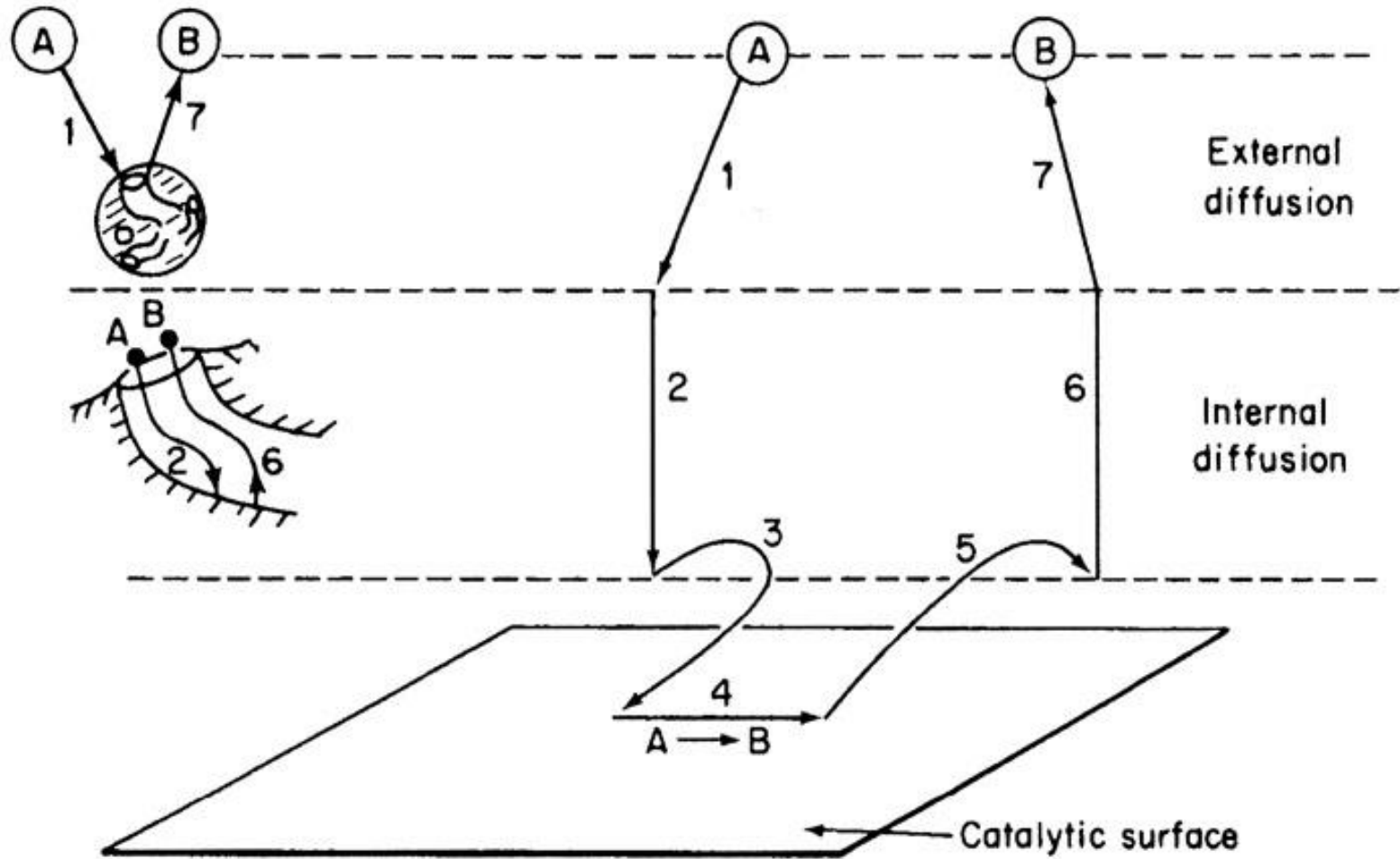
the corresponding surface reaction rate law is

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

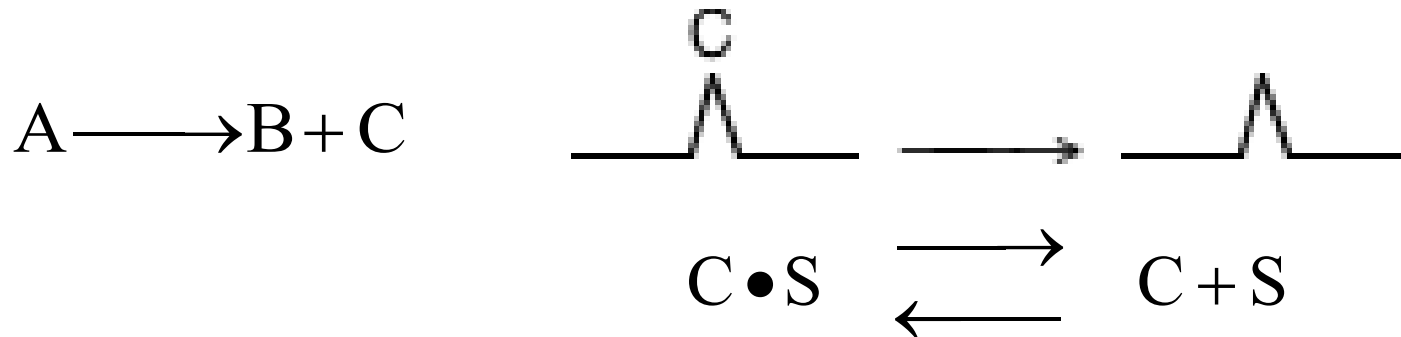This type of mechanism is referred to as an *Eley–Rideal mechanism.*

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

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

# Steps in a Catalytic Reaction

# Desorption from the Surface for the Reaction

$$A \longrightarrow B + C$$

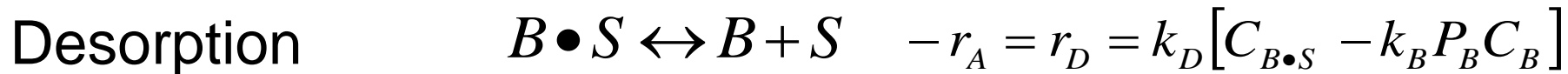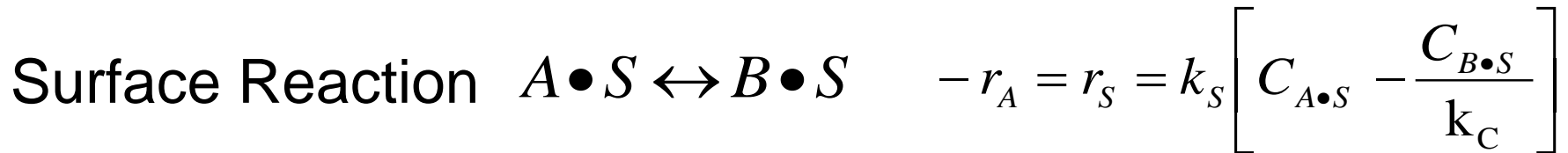$$C \bullet S \quad \rightleftharpoons \quad C + S$$

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

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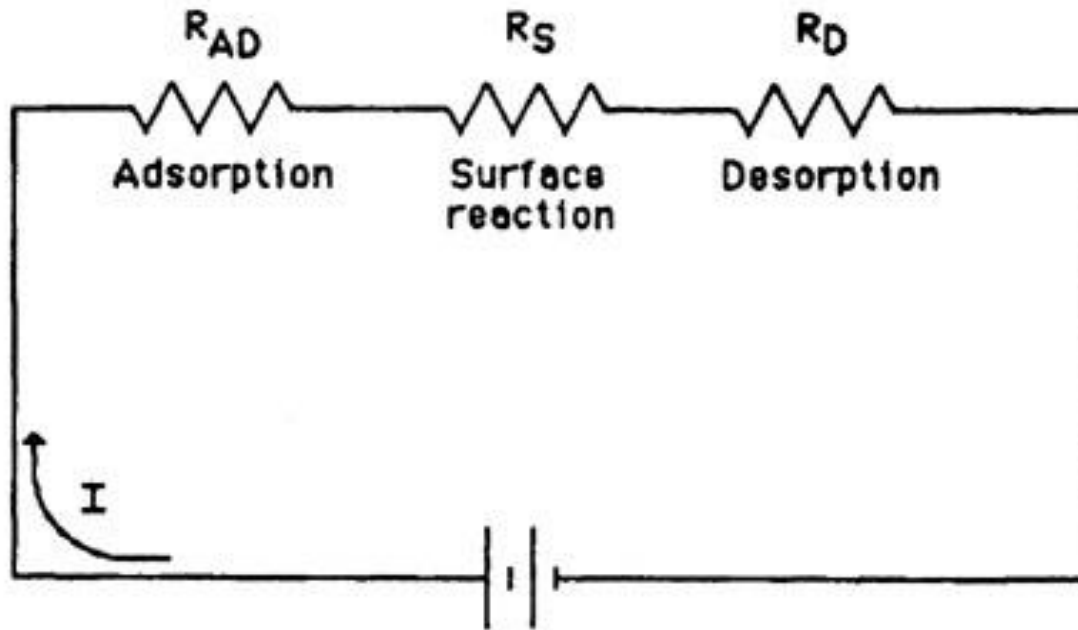
$$K_{DC} = \frac{1}{K_C}$$

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

# Steps in a Single-Site Catalytic Reactor

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

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

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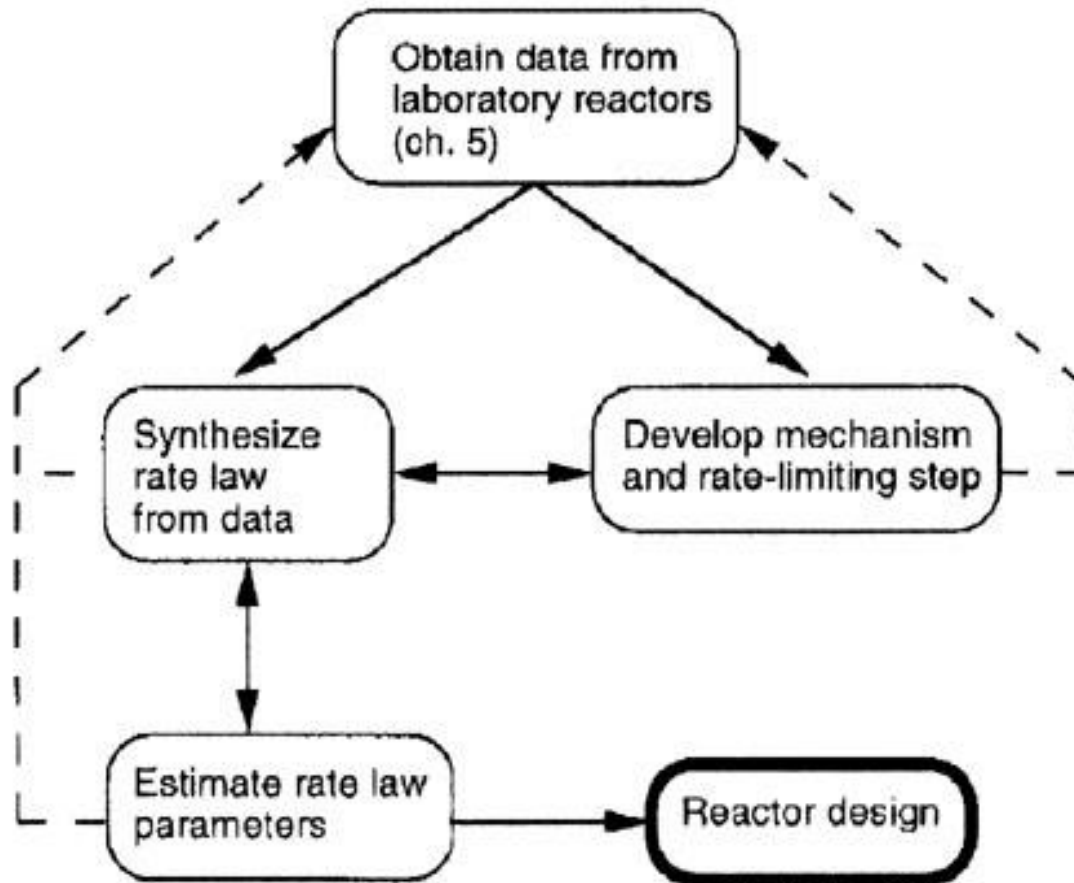
Which step is the **Rate** Limiting Step (RLS)?

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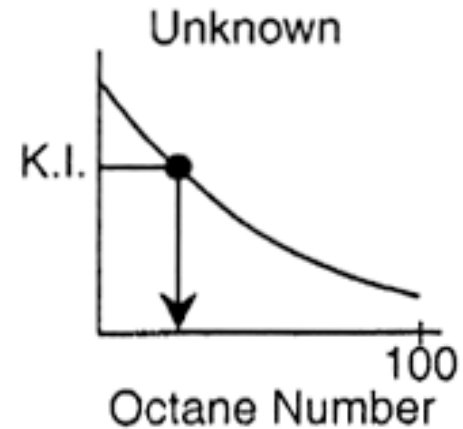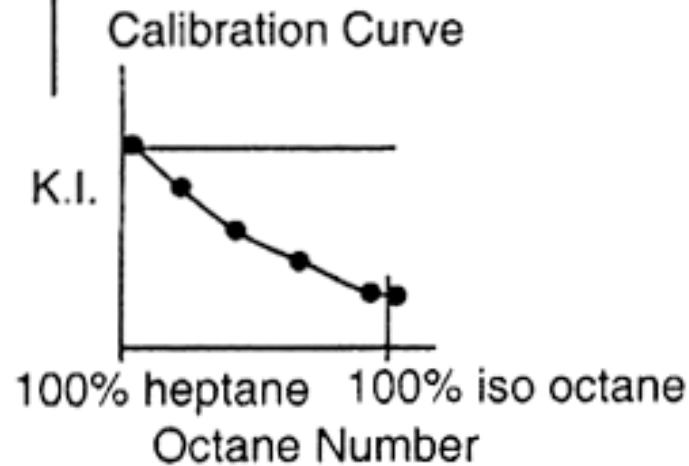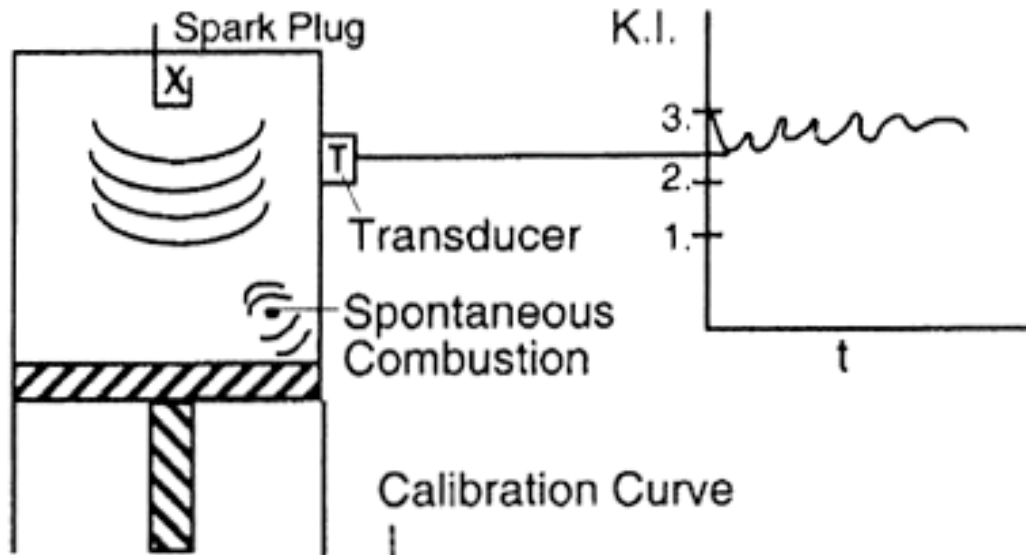# Which step has the largest resistance?



Electrical analog to heterogeneous reactions

# Collecting and Analyzing Data



Collecting information for catalytic reactor design

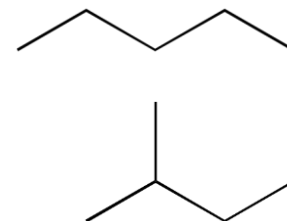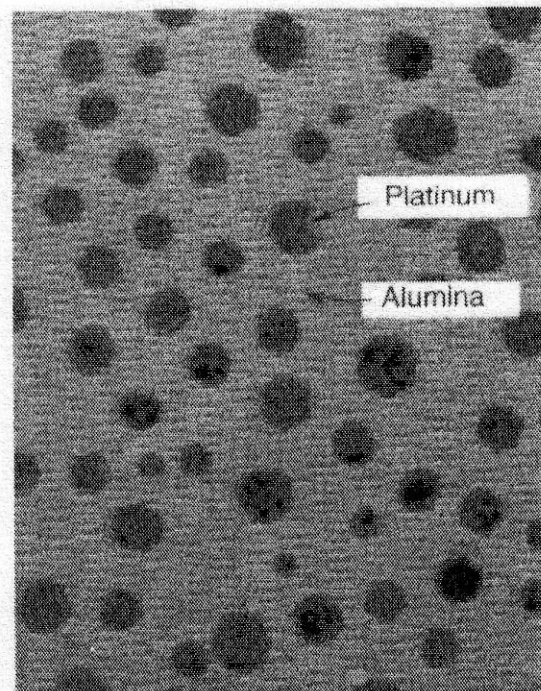# Collecting and Analyzing Data

# Catalytic Reformers

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

### Gasoline

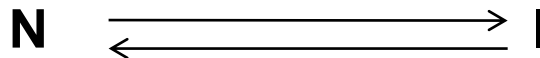| | |
|---|---|
| $C_5$ | 10% |
| $C_6$ | 10% |
| $C_7$ | 20% |
| $C_8$ | 25% |
| $C_9$ | 20% |
| $C_{10}$ | 10% |
| $C_{11-12}$ | 5% |

Platinum

Alumina

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

# Catalytic Reformers

$$n\text{-pentane} \quad \underset{Al_2O_3}{\overset{0.75 \text{ wt\% Pt}}{\rightleftarrows}} \quad i\text{-pentane}$$

$$n\text{-pentane} \xrightarrow[\text{Pt}]{-H_2} n\text{-pentene} \xrightarrow[]{Al_2O_3} i\text{-pentene} \xrightarrow[\text{Pt}]{+H_2} i\text{-pentane}$$

$$n\text{-pentene} \quad \overset{Al_2O_3}{\rightleftarrows} \quad i\text{-pentene}$$

$$\mathbf{N} \quad \rightleftarrows \quad \mathbf{I}$$
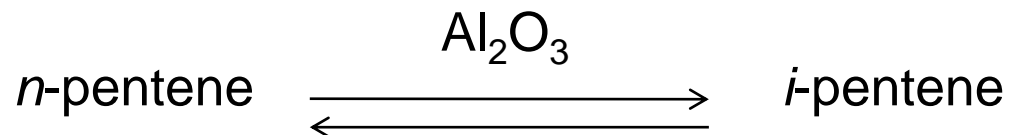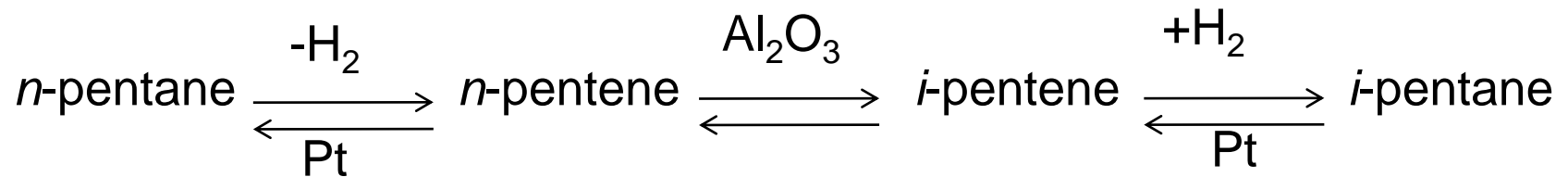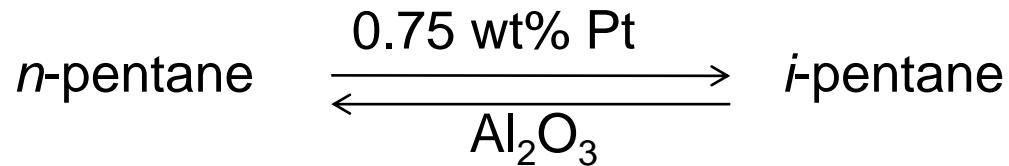
# Catalytic Reformers

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

$$N \xrightleftharpoons{Al_2O_3} I$$
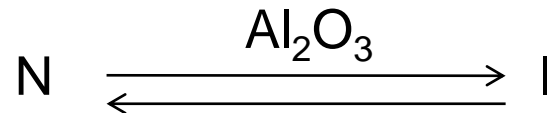
## 1*. Select a mechanism*  (Mechanism Single Site)

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

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

Desorption:     $I \bullet S \Leftrightarrow I + S$

Treat each reaction step as an elementary reaction when writing **rate laws.**

# Catalytic Reformers

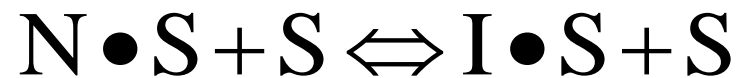2. *Assume a **rate**-limiting step.*
Choose the surface reaction first, since more than 75% of all heterogenous reactions that are not diffusion-limited are surface-reaction-limited. The **rate law** for the surface reaction step is:

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

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

# 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.*

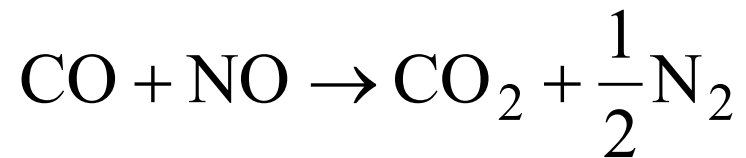$$C_t = C_\upsilon + C_{N \bullet S} + C_{I \bullet S}$$

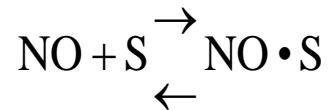5. *Derive the **rate law**. Combine steps 2, 3 and 4 to arrive at the **rate law** :

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

$$-r_N' = r_S = \frac{k(P_N - P_I/K_P)}{(1 + K_N P_N + K_I P_I)}$$
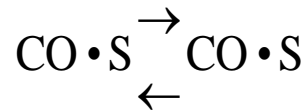
# Catalytic Conversion of Exhaust Gas

|      | 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

$$NO + S \underset{\leftarrow}{\overset{\rightarrow}{\phantom{x}}} NO \cdot S \qquad r_{ANO} = k_{NO}\left[ P_{NO}C_V - \frac{C_{NO \cdot S}}{K_{NO}} \right] \quad C_{NO \cdot S} = K_{NO}P_{NO}C_V$$

$$CO \cdot S \underset{\leftarrow}{\overset{\rightarrow}{\phantom{x}}} CO \cdot S \qquad r_{ACO} = k_{CO}\left[ P_{CO}C_V - \frac{C_{CO \cdot S}}{K_{CO}} \right] \quad C_{CO \cdot S} = K_{CO}P_{CO}C_V$$

$$CO \cdot S + NO \cdot S \rightarrow CO_2 + N \cdot S + S \quad r_S = k_S\left[ C_{CO \cdot S}C_{NO \cdot S} \right]$$
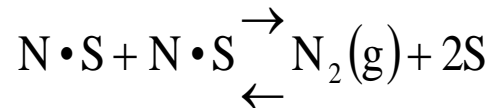
$$N \cdot S + N \cdot S \underset{\leftarrow}{\overset{\rightarrow}{\phantom{x}}} N_2(g) + 2S \qquad r_D = k_D\left[ C_{N \cdot S}^2 - K_{N_2}P_{N_2}C_V^2 \right] \quad C_{N \cdot S} = C_V\sqrt{K_N P_{N_2}}$$

# 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

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

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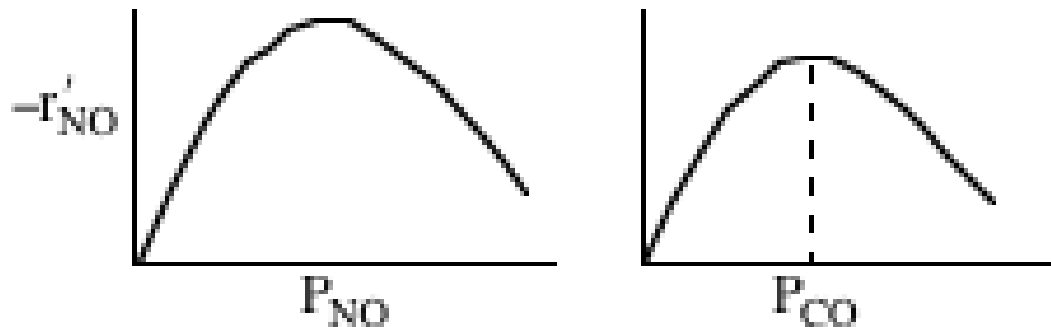
$$-r'_{NO} = \frac{kP_{NO}P_{CO}}{\left(1 + K_{NO}P_{NO} + K_{CO}P_{CO} + \sqrt{K_{N_2}P_{N_2}}\right)^2}$$

# 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