Advanced Reactor Design

Week 5

Catalysts and Catalysis

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Introduction

- This presentation covers catalysts and catalysis, including catalytic mechanisms, data analysis, and chemical vapor deposition (CVD).

Topics to be Addressed

- - Introduction to Catalysts and Catalysis
- - Catalytic Steps
- - Catalytic Mechanisms
- - Data Analysis
- - Chemical Vapor Deposition (CVD)

Objectives

- \- Understand the role of catalysts in chemical reactions
- \- Analyze catalytic mechanisms and reaction steps
- \- Apply data analysis methods for catalytic processes
- \- Explore applications of Chemical Vapor Deposition (CVD)

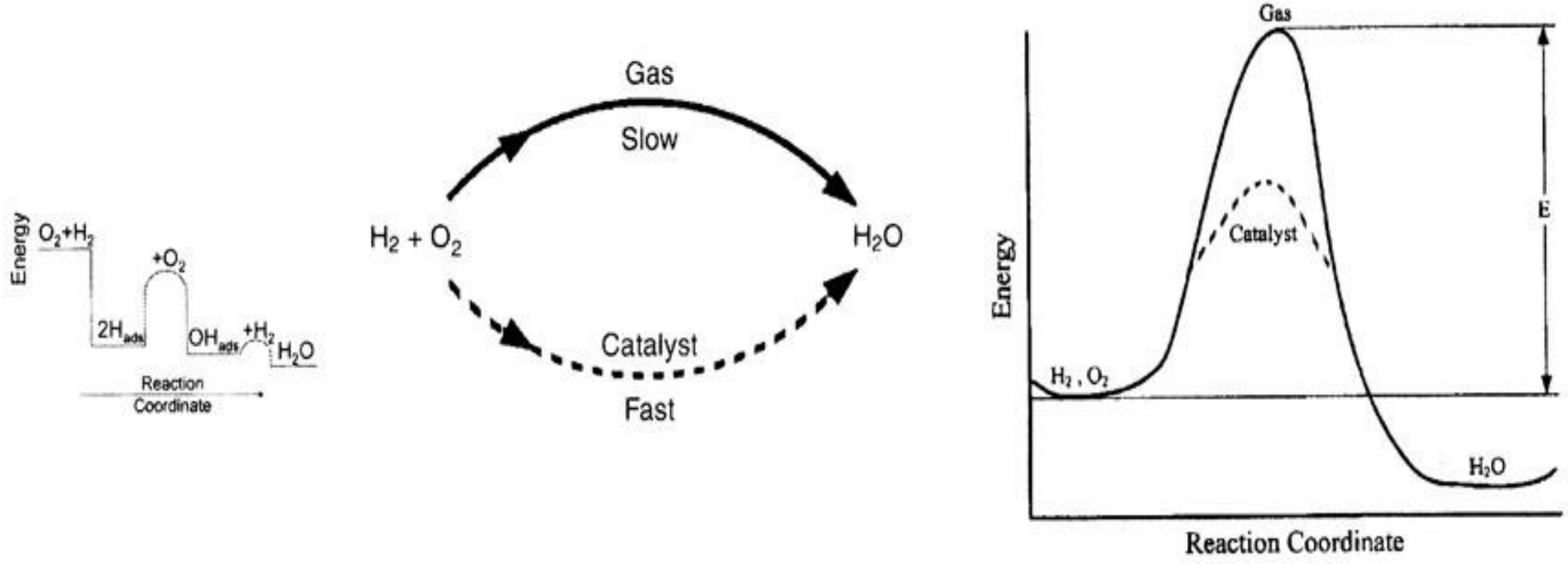
Catalysts and Catalysis

- 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

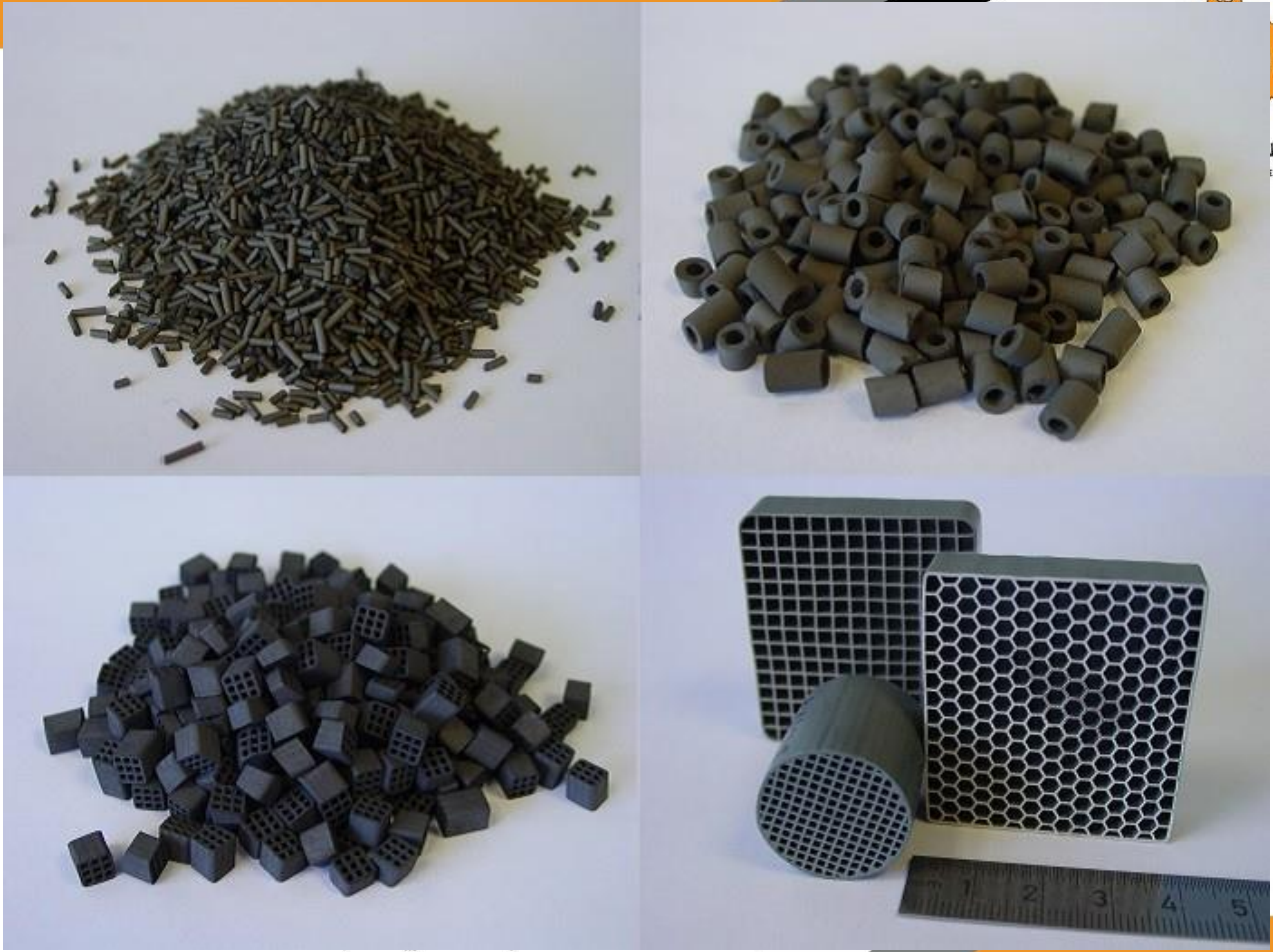
Catalysts affect both selectivity and yield



Different reaction paths

Catalysts and Catalysis

Different shapes and sizes of catalyst.


1
2
3
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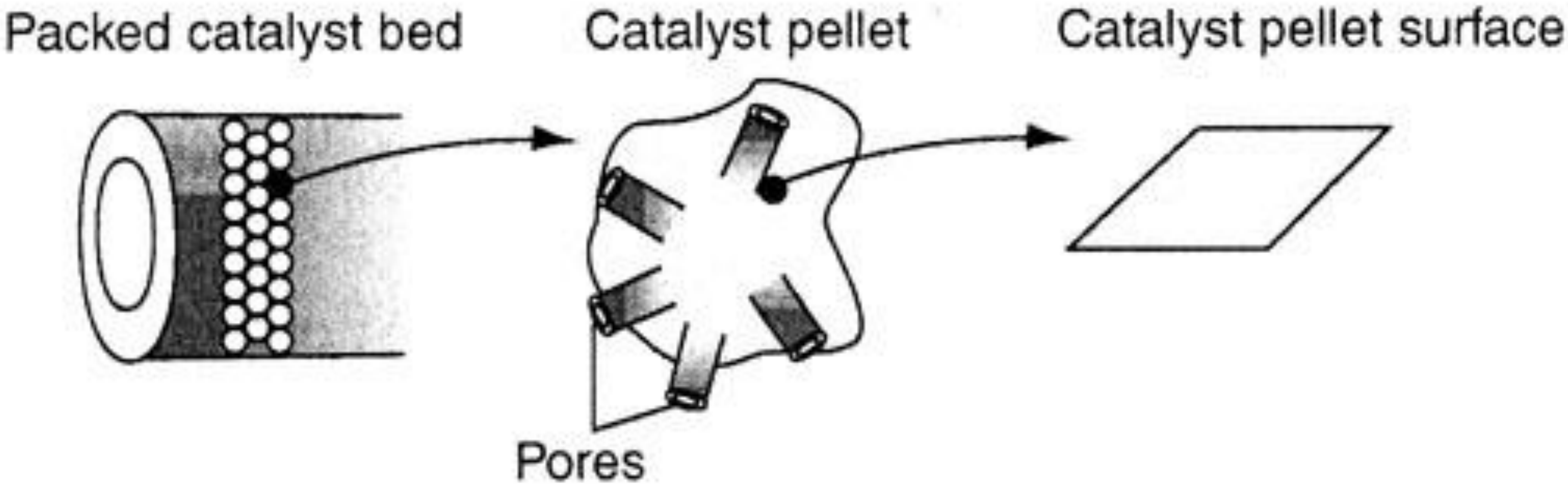
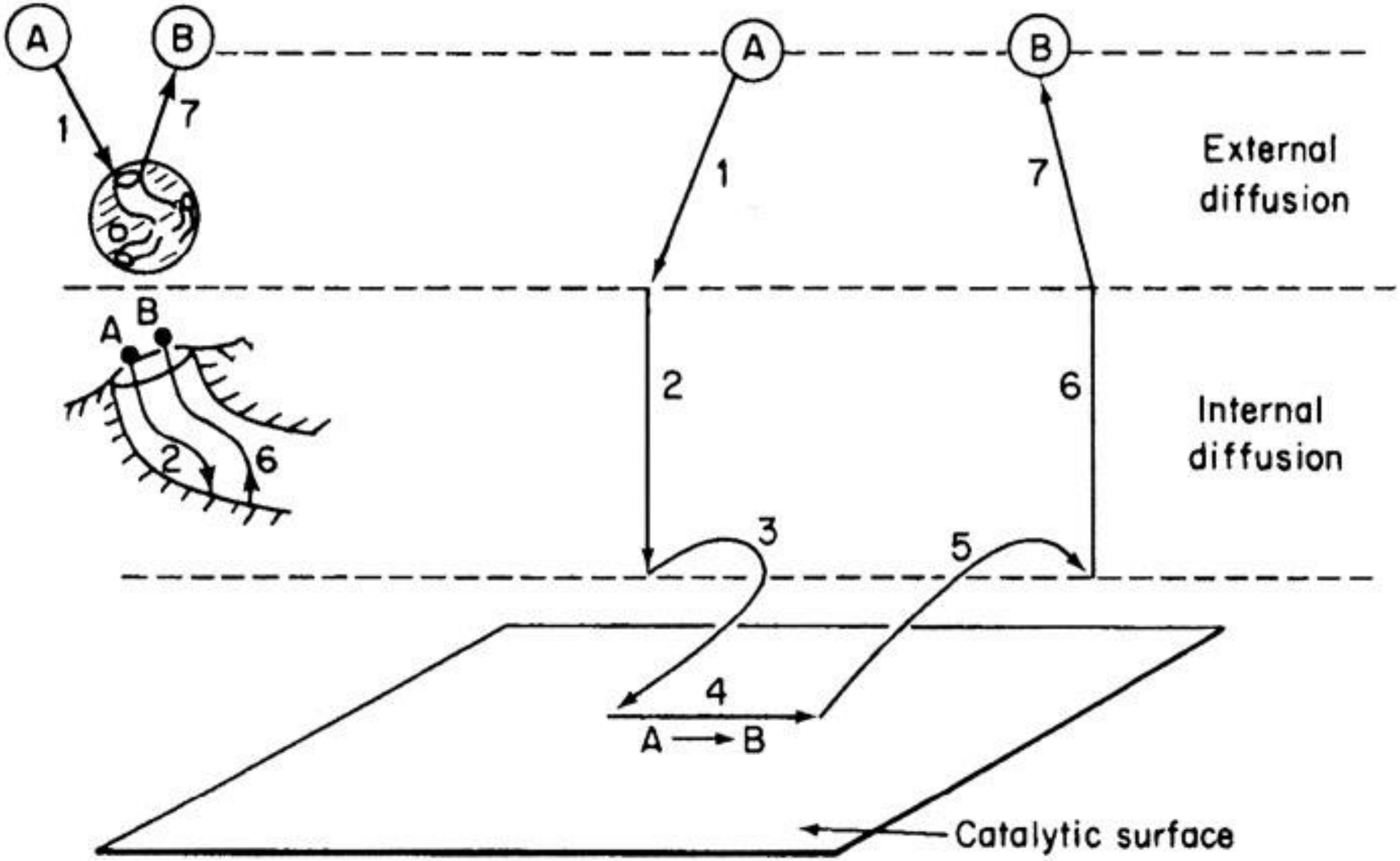
5

Catalysts and Catalysis

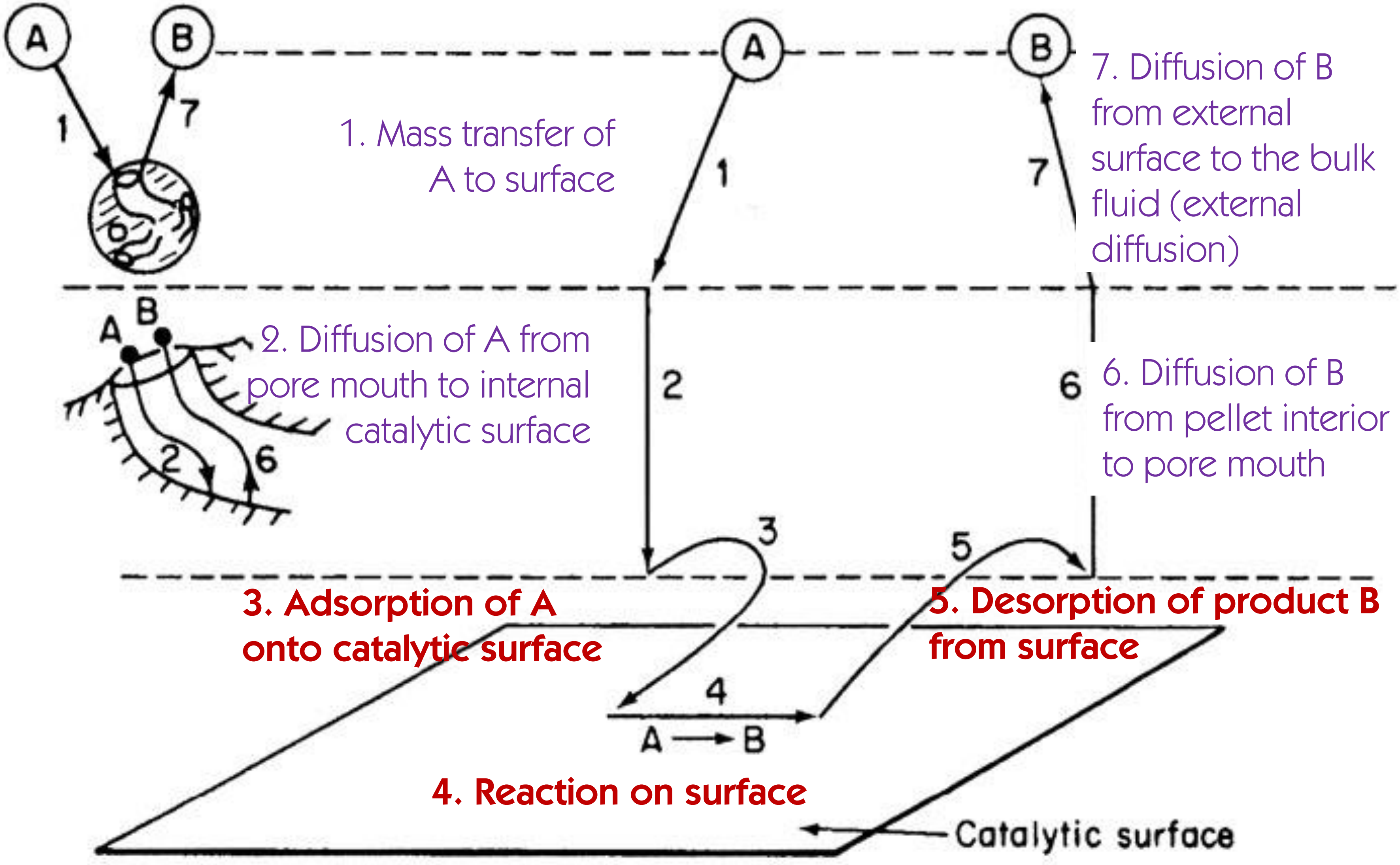


Catalytic packed-bed reactor, schematic.

Steps in a Catalytic Reaction



Steps in a Heterogeneous Catalytic Reaction



1. Mass transfer of A to surface

2. Diffusion of A from pore mouth to internal catalytic surface

3. Adsorption of A onto catalytic surface

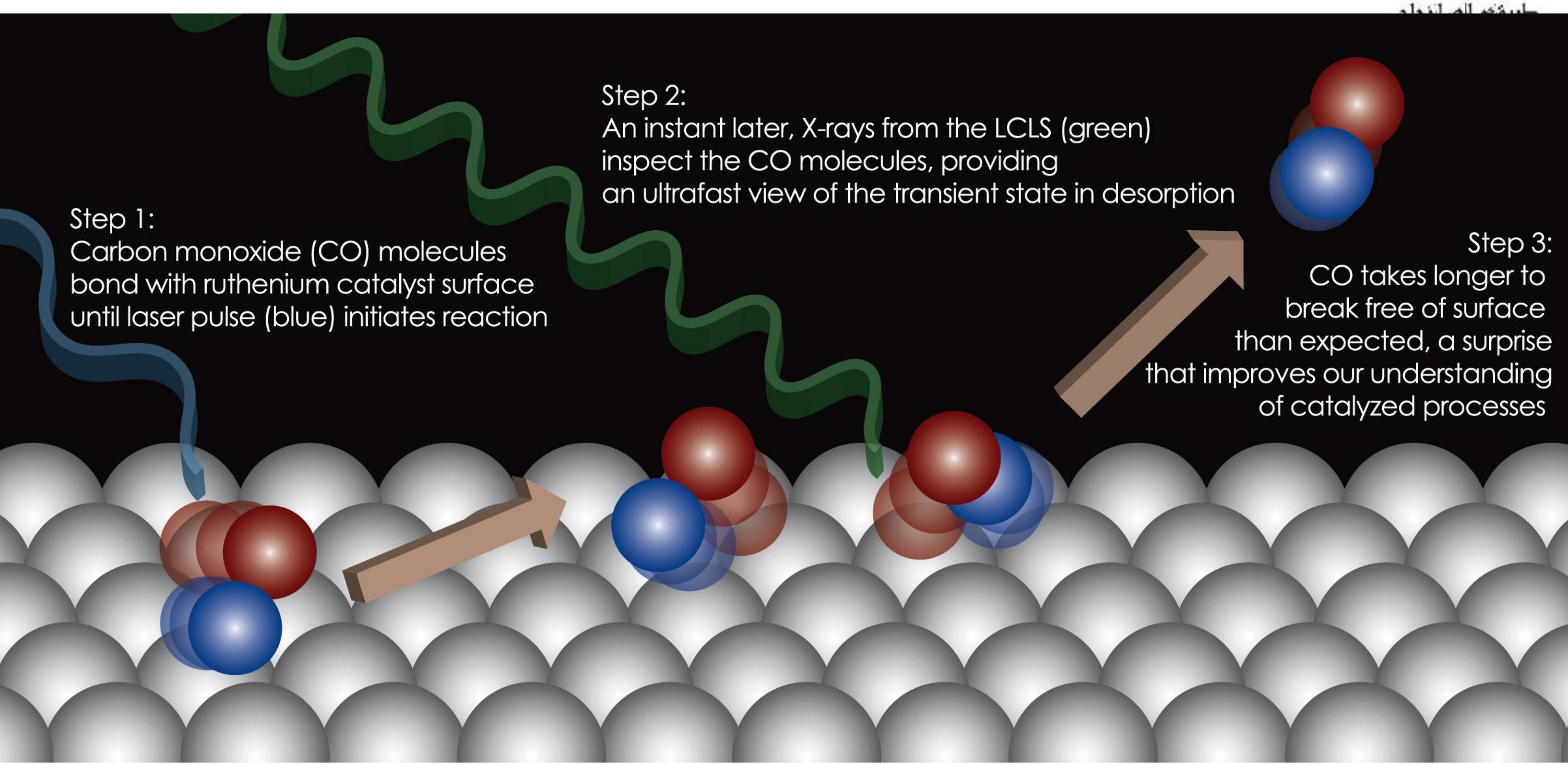
4. Reaction on surface

5. Desorption of product B from surface

6. Diffusion of B from pellet interior to pore mouth

7. Diffusion of B from external surface to the bulk fluid (external diffusion)

Assumes steps 1,2,6 & 7 are fast, so only steps 3, 4, and 5 need to be considered



Step 1:
Carbon monoxide (CO) molecules bond with ruthenium catalyst surface until laser pulse (blue) initiates reaction

Step 2:
An instant later, X-rays from the LCLS (green) inspect the CO molecules, providing an ultrafast view of the transient state in desorption

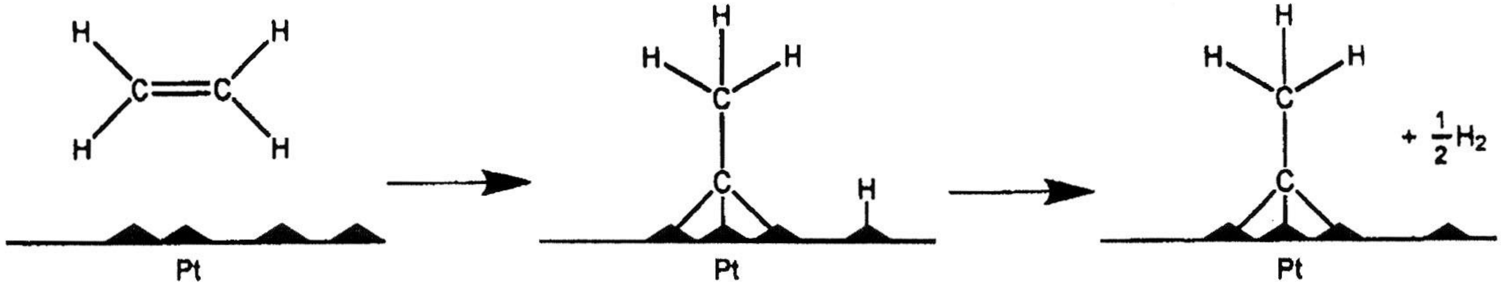
Step 3:
CO takes longer to break free of surface than expected, a surprise that improves our understanding of catalyzed processes

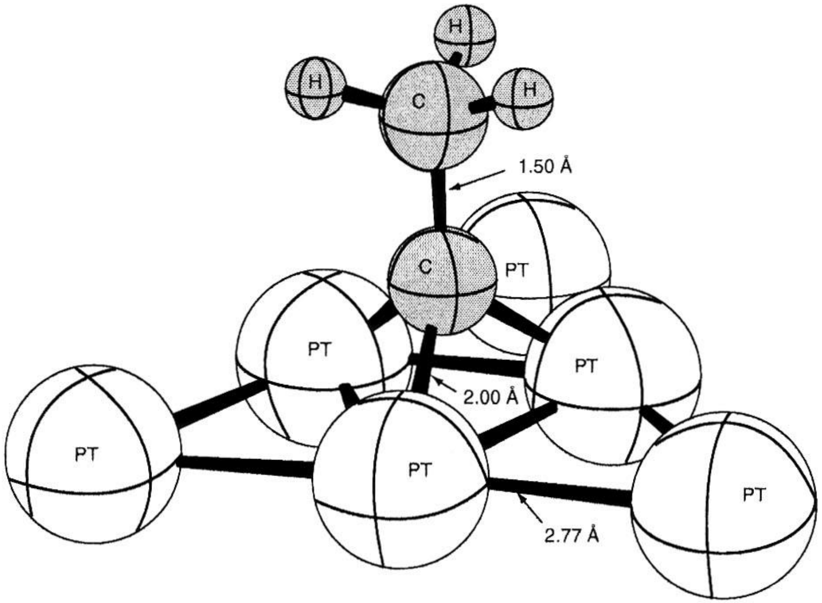
Active Sites

- 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



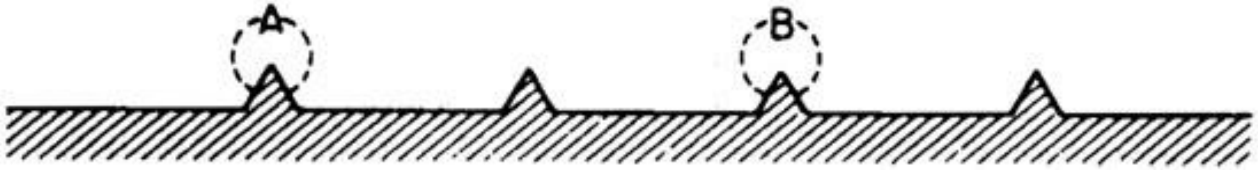


Pt (III) + ethylidyne

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

$$A + S \rightleftarrows A \cdot S$$



Vacant and occupied sites

For the system shown, the total concentration of sites is

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

Adsorption Step

The adsorption of A (gas phase) on an active site S is represented by:

A

-S-S-S-

$$A(g) + S \rightleftarrows A\cdot S$$

A

|

-S-S-S-

S: open (vacant) surface site   A·S: A bound to a surface site

Rate of adsorption = rate of attachment – rate of detachment

$$r_{AD} = k_A P_A C_v - k_{-A} C_{A\cdot S}$$

partial pressure of A

Molar conc of vacant sites on surface

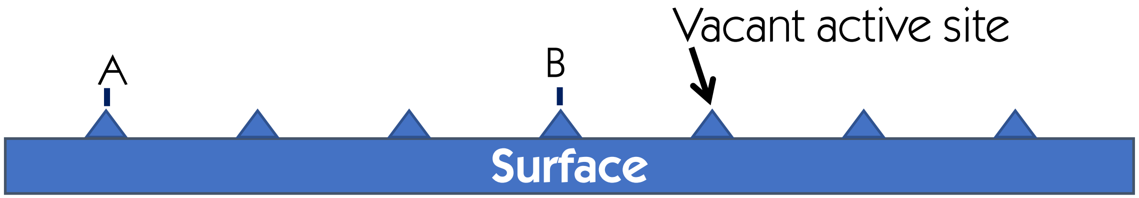
Using adsorption equilibrium constant (K_A)

$$K_A = \frac{k_A}{k_{-A}}$$

$$r_{AD} = k_A \left(P_A C_v - \frac{C_{A\cdot S}}{K_A} \right)$$

Equation I

Site Balance



C_v is not measurable, but the total # of sites, C_t can be measured

Assume the total # of active sites remains constant (no catalyst deactivation occurs):

Site balance: $\boxed{C_t = C_v + C_{A\cdot S} + C_{B\cdot S}}$

Use to express C_v in terms of measurable species

The Adsorption Step

$$\mathrm{A}+\mathrm{S}\leftrightarrow \mathrm{A}\bullet\mathrm{S}$$

$$r_{AD}=k_AP_AC_v \text{ - } \mathrm{k}_{\text{-A}}C_{A\bullet S} \;=k_A\left[P_AC_V-C_{A\bullet S}/K_A\right]$$

$$K_A=\mathrm{k}_{\mathrm{A}}/k_{-A} \quad [\mathrm{atm}^{-1}]$$

$$@\,\text{equilibrium}:\; r_{AD}=0 \qquad\qquad C_{AS}=k_AP_AC_V$$

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

$$C_t=C_V+C_{A\bullet S}=C_V+K_AP_AC_V=\;C_V(1+\;K_AP_A)$$

$$C_V=\frac{C_t}{1+K_AP_A}$$

Langmuir Adsorption Isotherm

طريقك إلى النجاح
YOUR WAY TO SUCCESS

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

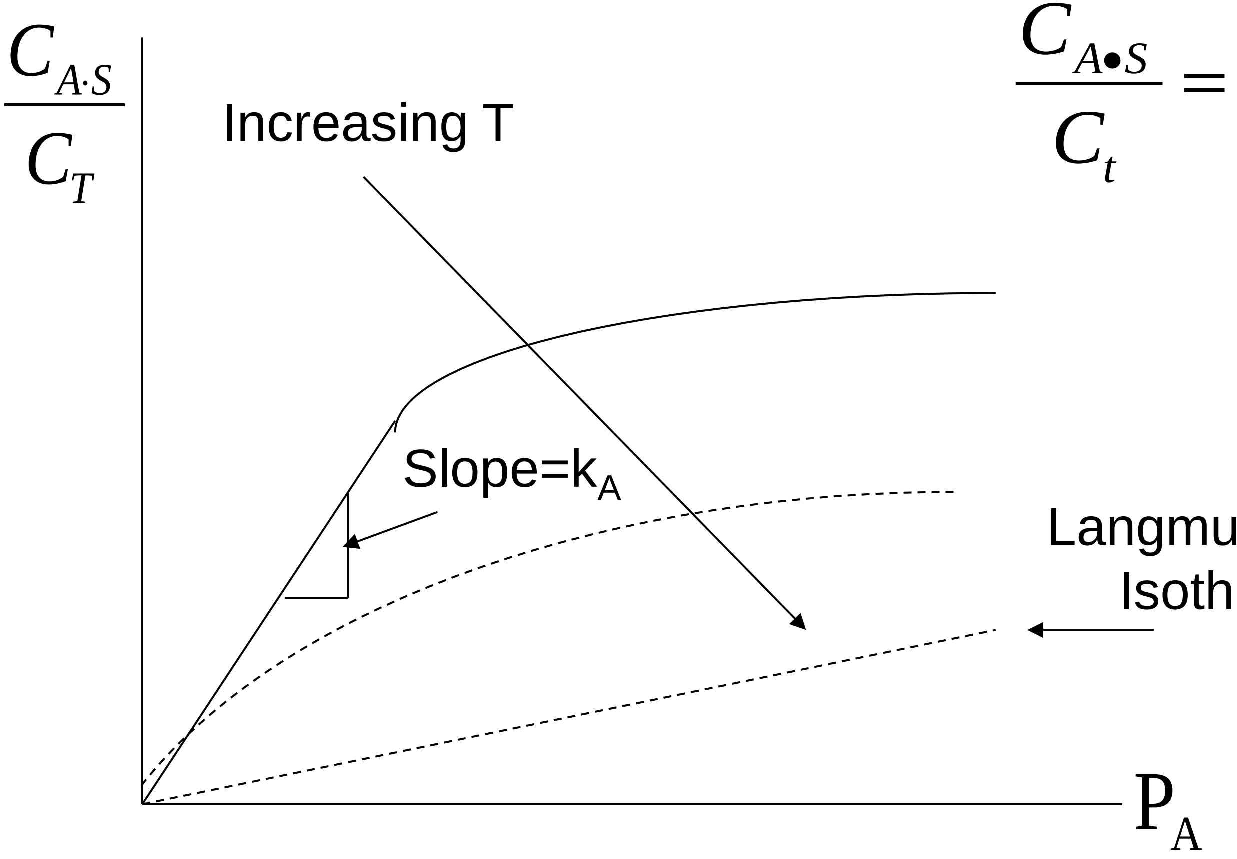
$$C_{A \cdot S} = K_A P_A C_V$$

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

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

Langmuir Adsorption Isotherm

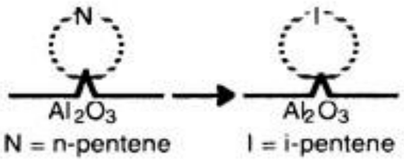
$$\frac{C_{A\bullet S}}{C_t} = \frac{K_A P_A}{1+K_A P_A}$$

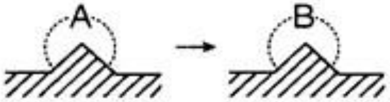


Langmuir Adsorption Isotherm

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





Single site

$$A\cdot S \rightleftarrows B\cdot S$$

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

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

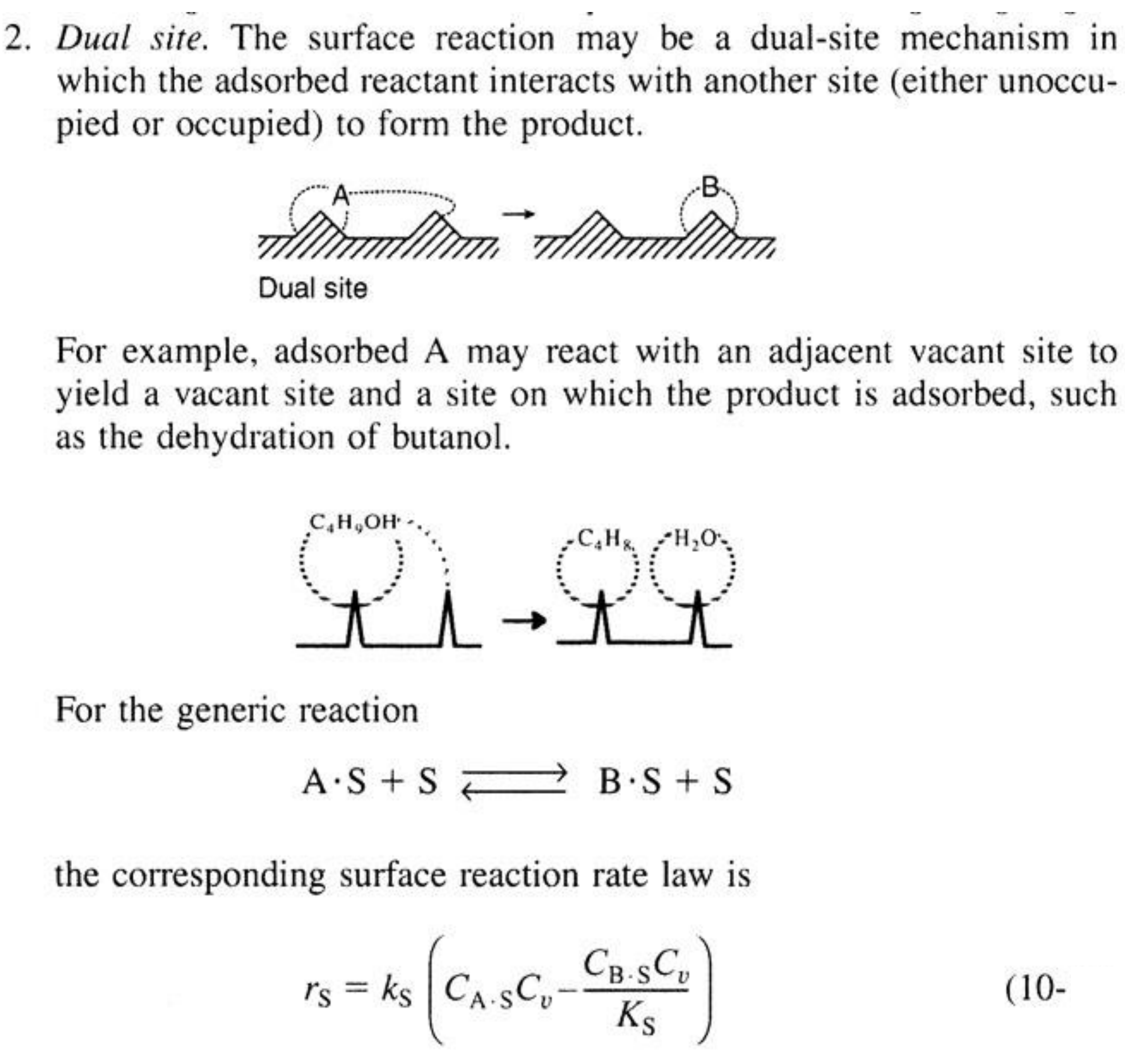
where K_S is the surface reaction equilibrium constant $K_S = k_S/k_{-S}$

Single Site

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

K_s = (dimensionless)

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

$$A\cdot S + S \rightleftarrows B\cdot S + S$$

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

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

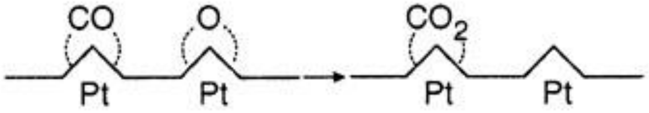
$$k_S = \left(\frac{\text{gcat}}{\text{mol} \cdot \text{s}}\right)$$

K_S = (dimensionless)

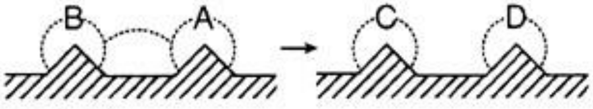
the corresponding surface reaction rate law is

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

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

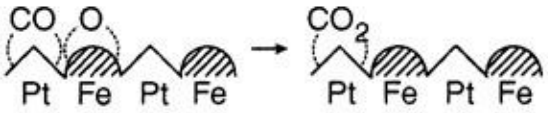
$$A \cdot S + B \cdot S \rightleftarrows C \cdot S + D \cdot S$$

the corresponding surface reaction rate law is

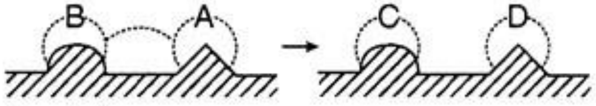
$$r_S = k_S \left(C_{A \cdot S} C_{B \cdot S} - \frac{C_{C \cdot S} C_{D \cdot S}}{K_S} \right)$$

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

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

the corresponding surface reaction rate law is

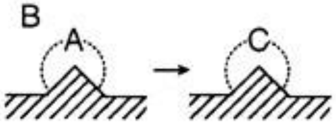
$$r_S = k_S \left(C_{A \cdot S} C_{B \cdot S'} - \frac{C_{C \cdot S'} C_{D \cdot S}}{K_S} \right)$$

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

$$A \cdot S + B(g) \rightleftarrows C \cdot S$$

the corresponding surface reaction rate law is

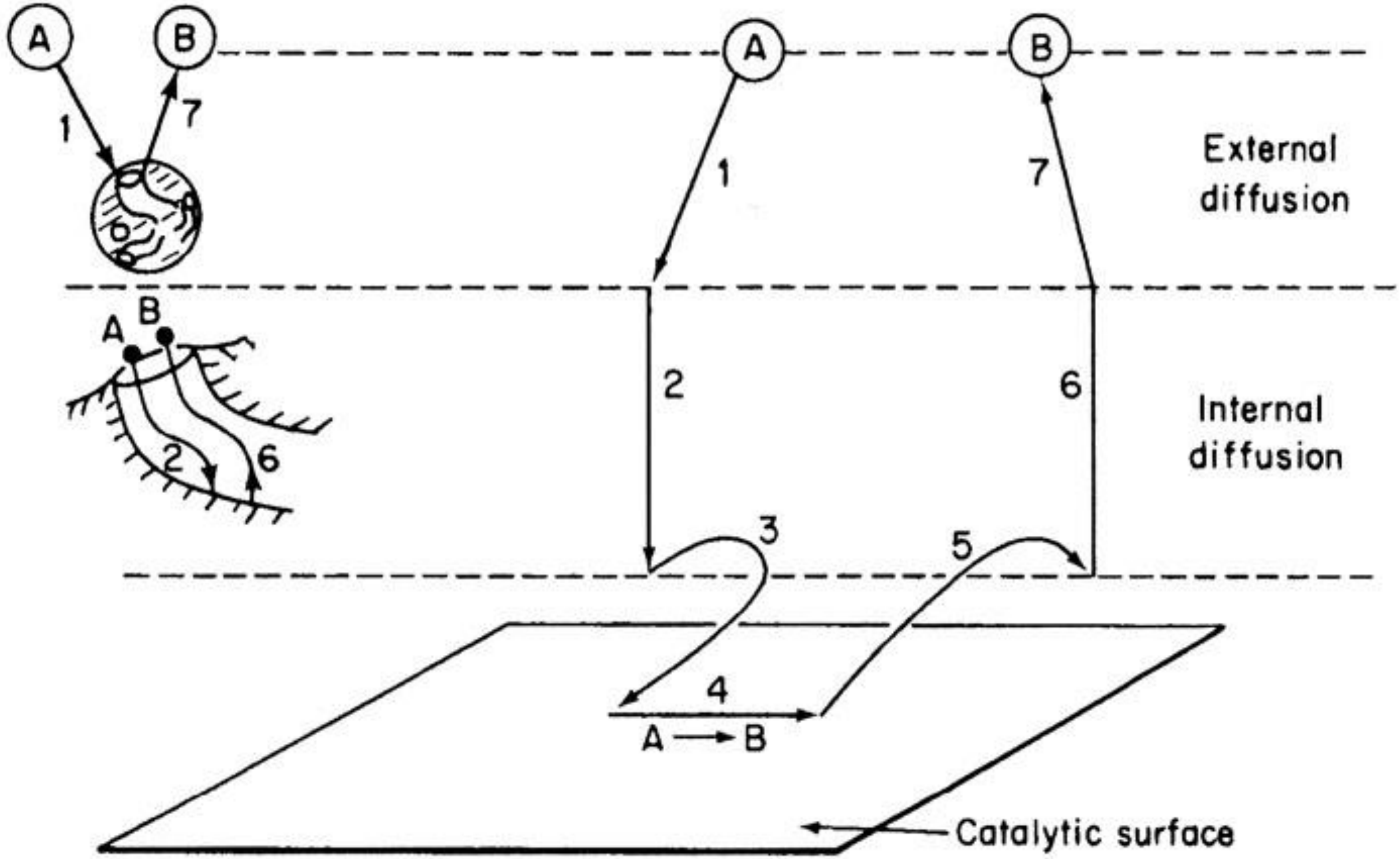
$$r_S = k_S \left(C_{A \cdot S} P_B - \frac{C_{C \cdot S}}{K_S} \right)$$

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

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

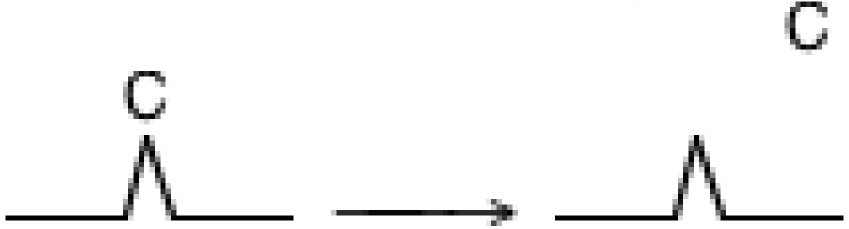
This type of mechanism is referred to as an *Eley–Rideal mechanism.*

Steps in a Catalytic Reaction



Desorption from the Surface for the Reaction

$$A \longrightarrow B + C$$



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

$$r_{DC} = k_D\left[C_{C\bullet S} - \frac{P_C C_\upsilon}{K_{DC}}\right]$$

$$r_{DC} = -r_{ADC}$$

$$K_{DC} = \frac{1}{K_C}$$

$$r_{DC} = k_D[C_{C\bullet S} - K_C P_C C_\upsilon]$$

Steps in a Single-Site Catalytic Reactor

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

$$-r_A = r_{Ad} = k_{Ad}\left[P_A C_v - \frac{C_{A\bullet S}}{\mathrm{k}_{\mathrm{A}}}\right]$$

Surface Reaction $A \bullet S \leftrightarrow B \bullet S$

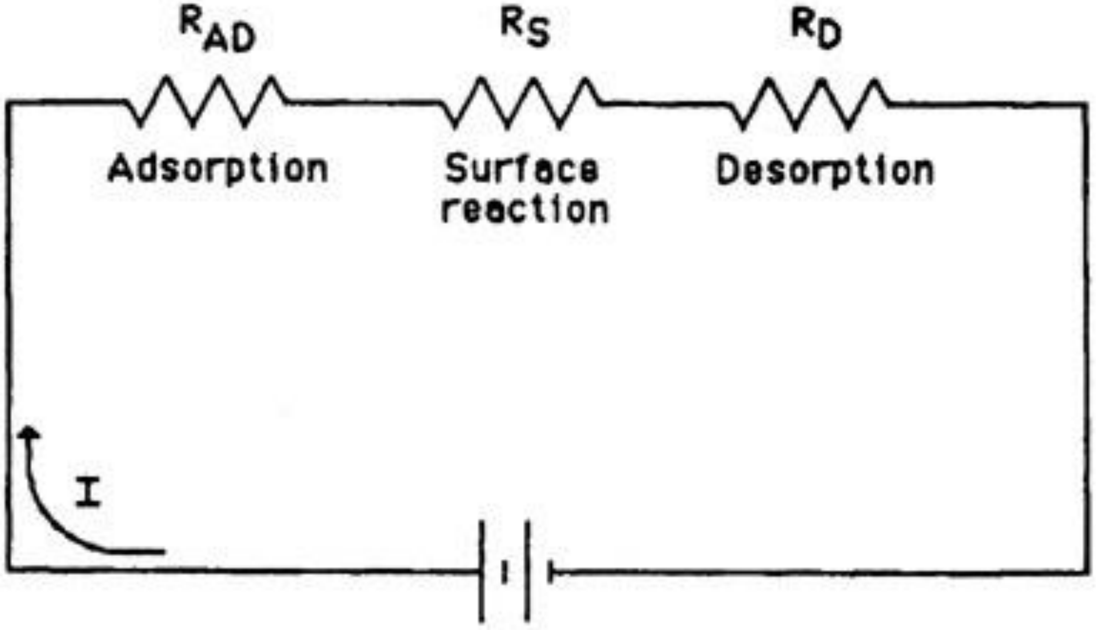
$$-r_A = r_S = k_S\left[C_{A\bullet S} - \frac{C_{B\bullet S}}{\mathrm{k}_{\mathrm{C}}}\right]$$

Desorption $B \bullet S \leftrightarrow B + S$

$$-r_A = r_D = k_D\left[C_{B\bullet S} - k_B P_B C_B\right]$$

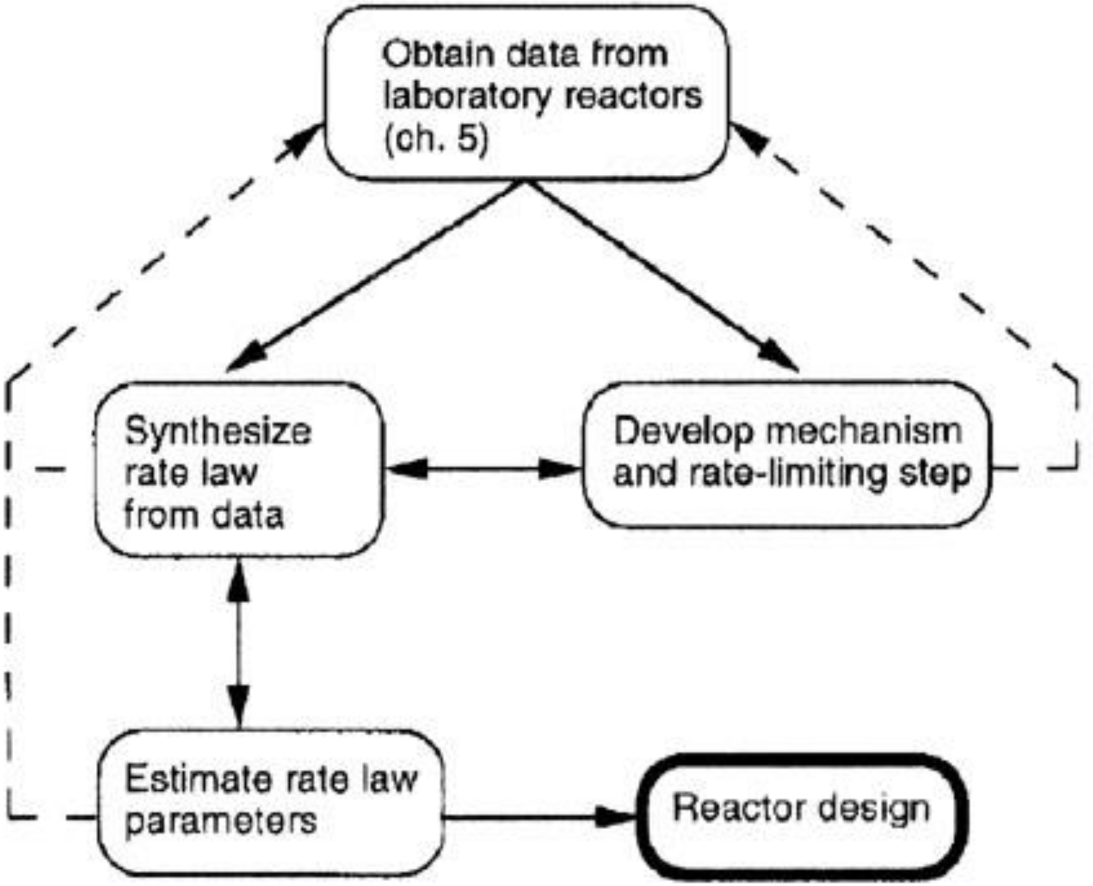
Which step is the Rate Limiting Step (RLS)?

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



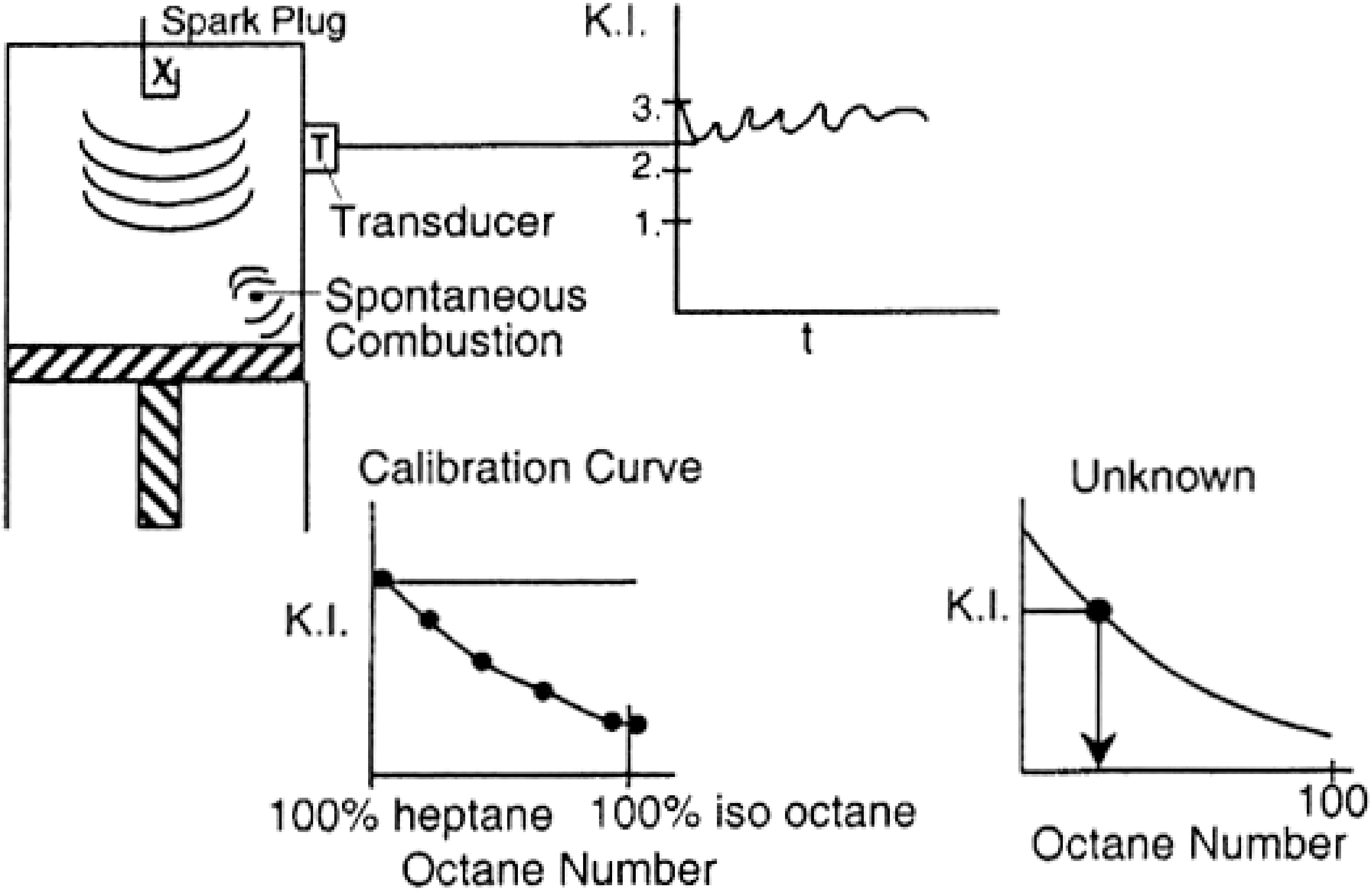
Electrical analog to heterogeneous reactions

Collecting and Analyzing Data



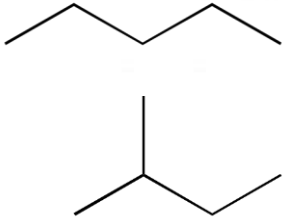
Collecting information for catalytic reactor design

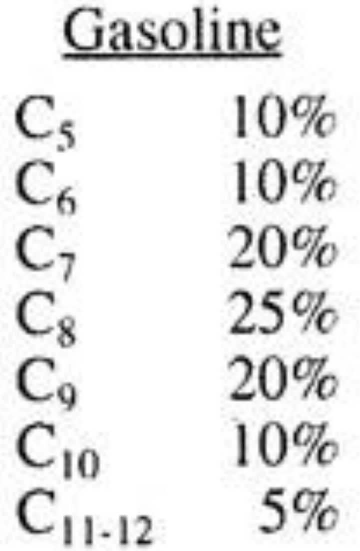
Collecting and Analyzing Data



Catalytic Reformers

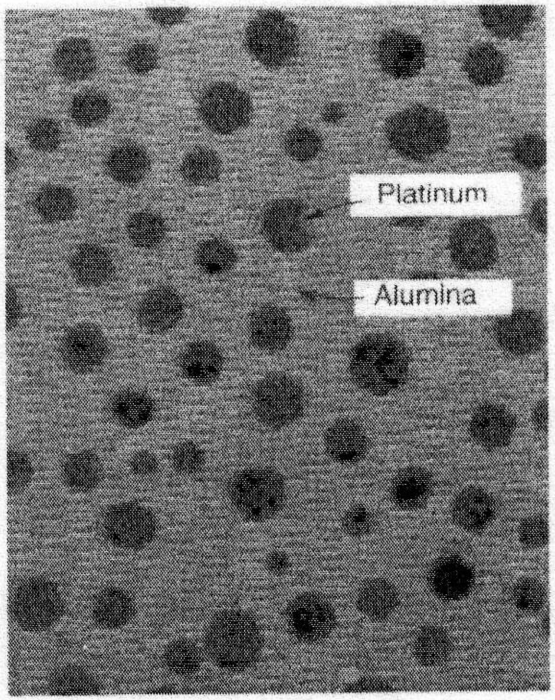
- Normal Pentane Octane Number = 62
- Iso-Pentane Octane Number = 95





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

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

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

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

$$\mathbf{N} \rightleftarrows \mathbf{I}$$

Catalytic Reformers

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

$$\mathrm{N} \overset{\mathrm{Al_2O_3}}{\rightleftarrows} \mathrm{I}$$

1. *Select a mechanism* (Mechanism Single Site)

Adsorption on Surface: $\mathrm{N} + \mathrm{S} \Leftrightarrow \mathrm{N} \bullet \mathrm{S}$

Surface Reaction: $\mathrm{N} \bullet \mathrm{S} \Leftrightarrow \mathrm{I} \bullet \mathrm{S}$

Desorption: $\mathrm{I} \bullet \mathrm{S} \Leftrightarrow \mathrm{I} + \mathrm{S}$

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

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

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

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

$$\mathrm{NO + S \rightleftarrows NO \bullet S} \qquad r_{ANO} = k_{NO}\left[P_{NO}C_V - \frac{C_{NO\bullet S}}{K_{NO}}\right] \qquad C_{NO\bullet S} = K_{NO}P_{NO}C_V$$

$$\mathrm{CO \bullet S \rightleftarrows CO \bullet S} \qquad r_{ACO} = k_{CO}\left[P_{CO}C_V - \frac{C_{CO\bullet S}}{K_{CO}}\right] \qquad C_{CO\bullet S} = K_{CO}P_{CO}C_V$$

$$\mathrm{CO \bullet S + NO \bullet S \rightarrow CO_2 + N \bullet S + S} \qquad r_S = k_S\left[C_{CO\bullet S}C_{NO\bullet S}\right]$$

$$\mathrm{N \bullet S + N \bullet S \rightleftarrows N_2(g) + 2S} \qquad r_D = k_D\left[C_{N\bullet S}^2 - K_{N_2}P_{N_2}C_V^2\right] \qquad C_{N\bullet S} = C_V\sqrt{K_N P_{N_2}}$$

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

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

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

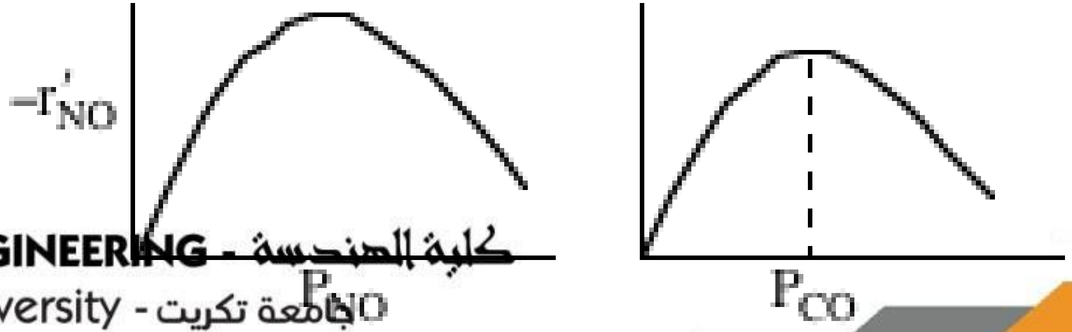
$$-r'_{NO} = \frac{k P_{NO} P_{CO}}{\left(1 + K_{NO}P_{NO} + K_{CO}P_{CO} + \sqrt{K_{N_2}P_{N_2}}\right)^2}$$

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

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



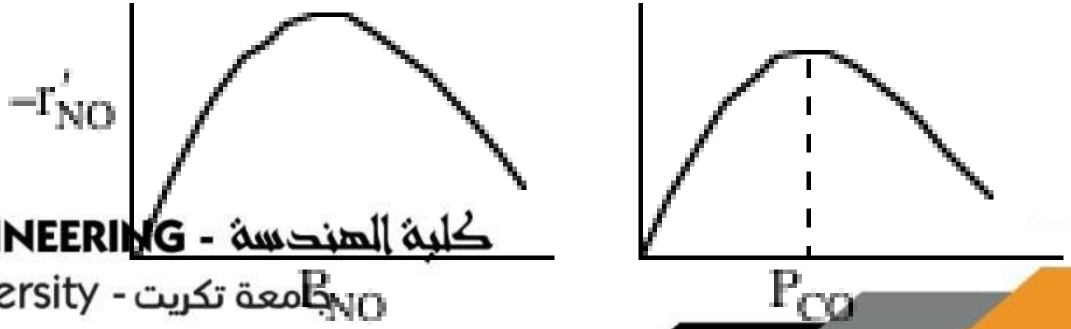
Catalytic Conversion of Exhaust Gas

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

Find optimum partial pressure of CO

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

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

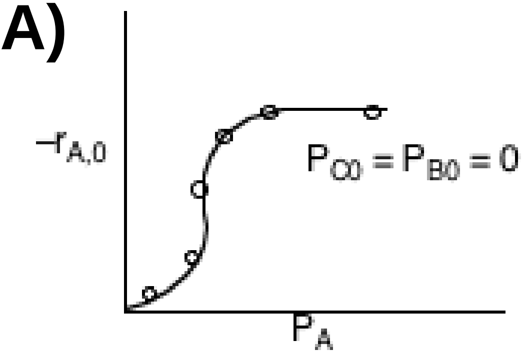


Catalytic Mechanisms

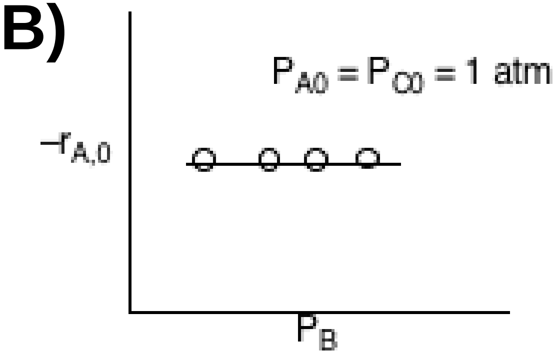
$$2A \underset{\text{cat}}{\rightleftarrows} B + C$$

(a) The initial rate of reaction is shown below

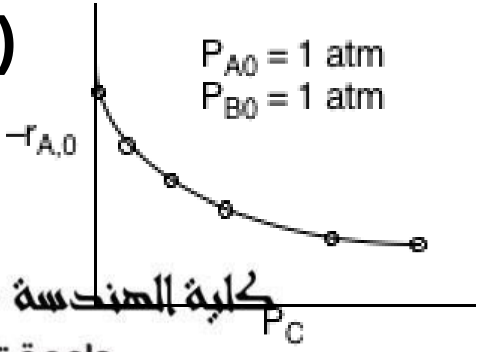
(A)



(B)



(C)



Catalytic Mechanisms

$$A \rightleftarrows B + C$$

(A)

$$-r_A = \frac{kP_A}{1 + K_A P_A + K_B P_B}$$

(B)

$$-r_A = \frac{kP_A}{\left(1 + K_A P_A + K_C P_C\right)}$$

(A)

$$A + S \rightleftarrows A \bullet S$$

$$A \bullet S \longrightarrow B \bullet S + C$$

$$B \bullet S \rightleftarrows B + S$$

(B)

$$A + S \rightleftarrows A \bullet S$$

$$A \bullet S \longrightarrow B + C \bullet S$$

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

Catalytic Mechanisms

$$2A \rightleftarrows B + C$$

(C)

$$-r_A = \frac{kP_A^2}{\left(1 + K_A P_A + K_C P_C\right)^2}$$

(D)

$$-r_A = \frac{kP_A^2}{\left(1 + K_A P_A + K_C P_C\right)^2}$$

(C)

$$A + S \rightleftarrows A \bullet S$$

$$A \bullet S + A(g) \longrightarrow B + C \bullet S$$

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

(D)

$$A + S \rightleftarrows A \bullet S$$

$$A \bullet S + A \bullet S \longrightarrow B + S + C \bullet S$$

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

Catalytic Mechanisms

$$2A \longrightarrow B + C$$

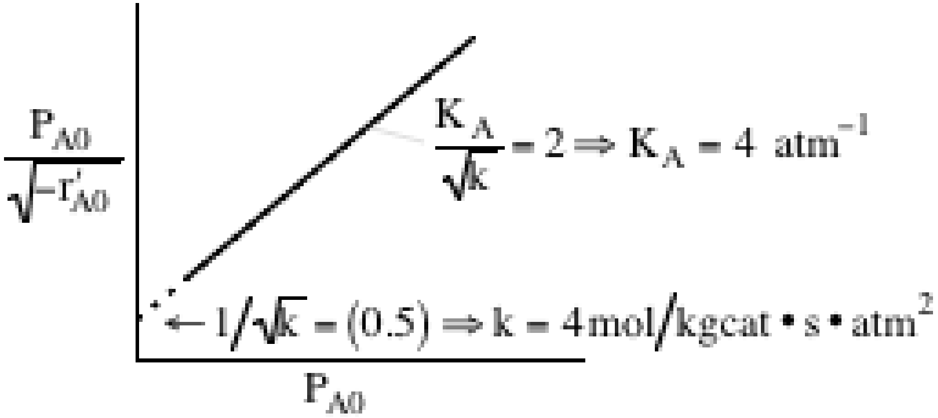
$$A + S \rightleftarrows A \bullet S$$

$$A \bullet S + A \bullet S \longrightarrow B + C \bullet S$$

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

$$-r'_A = \frac{kP_A^2}{\left(1 + K_A P_A + K_C P_C\right)^2}$$

Catalytic Mechanisms



$$-r'_{A0} = \frac{4P_A^2}{1 + 4P_{A0} + K_C P_{C0}}$$

For $P_{C0} = 2$ atm and $P_{A0} = 1$ atm, then $-r'_{A0} = 0.0138 \frac{\text{mol}}{\text{kgcat} \bullet \text{s}}$

$$-r'_{A0} = \frac{4}{(1 + 4 + 2K_C)^2} = 0.0138$$

One equation and one unknown

$$K_C = 6\ \text{atm}^{-1}$$

$$-r'_{A0} = \frac{4P_A^2}{(1 + 4P_A + 6P_C)^2}$$

Catalytic Mechanisms

$$2A \rightleftarrows B + C$$

$$A + S \rightleftarrows A \bullet S \qquad -r'_A = r_{A0} = k_A\left[P_A C_V - \frac{C_{A\bullet S}}{K_A}\right] \Rightarrow C_{A\bullet S} = K_A P_A C_V$$

$$A \bullet S + A \bullet S \rightleftarrows B + S + C \bullet S \qquad -r'_A = r_S = k_S C^2_{A\bullet S}$$

$$C \bullet S \rightleftarrows C + S \qquad -r_A = r_{DC} = k_{DC}\left[C_{C\bullet S} - P_C C_V K_C\right] \Rightarrow C_{C\bullet S} = K_C P_C C_V$$

Where $K_A = 4\ \text{atm}^{-1}$ and $K_C = 6\ \text{atm}^{-1}$

1) At what is the ratio of sites with A adsorbed to those sites with C adsorbed when the conversion is 50%?
2) What is the conversion when the sites with A adsorbed are equal to those with C adsorbed?

Catalytic Mechanisms

$$2A \longrightarrow B + C$$

$$A \longrightarrow \frac{B}{2} + \frac{C}{2}$$

$$K_A = 4 \text{ and } K_C = 6$$

Ratio of site concentrations

$$\frac{C_{A \bullet S}}{C_{C \bullet S}} = \frac{K_A\, P_A\, C_V}{K_C\, P_C\, C_V} = \frac{K_A\, P_A}{K_C\, P_C}$$

$$P_A = P_{A0}(1 - X)/(1 + \varepsilon X)$$

$$P_C = P_{A0}\frac{X}{2(1 + \varepsilon X)}$$

$$\frac{C_{A \bullet S}}{C_{C \bullet S}} = \frac{K_A\, P_{A0}\left(\dfrac{1 - X}{1 + \varepsilon X}\right)\dfrac{P}{P_0}}{K_C\, P_{A0}\left(\dfrac{X/2}{1 + \varepsilon X}\right)\dfrac{P}{P_0}} = 2\frac{K_A(1 - X)}{K_C\, X}$$

Catalytic Mechanisms

1) At X = 0.5

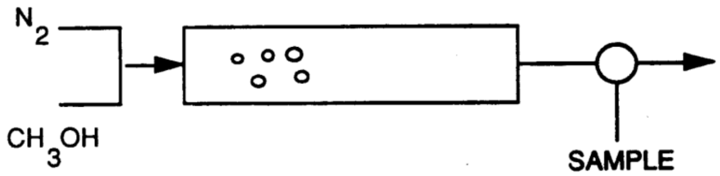
$$\frac{C_{A\bullet S}}{C_{C\bullet S}} =\sim \frac{(2)(4)(1-0.5)}{6(0.5)} = 1.33$$

2) At an equal concentrations of A and C sites, the conversion will be

$$\frac{C_{A\bullet S}}{C_{C\bullet S}} = 1 = \frac{2K_A(1-X)}{K_C\ X}\ ,\quad \text{then}\quad X = \frac{2K_A}{K_C + 2K_A} = \frac{(2)(4)}{6+(2)(4)} = \frac{8}{14}$$

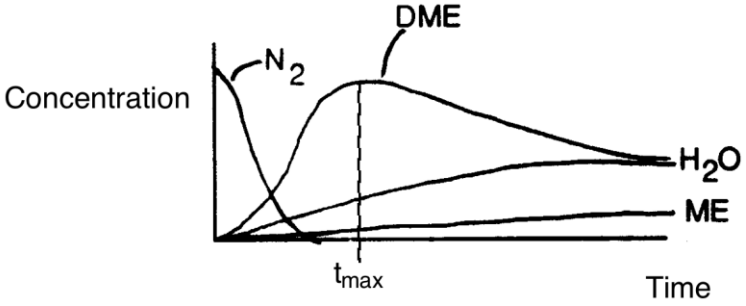
$$X = 0.57$$

Dimethyl Either



$$2CH_3OH \longrightarrow CH_3 - O - CH_3 + H_2O$$

$$2ME \longrightarrow DME + W$$



Initially water does not exit the reactor the same as DME because
Which of the following best describes the data

- **A** There is more DME than water.
- **B** Steady state has been reached.
- **C** Water reacts with ME.
- **D** Water is adsorbed on the surface.

Guidelines for Deducing Mechanisms

- More than 70% of heterogeneous reaction mechanisms are surface reaction limited
- If a species appears in the numerator of the rate law, it is probably a reactant
- If a species appears in the denominator of the rate law, it is probably adsorbed in the surface

The overall reaction for the hydrogenation (H) of ethylene (E) [illegible] a cobalt-molybdenum catalyst to form ethane (A) is $H_2(g) + C_2H_4(g) \rightarrow C_2H_6(g)$ and the observed rate law is:

$$-r'_E = \frac{kP_EP_H}{1+K_EP_E}$$

Suggest a mechanism and rate-limiting step that is consistent with the rate law

P_E appears in the denominator of the observed rate eq, so P_E is adsorbed on the surface. Neither P_H or P_A are in the denominator, so neither H or A are adsorbed on the surface.

$$\text{Adsorption:} \quad E + S \rightleftarrows E\cdot S \qquad r_{AD} = k_A\left(P_EC_V - \frac{C_{E\cdot S}}{K_{AD}}\right)$$

We'll assume that the surface reaction is rate limiting

$$\text{Surface rxn:} \quad E\cdot S + H \rightarrow A + S \qquad r_S = k_SC_{E\cdot S}P_H$$

No desorption step - P_A isn't in the denominator. Eliminate conc of occupied & vacant sites on surface:

$$\frac{r_{AD}}{k_A} = 0 = P_EC_V - \frac{C_{E\cdot S}}{K_{AD}} \rightarrow K_{AD}P_EC_V = C_{E\cdot S}$$

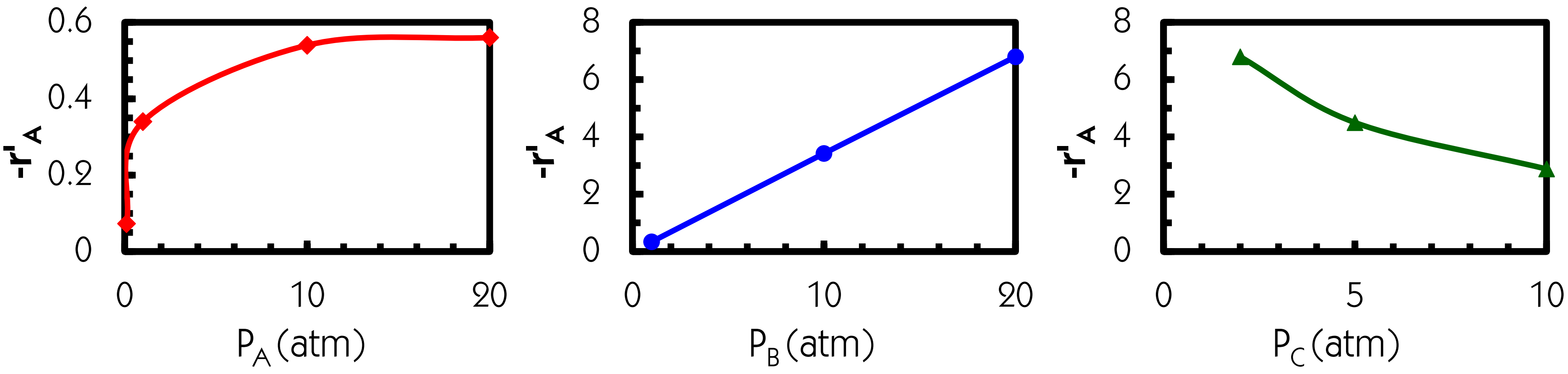
$$\text{site balance:}\ C_t = C_V + C_{E\cdot S} \rightarrow C_t = C_V + K_{AD}P_EC_V \rightarrow \frac{C_t}{1+K_{AD}P_E} = C_V$$

$$r_S = k_SC_{E\cdot S}P_H \rightarrow r_S = \frac{k_SK_{AD}P_EP_HC_t}{1+K_{AD}P_E} \quad k = k_SK_{AD}C_t \ \&\ K_{AD} = K_E \rightarrow r_S = \frac{kP_EP_H}{1+K_EP_E}$$

The experimental data for the gas-phase, catalytic, irreversible reaction A + B→C is given in the table. Suggest a rate law & mechanism consistent with the data.

Approach: Use graphs to show how $-r'_A$ varies with P_i when P_j and P_k are held constant

Run1	P_A (atm)	P_B (atm)	P_C (atm)	$-r'_A$(mol/g·s)
1	0.1	1	2	0.073
2	1	10	2	3.42
3	10	1	2	0.54
4	1	20	2	6.80
5	1	20	10	2.88
6	20	1	2	0.56
7	1	1	2	0.34
8	1	20	5	4.5



We need to use these graphs to determine whether A, B, & C are in the numerator, denominator, or both.

The experimental data for the gas-phase, catalytic, irreversible reaction A + B→C is given in the table. **Suggest a rate law & mechanism consistent with the data.**

Run	P_A (atm)	P_B (atm)	P_C (atm)	$-r'_A$(mol/g·s)
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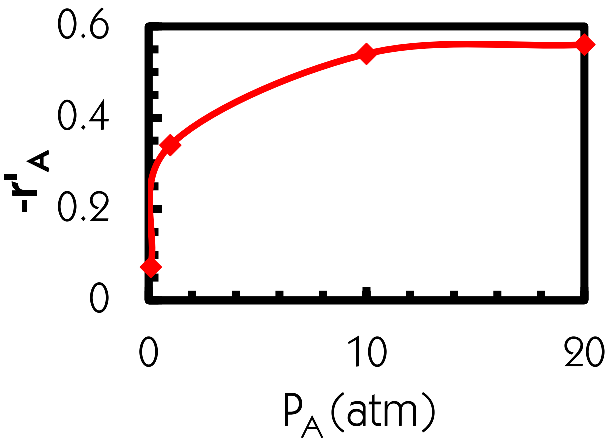
7	1	1	2	0.34
8	1	20	5	4.5

Approach: Use graphs to show how $-r'_A$ varies with P_i when P_j and P_k are held constant



$-r'_A$ increases rapidly at low P_A (means its in the numerator), but it levels off at high P_A (means its in the denominator)→ **P_A in numerator & denominator of $-r'_A$**

$$-r'_A = \frac{kP_A\ldots}{1+kP_A\ldots}$$

The experimental data for the gas-phase, catalytic, irreversible reaction A + B→C is given in the table. Suggest a rate law & mechanism consistent with the data.

Run	P_A (atm)	P_B (atm)	P_C (atm)	$-r'_A$(mol/g·s)
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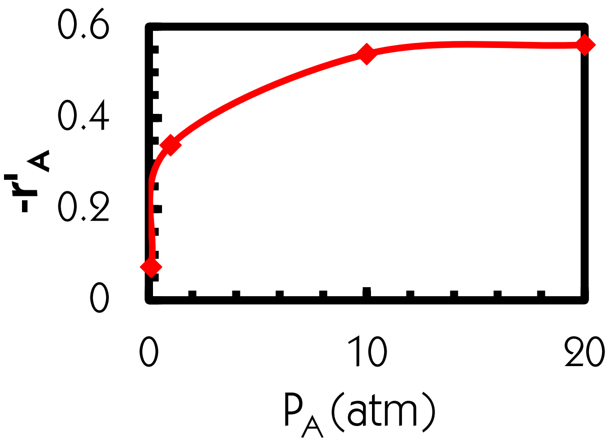
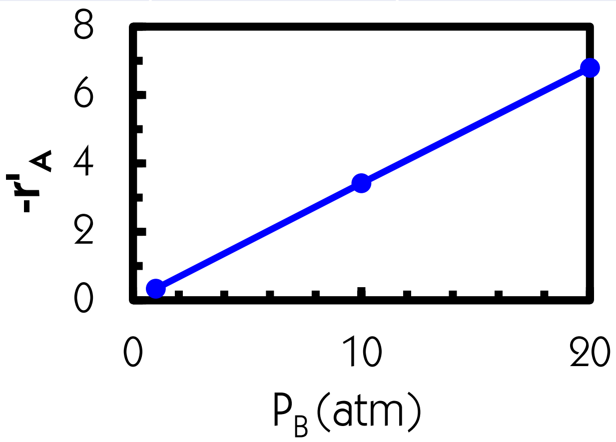
Approach: Use graphs to show how $-r'_A$ varies with P_i when P_j and P_k are held constant





$-r'_A$ increases linearly as P_B increases → P_B **is only in the numerator**

$$-r'_A = \frac{kP_A\ldots}{1+kP_A\ldots}$$

$$-r'_A = \frac{kP_AP_B\ldots}{1+kP_A\ldots}$$

The experimental data for the gas-phase, catalytic, irreversible reaction A + B→C is given in the table. Suggest a rate law & mechanism consistent with the data.

Run	P_A (atm)	P_B (atm)	P_C (atm)	$-r'_A$(mol/g·s)
1	0.1	1	2	0.073
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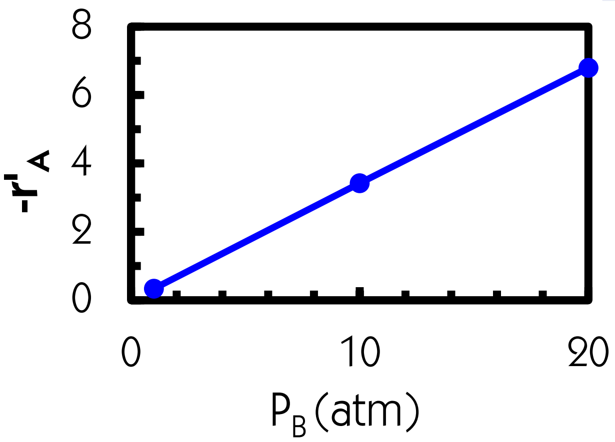
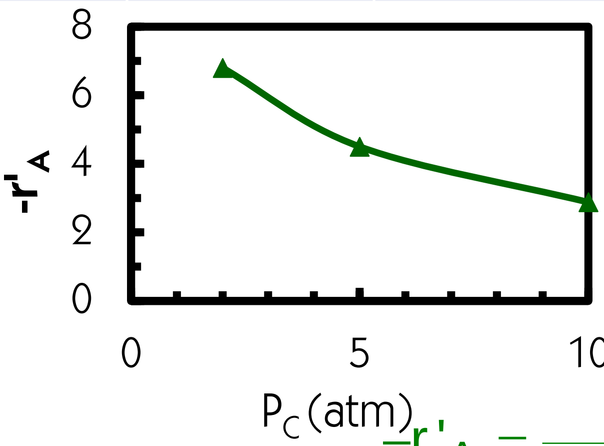
8	1	20	5	4.5

Approach: Use graphs to show how $-r'_A$ varies with P_i when P_j and P_k are held constant





$-r'_A$ ↓ with ↑P_C→ rnx is irreversible so P_C must be in the denominator of $-r'_A$. Therefore, C is adsorbed on surface

$$-r'_A = \frac{kP_AP_B}{1+K_AP_A+K_CP_C}$$

$$-r'_A = \frac{kP_AP_B\cdots}{1+kP_A\cdots}$$

The rate law suggested for the experimental data given for the gas-phase, catalytic, irreversible reaction A + B→C is:

$$-r'_A = \frac{kP_AP_B}{1+K_AP_A+K_CP_C}$$

Suggest a mechanism for this rate law.

P_A and P_C are in the denominator. A (reactant) and C (product) must be adsorbed on the surface, but B is not adsorbed on the surface:

Adsorption of reactant A:

$$A+S \rightleftarrows A\cdot S \quad r_{AD}=k_AP_AC_V-k_{-A}C_{A\cdot S} \quad \rightarrow r_{AD}=k_A\left(P_AC_V-\frac{C_{A\cdot S}}{K_A}\right)$$

Desorption of product C:

$$C\cdot S \rightleftarrows C+S \quad r_{DC}=k_DC_{C\cdot S}-k_{-D}P_CC_v \quad \rightarrow r_{DC}=k_D\left(C_{C\cdot S}-\frac{P_CC_V}{K_D}\right)$$

The rate law suggested for the experimental data given for the gas-phase, catalytic, irreversible reaction A + B→**C is:**

$$-r'_A = \frac{kP_AP_B}{1+K_AP_A+K_CP_C}$$

Suggest a mechanism for this rate law.

P_A and P_C are in the denominator. A (reactant) and C (product) must be adsorbed on the surface, but B is not:

Adsorption of reactant A:

$$A+S \rightleftarrows A\cdot S \quad r_{AD}=k_AP_AC_V-k_{-A}C_{A\cdot S} \quad \rightarrow r_{AD}=k_A\left(P_AC_V-\frac{C_{A\cdot S}}{K_A}\right)$$

Desorption of product C:

$$C\cdot S \rightleftarrows C+S \quad r_{DC}=k_DC_{C\cdot S}-k_{-D}P_CC_V \quad \rightarrow r_{DC}=k_D\left(C_{C\cdot S}-\frac{P_CC_V}{K_D}\right)$$

Surface reaction step: B is not adsorbed on the surface, so B must be in the gas phase when it reacts with A adsorbed on the surface.
The overall reaction is irreversible, so this step is likely irreversible.

$$A\cdot S+B \rightarrow C\cdot S \qquad r_S=k_SC_{A\cdot S}P_B$$

The rate law suggested for the experimental data given on sli for the gas-phase, catalytic, irreversible reaction A + B→C is:

$$-r'_A = \frac{kP_AP_B}{1+K_AP_A+K_CP_C}$$

Suggest a mechanism for this rate law.

Adsorption of reactant A: $A+S \rightleftarrows A\cdot S$ $\quad r_{AD}=k_A\left(P_AC_V-\frac{C_{A\cdot S}}{K_A}\right)$

Surface reaction: $A\cdot S+B\rightarrow C\cdot S$ $\quad r_S=k_SC_{A\cdot S}P_B$

Desorption of product C: $C\cdot S \rightleftarrows C+S$ $\quad r_{DC}=k_D\left(C_{C\cdot S}-\frac{P_CC_V}{K_D}\right)$

Postulate that the surface reaction is the rate limiting step since that is true the majority of the time. Check if that is consistent with the observed kinetics

$$-r'_A=r_S=k_SC_{A\cdot S}P_B$$

Eliminate $C_{A\cdot S}$ & C_V from rate eq

$$C_t=C_V+C_{A\cdot S}+C_{C\cdot S}$$

$$\frac{r_{AD}}{k_A}=0=P_AC_V-\frac{C_{A\cdot S}}{K_A}\quad\rightarrow P_AC_V=\frac{C_{A\cdot S}}{K_A}\quad\rightarrow K_AP_AC_V=C_{A\cdot S}$$

$$\frac{r_{DC}}{k_D}=0=C_{C\cdot S}-\frac{P_CC_V}{K_D}\quad\rightarrow C_{C\cdot S}=\frac{P_CC_V}{K_D}$$

Insert into site balance and solve for C_V

The rate law suggested for the experimental data given on slide 13 for the gas-phase, catalytic, irreversible reaction A + B→C is:

$$-r'_A = \frac{kP_AP_B}{1+K_AP_A+K_CP_C}$$

Suggest a mechanism for this rate law.

Adsorption of reactant A:

$$A + S \rightleftarrows A\cdot S$$

$$r_{AD} = k_A\left(P_AC_V - \frac{C_{A\cdot S}}{K_A}\right)$$

Surface reaction:

$$A\cdot S + B \rightarrow C\cdot S$$

$$r_S = k_SC_{A\cdot S}P_B$$

Desorption of product C:

$$C\cdot S \rightleftarrows C + S$$

$$r_{DC} = k_D\left(C_{C\cdot S} - \frac{P_CC_V}{K_D}\right)$$

Postulated surface reaction is rate limiting

$$-r'_A = r_S = k_SC_{A\cdot S}P_B = k_SK_AP_AC_VP_B$$

$$C_{A\cdot S} = K_AP_AC_V$$

$$C_{C\cdot S} = P_CC_V/K_D$$

$$C_t = C_v + C_{A\cdot S} + C_{C\cdot S} \rightarrow C_t = C_v + K_AP_AC_V + \frac{P_CC_V}{K_D} \rightarrow \frac{C_t}{1+K_AP_A+P_C/K_D} = C_v$$

$$-r'_A = r_S = k_SC_{A\cdot S}P_B = k_SK_AP_AC_VP_B \rightarrow r_S = \frac{k_SK_AP_AC_tP_B}{1+K_AP_A+P_C/K_D}$$

$$K_C = \frac{1}{K_D} \qquad k = k_SK_AC_t \qquad \rightarrow r_S = \frac{kP_AP_B}{1+K_AP_A+K_CP_C}$$

Chemical Reaction Engineering in the Electronics Industry

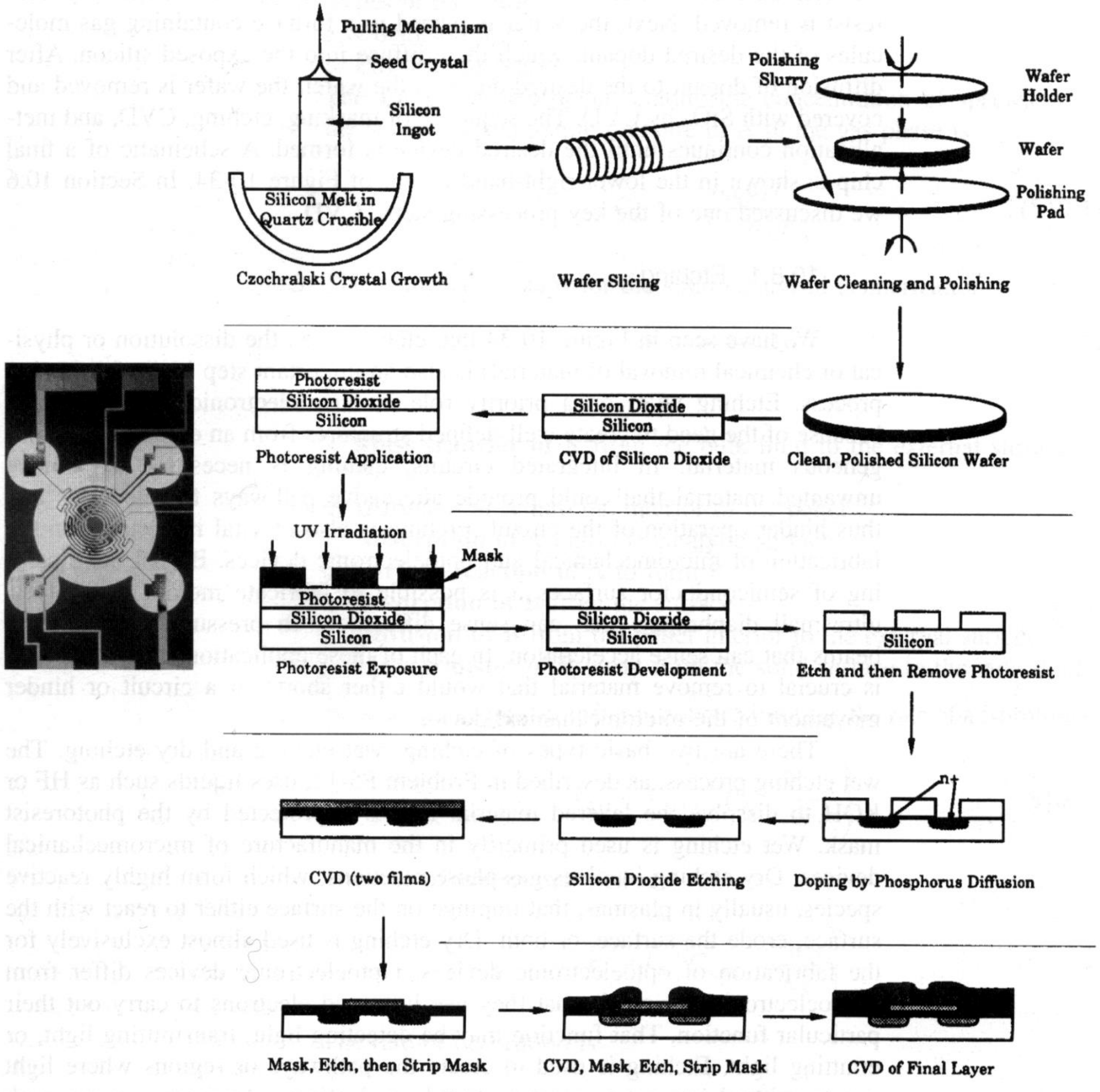
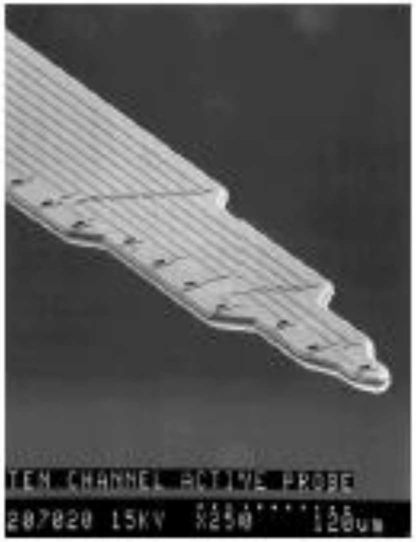


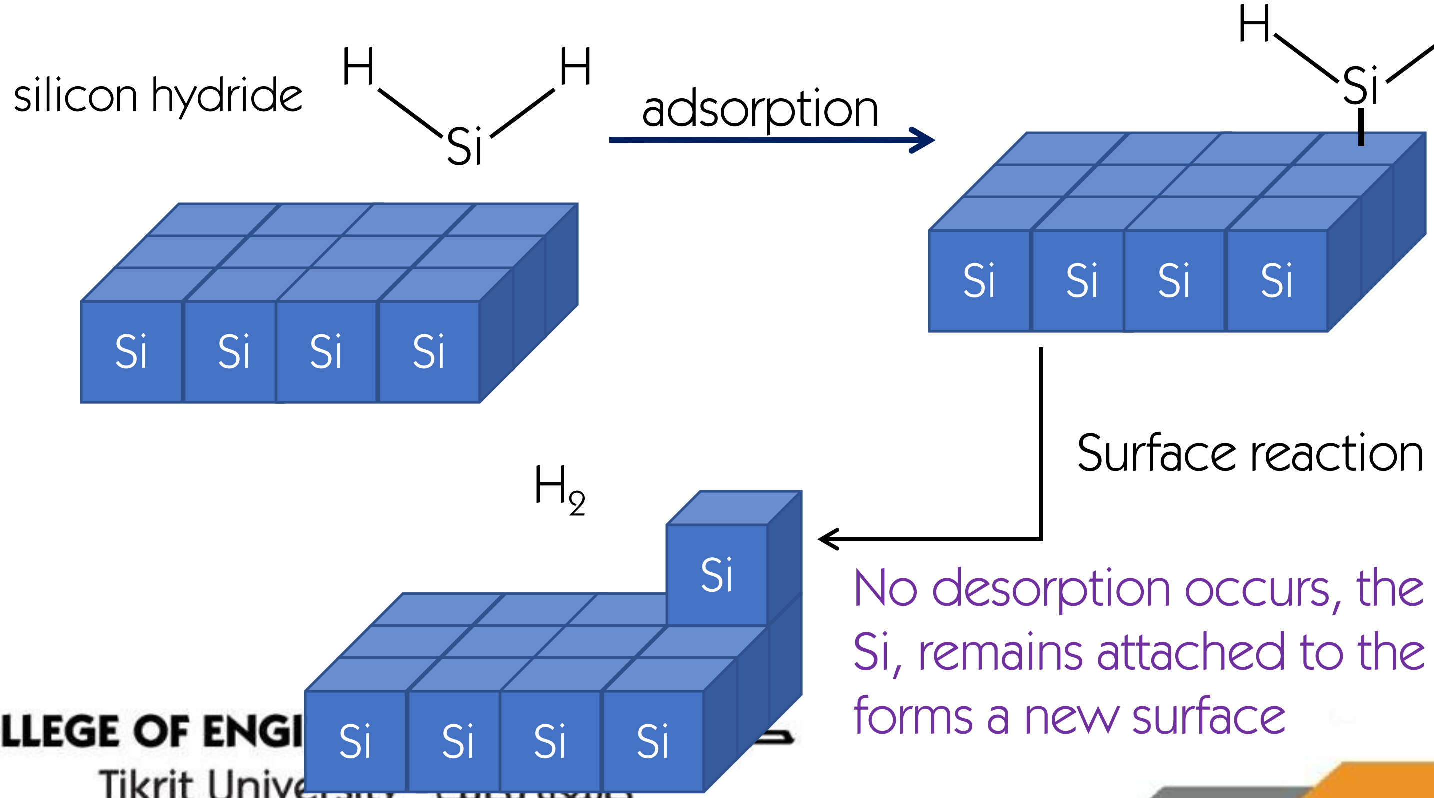
Figure 10-34 Microelectronic fabrication steps.

Chemical Reaction Engineering in the Electronics Industry



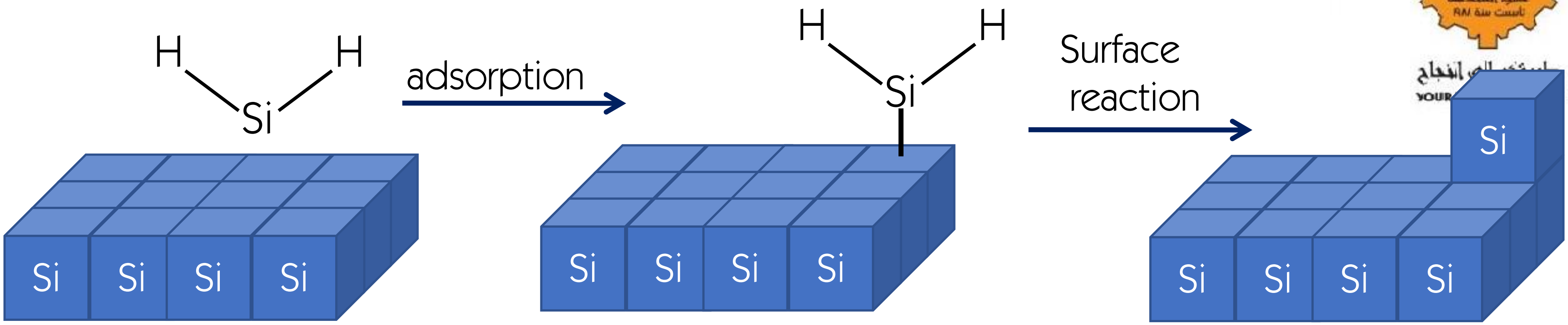
CVD

- Chemical vapor deposition (CVD)
  - Important process in the formation of microcircuits (electrically interconnected films ICs), microprocessors & solar cells
  - Used to deposit thin films of material, such as Si, SiO_2, & germanium (Ge)
  - Mechanism of CVD is similar to those of heterogeneous catalysis ***except*** that site concentration (C_V) is replaced w/ fraction of surface coverage (f_V)



No desorption occurs, the product, Si, remains attached to the surface, forms a new surface

Growth of Silicon Film by CVD



Write out elementary reactions and assume a rate-limiting step

1. Adsorption $SiH_2(g) + S \rightleftarrows SiH_2 \cdot S$

Rate of adsorption = rate of attachment – rate of detachment

$$r_{AD} = k_{SiH_2} P_{SiH_2} f_v - k_{-SiH_2} f_{SiH_2} \qquad \rightarrow r_{AD} = k_{SiH_2}\left(P_{SiH_2} f_v - \frac{f_{SiH_2}}{K_{SiH_2}} \right)$$

f_v & f_{SiH2}: fraction of the surface covered by vacant sites or SiH_2, respectively

2. Surface reaction: $SiH_2 \cdot S \rightleftarrows Si + S + H_2(g)$

$$r_S = k_S f_{SiH_2} - k_{-S} C_{Si} P_{H_2} f_v \qquad \rightarrow r_S = k_S\left(f_{SiH_2} - \frac{C_{Si} C_{H_2} f_v}{K_S} \right)$$

Surface coverage is in terms of fraction of surface, not conc of active sites

Growth of Germanium Films by CVD

Germanium films have applications in microelectronics & solar cell fabrication

Gas-phase dissociation $GeCl_{4(g)} \underset{k_{-dis}}{\overset{k_{dis}}{\rightleftharpoons}} GeCl_{2(g)} + Cl_{2(g)}$

Adsorption (1) $GeCl_{2(g)} + S \underset{k_{-A}}{\overset{k_{A}}{\rightleftharpoons}} GeCl_2 \cdot S$

Adsorption (2) $H_{2(g)} + 2S \underset{k_{-H}}{\overset{k_{H}}{\rightleftharpoons}} 2H \cdot S$

Surface reaction $GeCl_2 \cdot S + 2H \cdot S \xrightarrow{k_S} Ge(s) + 2HCl(g) + 2S$

Surface reaction is believed to be the rate-limiting step

What is the rate of Ge deposition if the surface reaction is rate limiting?

a) $r''_{Dep} = k_{dis}P_{GeCl4} - k_{-dis}P_{GeCl2}P_{Cl2}$
b) $r''_{Dep} = k_A P_{GeCl2} f_v - k_{-A} f_{GeCl2}$
c) $r''_{Dep} = k_H P_{H2} f_v^2 - k_{-H} f_H^2$
d) $r''_{Dep} = k_S f_{GeCl2} f_H^2 - k_{-S} C_{Ge} P_{HCl}^2 f_v^2$
e) $\boxed{r''_{Dep} = k_S f_{GeCl2} f_H^2}$

CVD

ermanium films have applications in microelectronics & solar cell fabrication

Gas-phase dissociation $GeCl_{4(g)} \underset{k_{-dis}}{\overset{k_{dis}}{\rightleftharpoons}} GeCl_{2(g)} + Cl_{2(g)}$

Adsorption (1) $GeCl_{2(g)} + S \underset{k_{-A}}{\overset{k_{A}}{\rightleftharpoons}} GeCl_2 \cdot S$

Adsorption (2) $H_{2(g)} + 2S \underset{k_{-H}}{\overset{k_{H}}{\rightleftharpoons}} 2H \cdot S$

Surface reaction $GeCl_2 \cdot S + 2H \cdot S \xrightarrow{k_S} Ge(s) + 2HCl(g) + 2S$

Surface reaction is believed to be the rate-limiting step:

Rate of Ge deposition (nm/s): $r''_{Dep} = k_S f_{GeCl_2} f_H{}^2$

k_s: surface specific reaction rate (nm/s)

f_{GeCl2}: fraction of the surface covered by $GeCl_2$

f_{H2}: fraction on the surface occupied by H_2

*Surface coverage is in terms of fraction of surface, not conc of active sites

Chemical Vapor Deposition

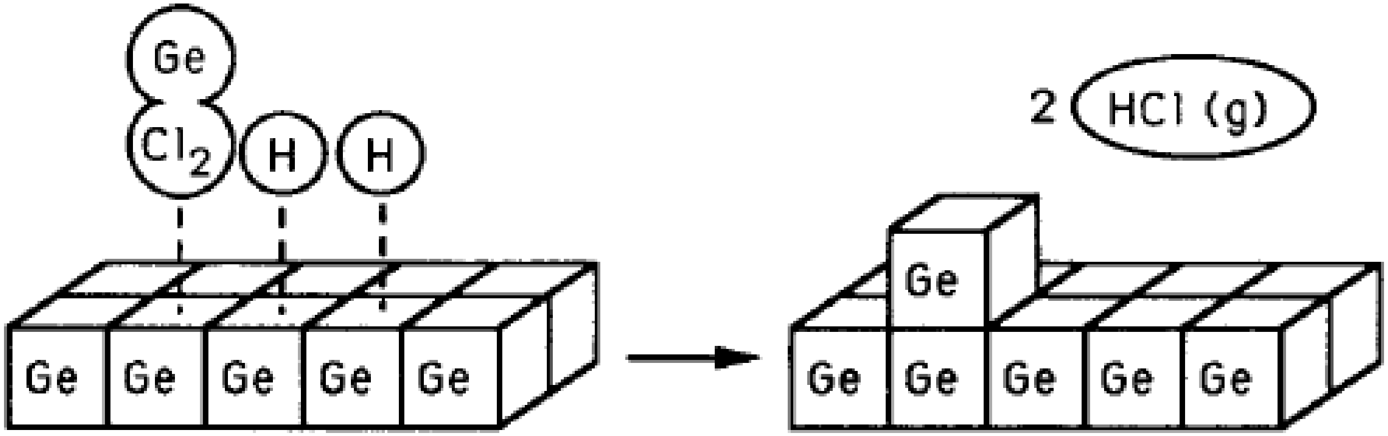
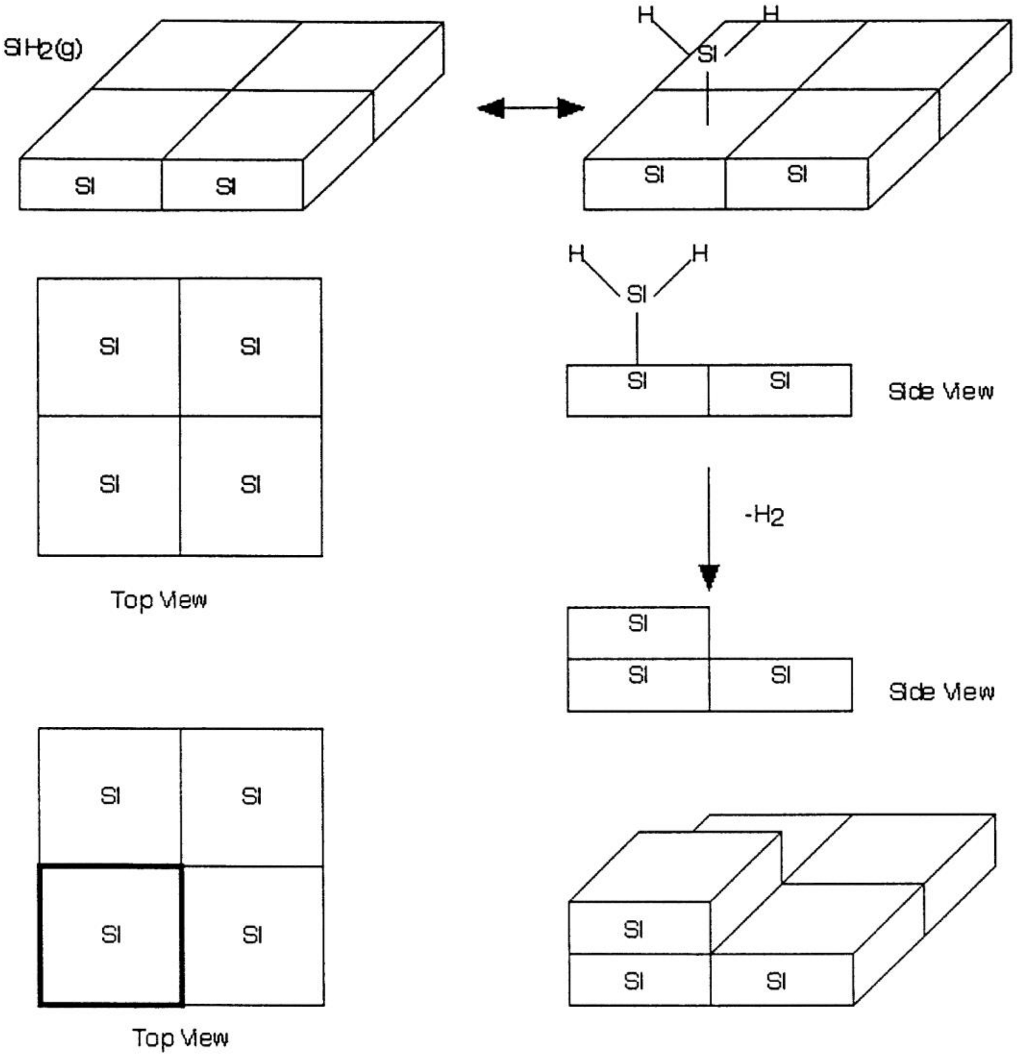


Figure 10-21 CVD surface reaction step for Germanium.

Chemical Vapor Deposition



Chemical Vapor Deposition

1) Mechanism

Gas Phase

Homogeneous

$$SiH_4 \rightleftarrows SiH_2 + H_2 \qquad -r_{SiH_4} = k_{SiH_4}\left[P_{SiH_4} - \frac{P_{H_2}P_{SiH_2}}{K_P}\right]$$

Heterogeneous

$$SiH_2 + \tilde{S} \rightleftarrows SiH_2 \bullet \tilde{S} \qquad r_{AD} = k_A\left[P_{SiH_2} f_V - \frac{f_{SiH_2}}{K_{SiH_2}}\right]$$

$$SiH_2 + \tilde{S} \longrightarrow \tilde{S} + H_2 \qquad r_{Dep} = r_S = k_S f_{SiH_2}$$

f_V = fraction of surface that is vacant

Chemical Vapor Deposition

2) Rate Limiting Step

$$r_{Dep} = r_S = k_S f_{SiH_2}$$

3) Express f_i in terms of P_i

$$\frac{r_{AD}}{k_A} \approx 0$$

$$f_{SiH_2} = K_{SiH_2} f_V P_{SiH_2}$$

4) Area Balance

$$1 = f_V + f_{SiH_2} = f_V + K_{SiH_2} P_{SiH_2} f_V$$

Chemical Vapor Deposition

4) Area Balance

$$1 = f_V + f_{SiH_2} = f_V + K_{SiH_2} P_{SiH_2} f_V$$

$$f_V = \frac{1}{1 + K_{SiH_2} P_{SiH_2}}$$

5) Combine

$$r_{Dep} = \frac{k_S K_{SiH_2} P_{SiH_2}}{1 + K_{SiH_2} P_{SiH_2}}$$

Homogeneous Reaction

$$SiH_4 \rightleftarrows SiH_2 + H_2 \qquad -r_{SiH_4} = k_{SiH_4}\left[P_{SiH_4} - \frac{P_{H_2}P_{SiH_2}}{K_P}\right]$$

$$\frac{-r_{SiH_4}}{k_{SiH_4}} \approx 0 \Rightarrow P_{SiH_2} = \frac{K_P P_{SiH_2}}{P_{H_2}}$$

$$r_{Dep} = \frac{k_S K_P K_{SiH_2} P_{SiH_4}}{P_{H_2} + K_{SiH_2} K_P P_{SiH_4}} = \frac{k_1 P_{SiH_4}}{P_{H_2} + K_1 P_{SiH_4}}$$

Summary

- This presentation discussed catalysts and catalysis, catalytic mechanisms, and data analysis, with a focus on CVD applications.