10. Catalysis & Catalytic Reaction

- Basic Define
  - Catalyst, catalytic mechanism, rate limit step.
- Catalytic Mechanism
  - Describe the steps
  - Derive a rate law and a mechanism and rate limiting step consistent with the experimental data
- Use Regression to discriminate between reaction rate laws and mechanisms

2. Steps in a Catalytic Reaction X

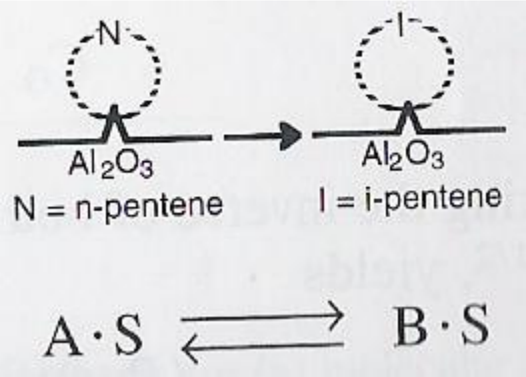
- **Step 4 : Surface Reaction 1**
- **Rate of adsorption of species A onto a solid surface**

$$A + S \leftrightarrow A \cdot S$$

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

- **Single site**

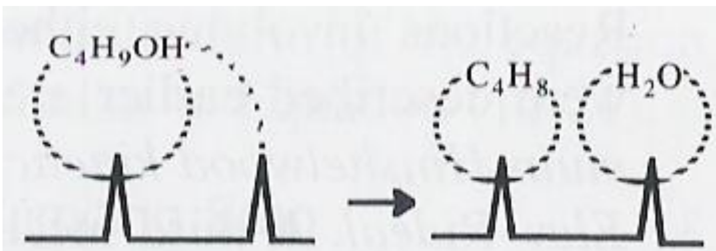
  - Only the site on which the reactant is adsorbed is involved in the reaction



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

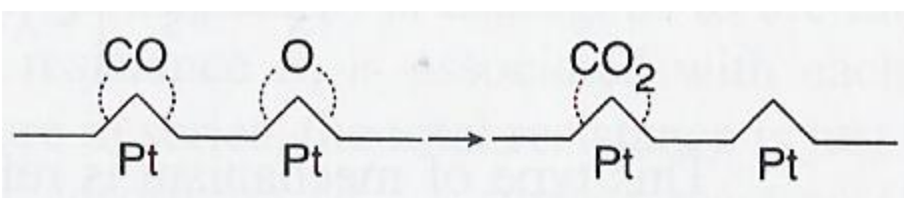
2. Steps in a Catalytic Reaction XI

- **Dual site**
  - **The adsorbed reactant interacts with another site (either occupied or unoccupied)**



$$\mathrm{A\cdot S + S \leftrightarrow B\cdot S + S}$$

$$r_{\mathrm{S}} = k_{\mathrm{S}}\left(C_{\mathrm{A\cdot S}} C_v - \frac{C_{\mathrm{B\cdot S}} C_v}{K_{\mathrm{S}}} \right)$$

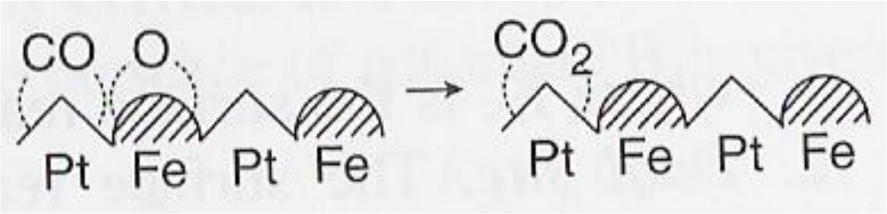


$$\mathrm{A\cdot S + B\cdot S \leftrightarrow C\cdot S + D\cdot S}$$

$$r_{\mathrm{S}} = k_{\mathrm{S}}\left(C_{\mathrm{A\cdot S}} C_{\mathrm{B\cdot S}} - \frac{C_{\mathrm{C\cdot S}} C_{\mathrm{D\cdot S}}}{K_{\mathrm{S}}} \right)$$

2. Steps in a Catalytic Reaction XII

○ **Dual site 2**



$$\mathrm{A\cdot S + B\cdot S' \leftrightarrow C\cdot S' + D\cdot S}$$

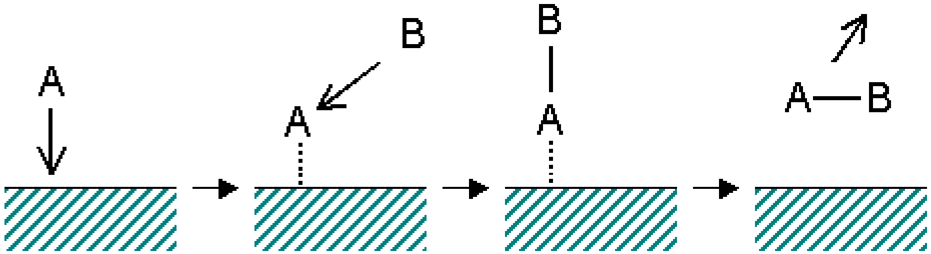
$$r_\mathrm{S} = k_\mathrm{S}\left(C_\mathrm{A\cdot S} C_\mathrm{B\cdot S'} - \frac{C_\mathrm{C\cdot S'} C_\mathrm{D\cdot S}}{K_\mathrm{S}} \right)$$

☞ **Langmuir-Hinshelwood Mechanism**

- Single or dual site mechanism reaction

2. Steps in a Catalytic Reaction XIII

- **Eley-Rideal**
  - **- Reaction between an adsorbed molecule and a molecule in the gas phase**



$$\mathrm{A\cdot S + B(g) \leftrightarrow C\cdot S}$$

$$r_{\mathrm{S}} = k_{\mathrm{S}}\left(C_{\mathrm{A\cdot S}} P_{\mathrm{B}} - \frac{C_{\mathrm{C\cdot S}}}{K_{\mathrm{S}}} \right)$$

2. Steps in a Catalytic Reaction XIV

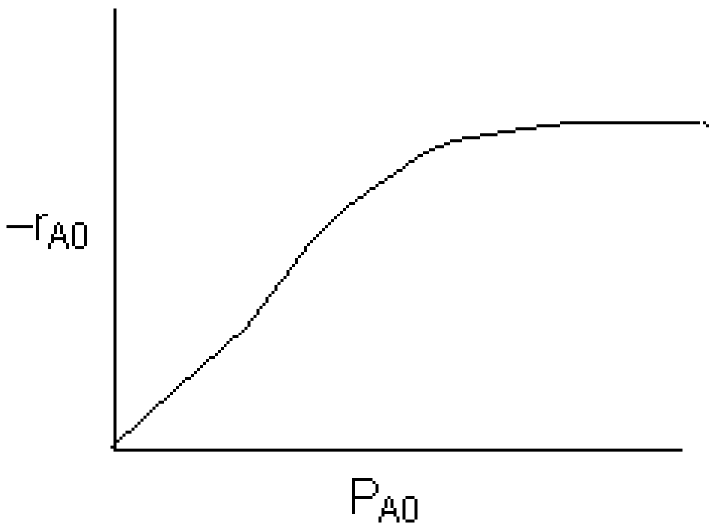
- **Summary**

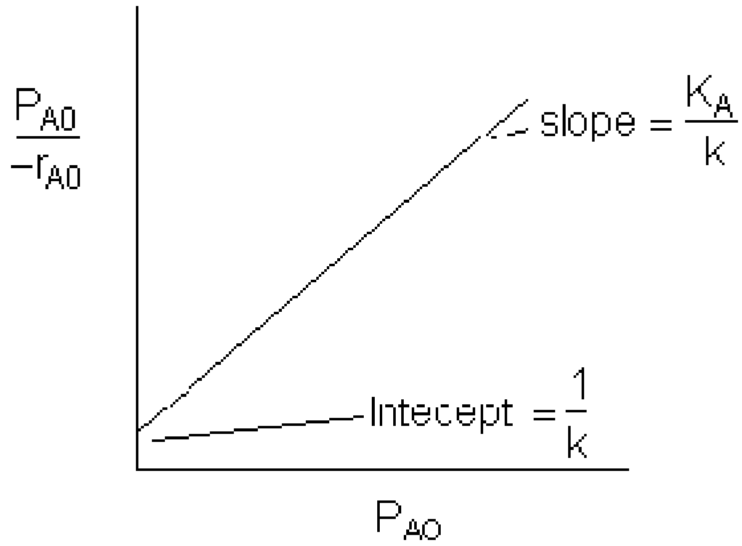
Single site			
a	$A+S \leftrightarrow A\cdot S$	$-r_A' = \dfrac{kP_A}{1+K_AP_A+K_BP_B}$	
Dual site			
b	$A\cdot S+S \leftrightarrow B\cdot S+S$	$-r_A' = \dfrac{kP_A}{(1+K_AP_A+K_BP_B)^2}$	
c	$A\cdot S+B\cdot S' \leftrightarrow C\cdot S'+D\cdot S$	$-r_A' = \dfrac{kP_AP_B}{(1+K_AP_A+K_BP_B+K_CP_C)^2}$	
Eley-Rideal			
d	$A\cdot S+B(g) \leftrightarrow C\cdot S$	$-r_A' = \dfrac{kP_AP_B}{1+K_AP_A+K_CP_C}$	

2. Steps in a Catalytic Reaction XV

- **Plot 1**

$$-r_A = \frac{kP_A}{1 + K_A P_A + K_B P_B} \;, \quad -r_{A0} = \frac{kP_{A0}}{1 + K_A P_{A0}}$$

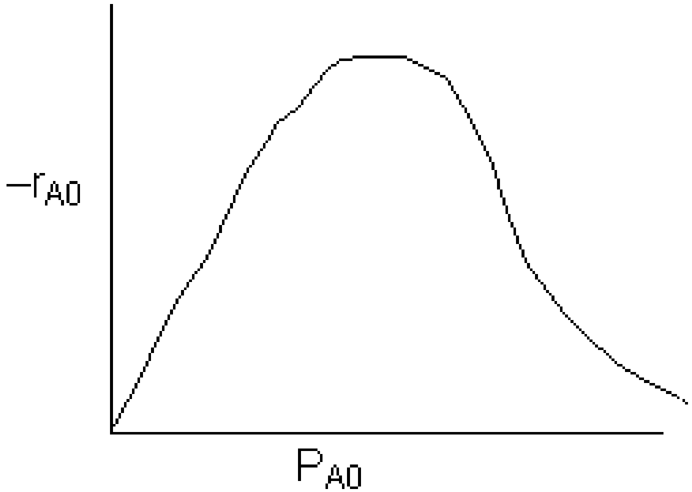


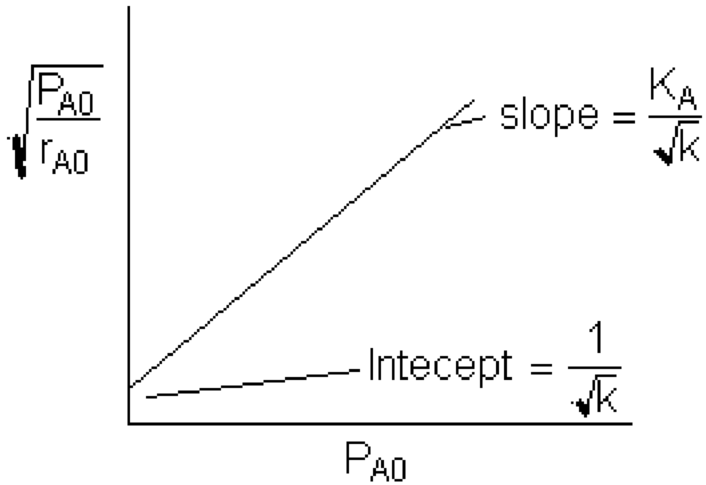


2. Steps in a Catalytic Reaction XVI

- **Plot 2**

$$-r_A = \frac{kP_A}{(1+K_AP_A+K_BP_B)^2} \qquad -r_{A0} = \frac{kP_{A0}}{(1+K_AP_{A0})^2}$$



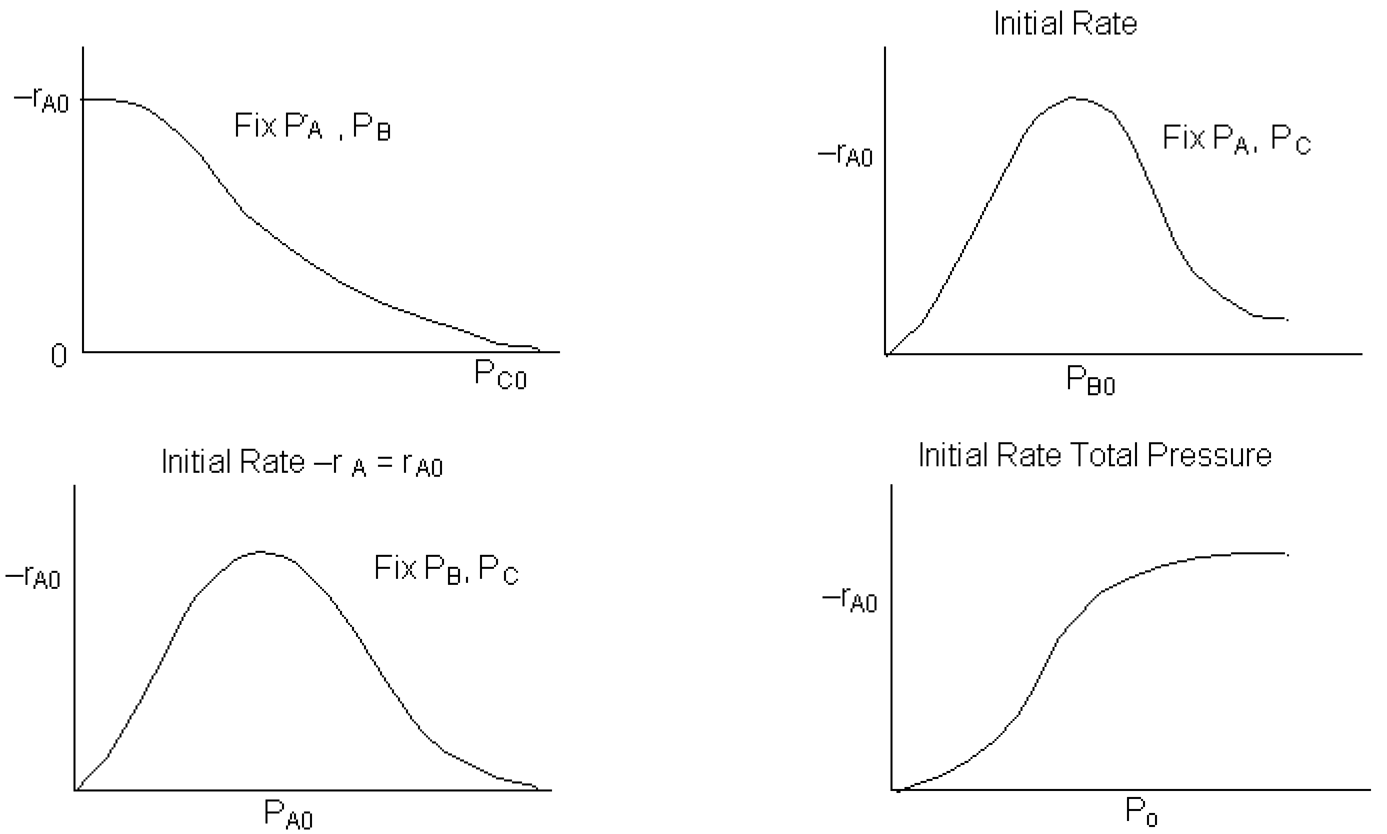


2. Steps in a Catalytic Reaction XVII

- **Plot 3**

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

$$-r_{A0} = \frac{kP_{A0} P_{B0}}{(1+K_A P_{A0} + K_B P_{B0} + K_C P_{C0})^2}$$

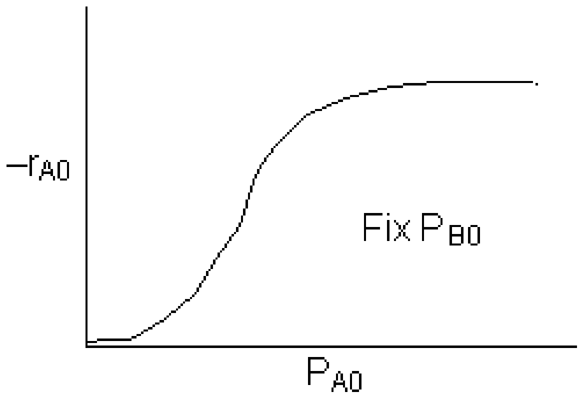


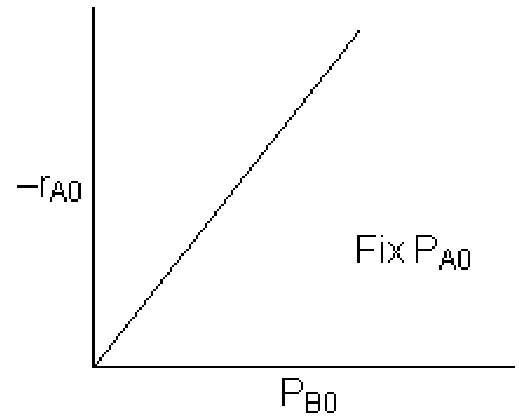
2. Steps in a Catalytic Reaction XIIIV

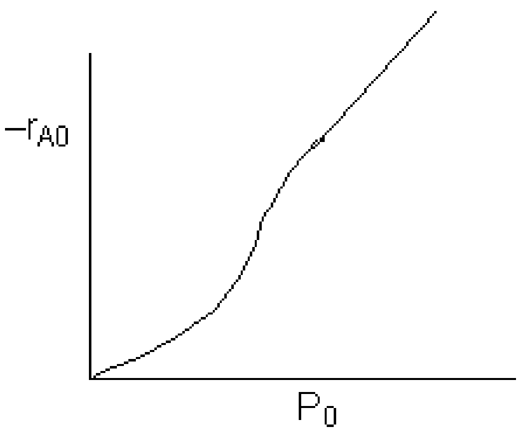
- **Plot 4**

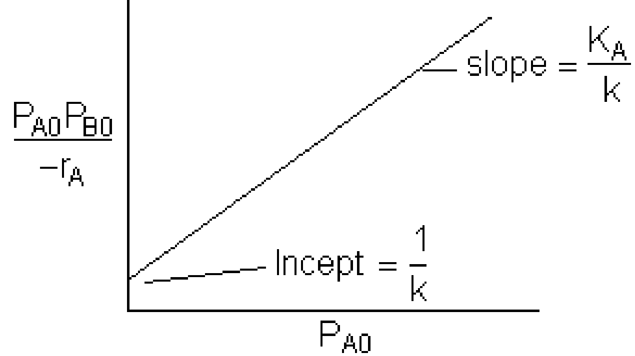
$$-r_A = \frac{kP_A P_B}{1 + K_A P_A + K_C P_C}$$

$$-r_{A0} = \frac{kP_{A0} P_{B0}}{1 + K_A P_{A0}}$$









2. Steps in a Catalytic Reaction XIX

- **Desorption**

$$C \cdot S \leftrightarrow C + S$$

$$r_{\mathrm{DC}} = k_{\mathrm{D}}\left(C_{\mathrm{C \cdot S}} - \frac{P_{\mathrm{C}} C_v}{K_{\mathrm{DC}}} \right)$$

- Desorption rate constant for C is just reverse of the adsorption step, $r_{DC} = -r_{ADC}$

- Desorption equilibrium constant for C is just reciprocal of the adsorption equilibrium constant

$$K_{\mathrm{DC}} = \frac{1}{K_{\mathrm{C}}}$$

$$r_{\mathrm{DC}} = k_{\mathrm{D}}\left(C_{\mathrm{C \cdot S}} - K_{\mathrm{C}} P_{\mathrm{C}} C_v \right)$$

2. Steps in a Catalytic Reaction XX

- **Rate-Limiting Step**
  - **- At steady state**

$$-r_A' = r_{AD} = r_S = r_D$$

  - **- One particular step in the series is found to be rate-limiting or rate-controlling**

☞ **Studied by Langmuir-Hinshelwood approach**

- **adsorption-limited reaction**
- **surface-limited reaction**
- **desorption-limited reaction**

2. Steps in a Catalytic Reaction XXI

- **Rate-Limiting Step 2**

- Example of adsorption-limited reaction

$$3H_2 + N_2 \rightarrow 2NH_3$$

$$H_2 + 2S \rightarrow 2H \cdot S \qquad \text{Rapid}$$

$$\left.\begin{aligned} &N_2 + S \leftrightarrow N_2 \cdot S \\ &N_2 \cdot S + S \leftrightarrow 2N \cdot S \end{aligned}\right\} \qquad \text{Rate-limiting}$$

$$\left.\begin{aligned} &N \cdot S + H \cdot S \leftrightarrow HN \cdot S + S \\ &NH \cdot S + H \cdot S \leftrightarrow H_2N \cdot S + S \\ &H_2N \cdot S + H \cdot S \leftrightarrow NH_3S + S \\ &NH_3S \leftrightarrow NH_3 + S \end{aligned}\right\} \qquad \text{Rapid}$$

3. Rate Law, Mechanism, and RLS I

○ **Modeling Reaction**

- Decomposition of cumene to benzene and propylene

$$C_6H_5CH(CH_3)_2 \rightarrow C_6H_6 + C_3H_6$$

TABLE 10-3. STEPS IN A LANGMUIR-HINSHELWOOD KINETIC MECHANISM

$C + S \underset{k_{-A}}{\overset{k_A}{\rightleftarrows}} C \cdot S$	Adsorption of cumene on the surface
$C \cdot S \underset{k_{-S}}{\overset{k_S}{\rightleftarrows}} B \cdot S + P$	Surface reaction to form adsorbed benzene and propylene in the gas phase
$B \cdot S \underset{k_{-D}}{\overset{k_D}{\rightleftarrows}} B + S$	Desorption of benzene from surface

3. Rate Law, Mechanism, and RLS II

- **Modeling Reaction 2**
  - **Treat each step as an elementary reaction**
  - **The species concentrations in the gas phase are replaced by their respective partial pressures**

$$C_C \rightarrow P_C$$

  - **Adsorption of cumene**

$$r_{\mathrm{AD}} = k_{\mathrm{A}} P_{\mathrm{C}} C_{\upsilon} - k_{-\mathrm{A}} C_{\mathrm{C \cdot S}}$$

$$\text{Adsorption}: r_{\mathrm{AD}} = k_{\mathrm{A}} \left(P_{\mathrm{C}} C_{v} - \frac{C_{\mathrm{C \cdot S}}}{K_{\mathrm{C}}} \right)$$

3. Rate Law, Mechanism, and RLS III

○ **Modeling Reaction 3**

- Surface reaction

$$r_S = k_S C_{C\cdot S} - k_{-S} P_P C_{B\cdot S}$$

$$\text{Surface reaction: } r_S = k_S \left(C_{C\cdot S} - \frac{P_P C_{B\cdot S}}{K_S} \right)$$

- Desorption

- **Propylene is not adsorbed on the surface**

$$C_{P\cdot S} = 0 \qquad r_D = k_D C_{B\cdot S} - k_{-D} P_B C_v$$

$$\text{Desorption: } r_D = k_D \left(C_{B\cdot S} - \frac{P_B C_v}{K_{DB}} \right)$$

3. Rate Law, Mechanism, and RLS IV

- **Modeling Reaction 4**
  - **Desorption 2**

$$K_{\mathrm{B}} = \frac{1}{K_{\mathrm{DB}}}$$

$$\text{Desorption}: r_{\mathrm{D}} = k_{\mathrm{D}}\left(C_{\mathrm{B\cdot S}} - K_{\mathrm{B}} P_{\mathrm{B}} C_{v}\right)$$

  - **No accumulation of reacting species on the surface**

$$-r_{\mathrm{C}}' = r_{\mathrm{AD}} = r_{\mathrm{S}} = r_{\mathrm{D}}$$

3. Rate Law, Mechanism, and RLS V

- **Modeling Reaction 5**

- Adsorption is RLS?

$$-r_{\mathrm{C}}^{'} = r_{\mathrm{AD}} = k_{\mathrm{A}}\left(P_{\mathrm{C}} C_{v} - \frac{C_{\mathrm{C \cdot S}}}{K_{\mathrm{C}}} \right)$$

- **surface reaction rate is**

$$r_{\mathrm{S}} = k_{\mathrm{S}}\left(C_{\mathrm{C \cdot S}} - \frac{C_{\mathrm{B \cdot S}} P_{\mathrm{P}}}{K_{\mathrm{S}}} \right)$$

- **surface specific reaction rate is large by comparison**

$$\frac{r_{\mathrm{S}}}{k_{\mathrm{S}}} \cong 0$$

3. Rate Law, Mechanism, and RLS VI

- **Modeling Reaction 5**
  - **Adsorption is RLS? 2**
    - **solving for $C_{C\cdot S}$**

$$C_{C\cdot S} = \frac{C_{B\cdot S} P_P}{K_S}$$

    - **to obtain $C_{B\cdot S}$**

$$r_D = k_D \left(C_{B\cdot S} - K_B P_B C_v \right)$$

    - **desorption rate constant is large by comparison**

$$\frac{r_D}{k_D} \cong 0$$

    - **solving for $C_{B\cdot S}$**

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

    - **solving for $C_{C\cdot S}$**

$$C_{C\cdot S} = K_B \frac{P_B P_P}{K_S} C_v$$

3. Rate Law, Mechanism, and RLS VII

- **Modeling Reaction 6**

  - Adsorption is RLS? 3

  - **replacing $C_{C\cdot S}$**

$$r_{AD} = k_A\left(P_C - \frac{K_B P_B P_P}{K_S K_C}\right)C_v = k_A\left(P_C - \frac{P_B P_P}{K_P}\right)C_v$$

  - **let** $\frac{K_S K_C}{K_B} = K_P$

  - **total site** $C_t = C_v + C_{C\cdot S} + C_{B\cdot S}$

  - **substituting**

$$C_v = \frac{C_t}{1 + P_B P_P K_B / K_S + K_B P_B}$$

3. Rate Law, Mechanism, and RLS VIII

- **Modeling Reaction 7**

  - Adsorption is RLS? 4

  - **reaction rate = rate of adsorption**

$$-r_{C}^{'} = r_{AD} = k_{A}\left(P_{C}C_{v} - \frac{C_{C\cdot S}}{K_{C}}\right)$$

$$C_{C\cdot S} = \frac{C_{B\cdot S}P_{P}}{K_{S}} = K_{B}\frac{P_{B}P_{P}}{K_{S}}C_{v} \qquad C_{B\cdot S} = K_{B}P_{B}C_{v}$$

$$C_{v} = \frac{C_{t}}{1 + P_{B}P_{P}K_{B}/K_{S} + K_{B}P_{B}}$$

- **substituting**

$$-r_{C}^{'} = r_{AD} = \frac{C_{t}k_{A}\left(P_{C} - P_{P}P_{B}/K_{P}\right)}{1 + K_{B}P_{B}P_{P}/K_{S} + K_{B}P_{B}}$$

3. Rate Law, Mechanism, and RLS IX

○ **Modeling Reaction 8**

- Surface Reaction is RLS?

- **reaction rate = rate of surface reaction**

$$-r_{\mathrm{C}}^{'} = r_{\mathrm{S}} = \frac{\overbrace{k_{\mathrm{S}} C_t K_{\mathrm{C}}}^{k} \left(P_{\mathrm{C}} - P_{\mathrm{P}} P_{\mathrm{B}} / K_{\mathrm{P}}\right)}{1 + P_{\mathrm{B}} K_{\mathrm{B}} + K_{\mathrm{C}} P_{\mathrm{C}}}$$

- Desorption is RLS?

- **reaction rate = rate of desorption**

$$-r_{\mathrm{C}}^{'} = r_{\mathrm{D}} = \frac{\overbrace{k_{\mathrm{D}} C_t K_{\mathrm{S}} K_{\mathrm{C}}}^{k} \left(P_{\mathrm{C}} - P_{\mathrm{B}} P_{\mathrm{P}} / K_{\mathrm{P}}\right)}{P_{\mathrm{P}} + P_{\mathrm{C}} K_{\mathrm{C}} K_{\mathrm{S}} + K_{\mathrm{C}} P_{\mathrm{P}} P_{\mathrm{C}}}$$