Catalytic Reaction Engineering

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Reaction Mechanism and Rate Equations of Heterogeneous Catalytic Reactions
Heterogeneous catalysis – reaction mechanisms

1. Bulk fluid → External surface
2. External surface → Internal surface
3. Surface adsorption
4. Surface reaction
5. Surface desorption
6. Internal surface → External surface
7. External surface → Bulk fluid

- The overall rate of reaction is limited by the rate of the slowest step in the sequence.
- The slowest step is called rate-determining step (RDS).
**Adsorption**

\[
\begin{align*}
\text{A} + \text{S} & \xrightleftharpoons[k_A]{k_{-A}} \text{A} \cdot \text{S} \\
\text{Rate of attachment} & = k_A P A C_V \\
\text{Rate of detachment} & = k_{-A} C_{A,S} \\
C_t & = C_{A,S} + C_V
\end{align*}
\]

**A:** atom, molecule, or some other atomic combination.

**S:** active site

**\(P_i\):** partial pressure of species i in the gas phase

**\(C_{i,S}\):** surface concentration of sites occupied by species i

**\(C_V\):** surface concentration of vacant sites

**\(K_A\):** Rate constant of the attachment processes

**\(K_{-A}\):** Rate constant of the detachment processes

**\(C_t\):** the total concentration of sites
Two types of adsorption:

Molecular adsorption

\[
\text{CO} + \overset{\text{Cr}}{-\text{Ni-Ni-Ni}} \rightleftharpoons \overset{\text{C}}{-\text{Ni-Ni-Ni}}
\]

Dissociative adsorption

\[
\text{CO} + \overset{\text{Cr}}{-\text{Fe-Fe-Fe}} \rightleftharpoons \overset{\text{C}}{-\text{Fe-Fe-Fe}}
\]
**Adsorption**

1. **Molecular adsorption**

\[
\text{CO} + \text{S} \xrightleftharpoons[k_A]{K_A} \text{CO} \cdot \text{S}
\]

\[
r_{AD} = k_A \left( P_{CO} C_V - \frac{C_{CO \cdot S}}{K_A} \right)
\]

\[
C_{CO \cdot S} = \frac{K_A P_{CO} C_t}{1 + K_A P_{CO}}
\]

![Molecular Adsorption Graph](image)

2. **Dissociative adsorption**

\[
\text{CO} + 2\text{S} \xrightleftharpoons[k_A]{K_A} \text{C} \cdot \text{S} + \text{O} \cdot \text{S}
\]

\[
r_{AD} = k_A \left( P_{CO} C_V^2 - \frac{C_{C \cdot S} C_{O \cdot S}}{K_A} \right)
\]

\[
C_{O \cdot S} = \frac{(K_A P_{CO})^{1/2} C_t}{1 + 2 (K_A P_{CO})^{1/2}}
\]

![Dissociative Adsorption Graph](image)
After adsorption, surface reaction can take place via

- Single site mechanism (Langmuir-Hinshelwood)
- Dual site mechanism (Langmuir-Hinshelwood)
- Adsorbed molecule can react with gas-phase component (Eley-Rideal)
Single site mechanism

In single site mechanism only one active surface site is involved.

For example, isomerization

\[ A + S \xrightleftharpoons[k_−A]{k_A} A \cdot S \]

\[ A \cdot S \xrightleftharpoons[k_−S]{k_+S} B \cdot S \]

\[ B \cdot S \xrightleftharpoons[k_−B]{k_B} B + S \]
Rate of surface reaction:

\[ r_S = k_+s C_{A\cdot S} - k_-s C_{B\cdot S} \]

\[ = k_+s \left( C_{A\cdot S} - \frac{C_{B\cdot S}}{K_s} \right) \]

Where \( K_s \) is the surface-reaction equilibrium constant

\[ K_s = \frac{k_+s}{k_-s} \]

\[ C_{A\cdot S} = \frac{K_A P_A C_t}{1 + K_A P_A + K_B P_B} \]

\[ C_{B\cdot S} = \frac{K_B P_B C_t}{1 + K_A P_A + K_B P_B} \]
Dual site mechanism

- In dual site mechanism **two** active surface site are involved
  - Adsorbed component A reacts with unoccupied site:
    \[ A\cdot S + S \leftrightarrow B\cdot S + S \]
  - Adsorbed component A reacts with another adsorbed component B:
    \[ A\cdot S + B\cdot S \leftrightarrow C\cdot S + D\cdot S \]
  - Also two different sites can be involved:
    \[ A\cdot S + B\cdot S' \leftrightarrow C\cdot S + D\cdot S' \]
1. Adsorbed component A reacts with unoccupied site as the rate determining step:

\[
\begin{align*}
A + S & \underset{k_{-A}}{\overset{k_A}{\longleftrightarrow}} A \cdot S \\
A \cdot S + S & \underset{k_{-S}}{\overset{k_{+S}}{\longleftrightarrow}} B \cdot S + S \\
B \cdot S & \underset{k_{-B}}{\overset{k_B}{\longleftrightarrow}} B + S
\end{align*}
\]

Rate of surface reaction:

\[
r_S = k_{+s}C_{A \cdot S}C_V - k_{-s}C_{B \cdot S}C_V = k_{+s} \left( C_{A \cdot S}C_V - \frac{C_{B \cdot S}C_V}{K_s} \right)
\]

\[
C_{A \cdot S} = \frac{K_A P_A C_t}{1 + K_A P_A + K_B P_B}
\]

\[
C_{B \cdot S} = \frac{K_B P_B C_t}{1 + K_A P_A + K_B P_B}
\]
2. Adsorbed component A reacts with another adsorbed component B:

\[ A + S \xrightleftharpoons[k_A]{k_{-A}} A \cdot S \]

\[ B + S \xrightleftharpoons[k_B]{k_{-B}} B \cdot S \]

\[ A \cdot S + B \cdot S \xrightleftharpoons[k_{+S}]{k_{-S}} C \cdot S + D \cdot S \]

\[ C \cdot S \xrightleftharpoons[k_C]{k_{-C}} C + S \]

\[ D \cdot S \xrightleftharpoons[k_D]{k_{-D}} D + S \]
Surface Reaction • Langmuir-Hinshelwood

Rate of surface reaction:

\[ r_S = k_{+s} C_{A.S} C_{B.S} - k_{-s} C_{C.S} C_{D.S} = k_{+s} \left( C_{A.S} C_{B.S} - \frac{C_{C.S} C_{D.S}}{K_s} \right) \]

\[ C_{A.S} = \frac{K_A P_A C_t}{1 + K_A P_A + K_B P_B + K_c P_c + K_d P_d} \]
\[ C_{B.S} = \frac{K_B P_B C_t}{1 + K_A P_A + K_B P_B + K_c P_c + K_d P_d} \]
\[ C_{C.S} = \frac{K_C P_C C_t}{1 + K_A P_A + K_B P_B + K_c P_c + K_d P_d} \]
\[ C_{D.S} = \frac{K_D P_D C_t}{1 + K_A P_A + K_B P_B + K_c P_c + K_d P_d} \]
3. Two species adsorbed on different types of sites S and S':

\[
A + S \overset{k_A}{\underset{k_{-A}}{\rightleftharpoons}} A \cdot S
\]

\[
B + S' \overset{k_B}{\underset{k_{-B}}{\rightleftharpoons}} B \cdot S'
\]

\[
A \cdot S + B \cdot S' \overset{k_{+S}}{\underset{k_{-S}}{\rightleftharpoons}} C \cdot S + D \cdot S'
\]

\[
C \cdot S \overset{k_C}{\underset{k_{-C}}{\rightleftharpoons}} C + S
\]

\[
D \cdot S' \overset{k_D}{\underset{k_{-D}}{\rightleftharpoons}} D + S'
\]
Rate of surface reaction:

\[ r_S = k_{+s}C_{A\cdot S}C_{B\cdot S'} - k_{-s}C_{C\cdot S}C_{D\cdot S'} = k_{+s} \left( C_{A\cdot S}C_{B\cdot S'} - \frac{C_{C\cdot S}C_{D\cdot S'}}{K_s} \right) \]

\[
C_{A\cdot S} = \frac{K_A P_A C_t}{1 + K_A P_A + K_C P_C} \quad \quad C_{B\cdot S'} = \frac{K_B P_B C_t}{1 + K_B P_B + K_D P_D}
\]

\[
C_{C\cdot S} = \frac{K_C P_C C_t}{1 + K_A P_A + K_C P_C} \quad \quad C_{D\cdot S'} = \frac{K_D P_D C_t}{1 + K_B P_B + K_D P_D}
\]
Surface Reaction • Eley-Rideal

Adsorbed molecule react with gas-phase component

\[ A + S \xrightleftharpoons[k_A \rightarrow k_{-A}]{k_A \leftarrow k_{-A}} A \cdot S \]

\[ A \cdot S + B \xrightleftharpoons[k_{+S} \rightarrow k_{-S}]{k_{+S} \leftarrow k_{-S}} C \cdot S \]

\[ C \cdot S \xrightleftharpoons[k_B \rightarrow k_{-B}]{k_B \leftarrow k_{-B}} C + S \]

Rate of surface reaction:

\[ r_S = k_{+s} C_{A \cdot S} P_B - k_{-s} C_{C \cdot S} = k_{+s} \left( C_{A \cdot S} P_B - \frac{C_{C \cdot S}}{K_s} \right) \]

\[ C_{A \cdot S} = \frac{K_A P_A C_t}{1 + K_A P_A + K_C P_C} \]

\[ C_{C \cdot S} = \frac{K_C P_C C_t}{1 + K_A P_A + K_C P_C} \]
Desorption

\[ C \cdot S \xrightleftharpoons[k_D]{k_D} C + S \]

The rate of desorption of C is

\[ r_D = k_D C_{C \cdot S} - k_D P_C C_V = k_D \left( C_{C \cdot S} - \frac{P_C C_V}{K_{DC}} \right) \]
• Assumption: Fast and slow reaction steps

• Slowest step determines overall reaction rate
  – Changes in slowest step decides reaction rate

• Fast steps are in equilibrium:
  E.g. \( r_{AD} = r_{+AD} - r_{-AD} = 0 \)
Rate-Determining Step

Reaction: \( A \rightarrow B + C \)

Step: 

\[ A + S \xrightleftharpoons[\kappa_A]{\kappa_{-A}} A \cdot S \]

\[ A \cdot S \xrightleftharpoons[\kappa_S]{\kappa_{-S}} B \cdot S + C \]

\[ B \cdot S \xrightleftharpoons[\kappa_B]{\kappa_{-B}} B + S \]
The rate of adsorption is
\[ r_{AD} = k_A P_A C_V - k_{-A} C_{A\cdot S} = k_A \left( P_A C_V - \frac{C_{A\cdot S}}{K_A} \right) \]

The rate of reaction is
\[ r_S = k_S C_{A\cdot S} - k_{-S} P_C C_{A\cdot B} = k_S \left( C_{A\cdot S} - \frac{P_C C_{B\cdot S}}{K_S} \right) \]

The rate of desorption is
\[ r_D = k_B C_{B\cdot S} - k_{-B} P_B C_V = k_B \left( C_{B\cdot S} - \frac{P_B C_V}{K_D} \right) \]

The B adsorption equilibrium constant \( K_B \) is just the reciprocal of the B desorption constant \( K_D \)
\[ K_B = \frac{1}{K_D} \]

The rate of desorption can be written as
\[ r_D = k_B (C_{B\cdot S} - K_B P_B C_V) \]
1. Adsorption is the RDS

\[-r_A' = r_{AD} = k_A \left( P_A C_V - \frac{C_{A:S}}{K_A} \right)\]

For adsorption-limited reaction, \( k_A \) is very small and \( k_S, k_B \) are very large in comparison. Consequently, the ratios \( r_S/k_S, r_D/k_B \) are very small (approximately zero), whereas the ratio \( r_{AD}/k_A \) is relatively large.

**Reaction:**

\[r_S = k_S \left( C_{A:S} - \frac{P_C C_{B:S}}{K_S} \right) \quad \frac{r_S}{k_S} \approx 0 \quad \text{So:} \quad C_{A:S} = \frac{P_C C_{B:S}}{K_S}\]

**Desorption:**

\[r_D = k_B (C_{B:S} - K_B P_B C_V) \quad \frac{r_D}{k_B} \approx 0 \quad \text{So:} \quad C_{B:S} = K_B P_B C_V\]

So:

\[C_{A:S} = \frac{K_B P_B P_C}{K_S} C_V\]
Replacing $C_{A.S}$ in the rate equation and then factoring $C_V$, we obtain:

$$r_{AD} = k_A \left( P_A - \frac{K_B P_B P_C}{K_A K_S} \right) C_V = k_A \left( P_A - \frac{P_B P_C}{K_P} \right) C_V$$

Where:

$$K_P = \frac{K_A K_S}{K_B}$$

Total amount of sites:

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

Substituting for $C_{B.S}$ and $C_{A.S}$ in the Equation:

$$C_t = C_V + \frac{K_B P_B P_C}{K_S} C_V + K_B P_B C_V$$
Solving for amount of vacant sites:

\[ C_V = \frac{C_t}{1 + K_B P_B P_C / K_S + K_B P_B} \]

So:

\[ -r'_A = r_{AD} = k_A \left( P_A C_V - \frac{C_A \cdot S}{K_A} \right) = k_A \left( P_A - \frac{P_B P_C}{K_P} \right) C_V \]

\[ = \frac{C_t k_A (P_A - P_B P_C / K_P)}{1 + K_B P_B P_C / K_S + K_B P_B} \]

Where:

\[ K_P = \frac{K_A K_S}{K_B} \]
2. Surface Reaction is the RDS

\[ -r'_A = r_S = k_S \left( C_{A\cdot S} - \frac{P_C C_{B\cdot S}}{K_S} \right) \]

Adsorption

\[ r_{AD} = k_A \left( P_A C_V - \frac{C_{A\cdot S}}{K_A} \right) \quad \frac{r_{AD}}{k_A} \approx 0 \quad \text{So:} \quad C_{A\cdot S} = K_A P_A C_V \]

Desorption:

\[ r_D = k_B (C_{B\cdot S} - K_B P_B C_V) \quad \frac{r_D}{k_B} \approx 0 \quad \text{So:} \quad C_{B\cdot S} = K_B P_B C_V \]
Substituting for \( C_{B.S} \) and \( C_{A.S} \) in the rate equation, we obtain:

\[
\begin{align*}
  r_S &= k_S \left( K_A P_A - \frac{K_B P_B P_C}{K_S} \right) C_V \\
  &= k_S K_A \left( P_A - \frac{P_B P_C}{K_P} \right) C_V
\end{align*}
\]

Where:

\[ K_P = \frac{K_A K_S}{K_B} \]

Total amount of sites:

\[ C_t = C_V + C_{A.S} + C_{B.S} \]

Substituting for \( C_{B.S} \) and \( C_{A.S} \), factoring out \( C_V \):

\[
C_V = \frac{C_t}{1 + K_A P_A + K_B P_B}
\]
So:

\[-r'_A = r_S = k_S K_A \left( P_A - \frac{P_B P_C}{K_P} \right) \]

\[C_V = \frac{C_t k_S K_A (P_A - P_B P_C/K_P)}{1 + K_A P_A + K_B P_B} \]

\[= \frac{k (P_A - P_B P_C/K_P)}{1 + K_A P_A + K_B P_B} \]

Where: \[k = C_t k_S K_A \]
3. Desorption is the RDS

\[-r'_A = r_D = k_B(C_{B\cdot S} - K_B P_B C_V)\]

Adsorption

\[r_{AD} = k_A \left( P_A C_V - \frac{C_{A\cdot S}}{K_A} \right) \quad \frac{r_{AD}}{k_A} \approx 0 \quad \text{So:} \quad C_{A\cdot S} = K_A P_A C_V\]

Reaction:

\[r_S = k_S \left( C_{A\cdot S} - \frac{P_C C_{B\cdot S}}{K_S} \right) \quad \frac{r_S}{k_S} \approx 0 \quad \text{So:} \quad C_{B\cdot S} = \frac{K_S C_{A\cdot S}}{P_C}\]
Substituting for $C_{B\cdot S}$ and $C_{A\cdot S}$ in the rate equation, we obtain:

$$r_D = k_B \left( \frac{K_A K_S P_A}{P_C} - K_B P_B \right) C_V = k_B K_A K_S \left( \frac{P_A}{P_C} - \frac{P_B}{K_P} \right) C_V$$

Where: $K_P = \frac{K_A K_S}{K_B}$

Total amount of sites: $C_t = C_V + C_{A\cdot S} + C_{B\cdot S}$

Substituting for $C_{B\cdot S}$ and $C_{C\cdot S}$, factoring out $C_V$:

$$C_V = \frac{C_t}{1 + K_A K_S P_A / P_C + K_A P_A}$$
Rate-Determining Step

So:

\[-r'_A = r_D = k_B K_A K_S \left( \frac{P_A}{P_C} - \frac{P_B}{K_P} \right) \]

\[C_V = \frac{C_t k_B K_A K_S (P_A/P_C - P_B/K_P)}{1 + K_A P_A + K_A K_S P_A/P_C} \]

\[= \frac{k (P_A/P_C - P_B/K_P)}{1 + K_A P_A + K_A K_S P_A/P_C} \]

Where: \[k = C_t k_B K_A K_S\]
A! Rate-Determining Step

Overall equilibrium constant is the product of the equilibrium constants of the steps, thus in this case:

\[ K_p = \frac{K_A \cdot K_S}{K_B} \]

For irreversible reaction \( K_p \) is large, so \( 1/K_p \) is small

**Adsorption is RDS:**

\[ -r_A' = \frac{k(P_A - P_B P_C/K_P)}{1 + K_B P_B P_C/K_S + K_B P_B} = \frac{kP_A}{1 + K_B P_B P_C/K_S + K_B P_B} \]

**Surface reaction is RDS:**

\[ -r_A' = \frac{k(P_A - P_B P_C/K_P)}{1 + K_A P_A + K_B P_B} = \frac{kP_A}{1 + K_A P_A + K_B P_B} \]

**Desorption is RDS:**

\[ -r_A' = \frac{k(P_A/P_C - P_B/K_P)}{1 + K_A P_A + K_A K_S P_A/P_C} = \frac{k P_A/P_C}{1 + K_A P_A + K_A K_S P_A/P_C} \]
Initial rate of reaction:

**Adsorption is RDS:**

\[-r'_A = \frac{kP_A}{1 + K_B P_B P_C / K_S + K_B P_B} \rightarrow -r'_{A0} = kP_{A0}\]

**Surface reaction is RDS:**

\[-r'_A = \frac{kP_A}{1 + K_A P_A + K_B P_B} \rightarrow -r'_{A0} = \frac{kP_{A0}}{1 + K_A P_{A0}}\]

**Desorption is RDS:**

\[-r'_A = \frac{k P_A / P_C}{1 + K_A P_A + K_A K_S P_A / P_C} \rightarrow -r'_{A0} = k'\]
Rate-Determining Step

**Reaction:** \( A \rightarrow B + C \)

Adsorption is RDS:
\[-r_{A0} = kP_{A0}\]

Desorption is RDS:
\[-r_{A0} = k'\]

Surface reaction is RDS:
\[-r_{A0} = \frac{kP_{A0}}{1 + K_A P_{A0}}\]

At low partial pressures of A: \( 1 \gg K_A P_{C0} \)
\[-r_{A0} = k P_{A0}\]

At high partial pressures of A: \( 1 \ll K_A P_{C0} \)
\[-r_{A0} = \frac{k P_{A0}}{K_A P_{A0}} = k'\]
Rate-Determining Step

**Adsorption**

\[ r_0 \]

\[ T_3 \rightarrow T_2 \rightarrow T_1 \]

\[ -p_A \rightarrow \]

**Surface**

\[ T_3 \rightarrow T_2 \rightarrow T_1 \]

\[ -p_A \rightarrow \]

**Desorption**

\[ T_3 \]

\[ T_2 \]

\[ T_1 \]

\[ -p_A \rightarrow \]
Derivation of rate laws

- Assumptions needs to be made on
  1. Adsorption
     - Molecular or dissociative
     - Same or different active sites (competitive adsorption or not)
  2. Mechanism of surface reaction
     - Langmuir-Hinshelwood (single or dual site)
     - Eley-Rideal
  3. Desorption
  4. Rate-Determining step
    - Reaction rate laws for each step
    - Elimination of unknowns
Derivation of rate laws

Instructions:

1. Make rate law for each step (steps are elementary)
2. Reaction rate constant of RDS is small
   → For others \(-r/k \approx 0\)
   → Solve surface concentrations
3. Make site balance and solve \(C_v\)
4. Substitute surface concentrations and \(C_v\) into rate law
5. Substitute \(K_p\) (if overall reaction is irreversible)
6. Compare the rate law with experimental data
Example 1:  \[ C_6H_5CH(CH_3)_2 \rightarrow C_6H_6 + C_3H_6 \]

Step:

- \[ C + S \xrightleftharpoons[k_A]{k_{-A}} C \cdot S \quad \text{C=cumene} \]
  - B=benzene

- \[ C \cdot S \xrightleftharpoons[k_S]{k_{-S}} B \cdot S + P \quad \text{P=propylene} \]

- \[ B \cdot S \xrightleftharpoons[k_D]{k_{-D}} B + S \]

Diagram:
- Adsorption of cumene
- Surface reaction
- Desorption of benzene
Derivation of rate laws

Adsorption is RDS:

\[-r'_C = \frac{C_t k_A (P_C - P_B P_P/K_P)}{1 + K_B P_B P_P/K_S + K_B P_B}\]

Surface reaction is RDS:

\[-r'_C = \frac{C_t k_S K_C (P_C - P_B P_P/K_P)}{1 + K_B P_B + K_C P_C}\]

Desorption is RDS:

\[-r'_C = \frac{C_t k_D K_C K_S (P_C - P_B P_P/K_P)}{P_P + K_C P_C P_P + K_C K_S P_C}\]

Which rate law is correct?

Actual initial rate as a function of partial pressure of cumene.

The rate law derived by assuming that the surface reaction is rate-Determining agrees with the data.
Derivation of rate laws

The rate law for the case of no inerts adsorbing on the surface is:

$$-r'_C = \frac{C_t k_S K_C (P_C - P_B P_P / K_P)}{1 + K_B P_B + K_C P_C}$$

If we were to have an adsorbing inert in the feed, the inert would not participate in the reaction but would occupy active sites on the catalyst surface:

$$I + S \Leftrightarrow I \cdot S$$

The site balance:

$$C_t = C_v + C_{A\cdot S} + C_{B\cdot S} + C_{I\cdot S}$$

Because the adsorption of the inert is at equilibrium, the concentration of sites occupied by the inert is

$$C_{I\cdot S} = K_I P_I C_v$$
Substituting for the inert sites in the site balance, the rate law for surface reaction control when an adsorbing inert is present is

\[-r'_C = \frac{C_t k_S K_C (P_C - P_B P_P / K_P)}{1 + K_B P_B + K_C P_C + K_I P_I}\]

\[= \frac{k (P_C - P_B P_P / K_P)}{1 + K_B P_B + K_C P_C + K_I P_I}\]
Example 2: Propene hydrogenation

Propene (PE) + H₂ → Propane (PA)

Derive reaction rate law when propene (PE) adsorbs molecularly, surface reaction is rate-determining step, propane (PA) is formed on active site and mechanism is

1. Langmuir-Hinshelwood, hydrogen adsorbs dissociatively

2. Eley-Rideal (hydrogen reacts directly from gas-phase)

3. Langmuir-Hinshelwood, hydrogen adsorbs molecularly
1. Langmuir-Hinshelwood, hydrogen adsorbs dissociatively

\[
\begin{align*}
\text{PE} + S & \xrightleftharpoons[k_{-PE}]{k_{PE}} \text{PE} \cdot S \\
\text{H}_2 + 2S & \xrightleftharpoons[k_{-H_2}]{k_{H_2}} 2\text{H} \cdot S \\
\text{PE} \cdot S + 2\text{H} \cdot S & \xrightleftharpoons[k_S]{k_{S}} \text{PA} \cdot S + 2S \\
\text{PA} \cdot S & \xrightleftharpoons[k_{-PA}]{k_{PA}} \text{PA} + S
\end{align*}
\]
A! Derivation of rate laws

Adsorption: \[ r_{APE} = k_{PE}P_{PE}C_V - k_{-PE}C_{PE\cdot S} = k_{PE}\left( P_{PE}C_V - \frac{C_{PE\cdot S}}{K_{PE}} \right) \]

Adsorption: \[ r_{AH_2} = k_{H_2}P_{H_2}C_V^2 - k_{-H_2}C_{H\cdot S}^2 = k_{H_2}\left( P_{H_2}C_V^2 - \frac{C_{H\cdot S}^2}{K_{H_2}} \right) \]

Surface reaction: \[ r_S = k_SC_{PE\cdot S}C_{H\cdot S}^2 \]

Desorption \[ r_{DPA} = k_{PA}C_{PA\cdot S} - k_{-PA}P_{PA}C_V = k_{PA}\left( C_{PA\cdot S} - \frac{P_{PA}C_V}{K_D} \right) \]

\[ K_{PA} = \frac{1}{K_D} \]

So the rate of desorption is \[ r_{DPA} = k_{PA}(C_{PA\cdot S} - K_{PA}P_{PA}C_V) \]
Since the surface reaction is rate-determining

\[ r_{APE} = k_{PE} \left( P_{PE} C_V - \frac{C_{PE \cdot S}}{K_{PE}} \right) \]

\[ \frac{r_{APE}}{k_{PE}} \approx 0 \quad C_{PE \cdot S} = K_{PE} P_{PE} C_V \]

\[ r_{AH_2} = k_{H_2} \left( P_{H_2} C_V^2 - \frac{C_{H \cdot S}^2}{K_{H_2}} \right) \]

\[ \frac{r_{AH_2}}{k_{H_2}} \approx 0 \quad C_{H \cdot S} = \sqrt{K_{H_2} P_{H_2} C_V} \]

\[ r_{DPA} = k_{PA} (C_{PA \cdot S} - K_{PA} P_{PA} C_V) \]

\[ \frac{r_{DPA}}{k_{PA}} \approx 0 \quad C_{PA \cdot S} = K_{PA} P_{PA} C_V \]

Substituting for \( C_{PE \cdot S} \) and \( C_{H \cdot S} \) in the rate equation

\[ r_S = k_S C_{PE \cdot S} C_{H \cdot S}^2 = k_S K_{PE} K_{H_2} P_{PE} P_{H_2} C_V^3 \]
Derivation of rate laws

Total amount of sites: \[ C_t = C_V + C_{PE\cdot S} + C_{H\cdot S} + C_{PA\cdot S} \]

Substituting for \( C_{PE\cdot S}, C_{H\cdot S} \) and \( C_{PA\cdot S} \), factoring out \( C_V \): \[ C_V = \frac{C_t}{1 + K_{PE}P_{PE} + \sqrt{K_{H_2}P_{H_2}} + K_{PA}P_{PA}} \]

So, the rate equation:

\[
-r_A = \frac{k_S K_{PE} K_{H_2} P_{PE} P_{H_2} C_t^3}{(1 + K_{PE} P_{PE} + \sqrt{K_{H_2} P_{H_2}} + K_{PA} P_{PA})^3}
\]

\[
= \frac{k P_{PE} P_{H_2}}{(1 + K_{PE} P_{PE} + \sqrt{K_{H_2} P_{H_2}} + K_{PA} P_{PA})^3}
\]

Where: \( k = C_t^3 k_S K_{PE} K_{H_2} \)
Derivation of rate laws

Reaction rate laws (surface reaction RDS):

1. Langmuir-Hinshelwood, hydrogen adsorbs dissociatively

\[-r_A = \frac{kP_{PE}P_{H2}}{1 + \sqrt[3]{K_{H2}P_{H2} + K_{PE}P_{PE} + K_{PA}P_{PA}}}\]

2. Eley-Rideal (hydrogen reacts directly from gas-phase)

\[-r_A = \frac{kP_{PE}P_{H2}}{1 + K_{PE}P_{PE} + K_{PA}P_{PA}}\]

3. Langmuir-Hinshelwood, hydrogen adsorbs molecularly

\[-r_A = \frac{kP_{PE}P_{H2}}{\left(1 + K_{H2}P_{H2} + K_{PE}P_{PE} + K_{PA}P_{PA}\right)^2}\]

Homework: Derive rest of rate laws!
It is known that the rate law for irreversible gas-phase reaction \( A + B_2 \rightarrow C \) is

\[
-r_A = \frac{k' P_A P_B}{(1 + \sqrt{K_B P_B + K_C P_C})^2}
\]

What is the mechanism behind this rate law?
From rate law to mechanism

It is known that rate law for irreversible gas-phase reaction \( A + B_2 \rightarrow C \) is

\[
-r_A = \frac{k' P_A P_B}{\left(1 + \sqrt{K_B P_B + K_C P_C}\right)^2}
\]

Thus, mechanism is

\( B_2 (g) + 2 \text{S} \leftrightarrow 2 \text{B} \cdot \text{S} \)  
Adsorption of B  
occupying two sites (dissociative adsorption)

\( A (g) + 2 \text{B} \cdot \text{S} \leftrightarrow \text{C} \cdot \text{S} + \text{S} \)  
Surface reaction, RDS.  
where A reacts from gas phase

\( \text{C} \cdot \text{S} \leftrightarrow \text{C} + \text{S} \)  
Desorption of C
Irreversible Surface-Reaction-Limited Rate Laws

Single site

\[ A \cdot S \rightarrow B \cdot S \]

\[ -r'_A = \frac{kP_A}{1 + K_A P_A + K_B P_B} \]

Dual site

\[ A \cdot S + S \rightarrow B \cdot S + S \]

\[ -r'_A = \frac{kP_A}{(1 + K_A P_A + K_B P_B)^2} \]

\[ A \cdot S + B \cdot S \rightarrow C \cdot S + S \]

\[ -r'_A = \frac{kP_A P_B}{(1 + K_A P_A + K_B P_B + K_C P_C)^2} \]

Eley–Rideal

\[ A \cdot S + B(g) \rightarrow C \cdot S \]

\[ -r'_A = \frac{kP_A P_B}{1 + K_A P_A + K_C P_C} \]
Deducing rate law from experimental data

Cyclohexanol (A) → Cyclohexene (B) + Water (W)

<table>
<thead>
<tr>
<th>run</th>
<th>Reaction rate (mol/dm$^3$ s)</th>
<th>Cyclohexanol $P_A$ (atm)</th>
<th>Cyclohexene $P_B$ (atm)</th>
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# Deducing rate law from experimental data

## Dependence of reaction rate on cyclohexanol (runs 1, 2 and 3)

<table>
<thead>
<tr>
<th>run</th>
<th>Reaction rate (mol/dm³ s)</th>
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\[ -r_A \sim \frac{P_A}{1 + K_A P_A + \ldots} \]

**Explanation:** When \( P_A \) is small, \(-r_A\) increases linearly with increasing \( P_A \). When \( P_A \) is high, rate becomes constant
**Dependence of reaction rate on cyclohexene (runs 6, 7 and 9)**

<table>
<thead>
<tr>
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<th>Reaction rate (mol/dm³ s)</th>
<th>Cyclohexanol Pₐ (atm)</th>
<th>Cyclohexene Pₜ (atm)</th>
<th>Water Pₜ (atm)</th>
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**Explanation:** When Pₜ increases, -rₐ decreases linearly.
Deducing rate law from experimental data

Dependence of reaction rate on water (runs 4, 5 and 8)

<table>
<thead>
<tr>
<th>run</th>
<th>Reaction rate (mol/dm$^3$ s)</th>
<th>Cyclohexanol $P_A$ (atm)</th>
<th>Cyclohexene $P_B$ (atm)</th>
<th>Water $P_W$ (atm)</th>
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Explanation: When $P_W$ increases, $-r_A$ decreases linearly.
Deducing rate law from experimental data

Dependence of reaction rate on $P_A = P_B = P_W = P$ (runs 1, 10 and 11)

<table>
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<tr>
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<th>Reaction rate (mol/dm$^3$ s)</th>
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Explanation: When $P$ is small, $-r_A$ increases linearly with increasing $P$. When $P$ is high, rate becomes constant

$$-r_A \sim \frac{P_A}{(1 + K_A P_A + K_B P_B + K_W P_W)^2}$$
Based on given data, rate law for cyclohexanol dehydration is

\[-r_A = \frac{kP_A}{(1 + K_A P_A + K_B P_B + K_W P_W)^2}\]

Thus mechanism is

- A + S ↔ A∙S  \hspace{1cm} \text{adsorption of cyclohexanol (A)}
- A∙S + S → B∙S + W∙S  \hspace{1cm} \text{surface reaction on two sites, RDS}
- B∙S ↔ B + S  \hspace{1cm} \text{desorption of cyclohexene (B)}
- W∙S ↔ W + S  \hspace{1cm} \text{desorption of water}
PSSH = Pseudo-Steady-State Hypothesis

Applied in reactions which contain active intermediate species (e.g. reactions involving free radicals)

Net formation rate of active intermediate species is zero:

\[ r_i^* S = 0 \]

(Compare to \( r/k \approx 0 \))

PSSH useful when

Two or more steps are rate-limiting
Some steps are irreversible

See example in the course book:

Chapter 10.3.6 (4th ed.)
Chapter 10.3.5 (3rd ed.)
Example: the gas-phase decomposition of azomethane

\[(\text{CH}_3)_2\text{N}_2 \rightarrow \text{C}_2\text{H}_6 + \text{N}_2\]

Mechanism:

Reaction 1: \[(\text{CH}_3)_2\text{N}_2 + (\text{CH}_3)_2\text{N}_2 \xrightarrow{k_1\text{AZO}^*} (\text{CH}_3)_2\text{N}_2 + [(\text{CH}_3)_2\text{N}_2]^*\]

Reaction 2: \[(\text{CH}_3)_2\text{N}_2 + [(\text{CH}_3)_2\text{N}_2]^* \xrightarrow{k_2\text{AZO}^*} (\text{CH}_3)_2\text{N}_2 + (\text{CH}_3)_2\text{N}_2\]

Reaction 3: \[[(\text{CH}_3)_2\text{N}_2]^* \xrightarrow{k_3\text{AZO}^*} \text{C}_2\text{H}_6 + \text{N}_2\]
Because each of the reaction steps is elementary, the corresponding rate laws for the active intermediate AZO* in reactions 1, 2, 3 are

\[
\begin{align*}
    r_{1AZO^*} &= k_1 C_{AZO}^2 \\
    r_{2AZO^*} &= -k_2 C_{AZO} C_{AZO^*} \\
    r_{3AZO^*} &= -k_3 C_{AZO}^*
\end{align*}
\]

(Let \( k_1 = k_{1AZO^*} \), \( k_2 = k_{2AZO^*} \), \( k_3 = k_{3AZO^*} \))

The concentration of the active intermediate AZO* is not readily measurable, so we will use the Pseudo-Steady-State-Hypothesis (PSSH) to obtain a rate law in terms of measurable concentrations.
The rate of formation of product:

\[ r_{C_2H_6} = k_3 C_{AZO^*} \]

To find the concentration of the active intermediate AZO*, we set the net rate of formation of AZO* equal to zero, \( r_{AZO^*} \equiv 0 \)

\[ r_{AZO^*} = r_{1AZO^*} + r_{2AZO^*} + r_{3AZO^*} = 0 \]

\[ = k_1 C_{AZO}^2 - k_2 C_{AZO} C_{AZO^*} - k_3 C_{AZO^*} = 0 \]

Solving for \( C_{AZO^*} \):

\[ C_{AZO^*} = \frac{k_1 C_{AZO}^2}{k_2 C_{AZO} + k_3} \]

Substituting for \( C_{AZO^*} \) in the rate Equation:

\[ r_{C_2H_6} = \frac{k_1 k_3 C_{AZO}^2}{k_2 C_{AZO} + k_3} \]
1. Quasi-Equilibrium Hypothesis

1. Select mechanism
2. Make rate law for each step (steps are elementary)
3. Assume rate-limiting step (RDS)
   - For RDS, $k$ is small
   - For others $-r/k \approx 0$
4. Solve surface concentrations
5. Write site balance and solve $C_v$
6. Substitute surface concentrations and $C_v$ into rate law
7. Substitute $K_p$ (if overall reaction is irreversible)
8. Compare with data
9. Extract parameters
2. Pseudo-Steady-State Hypothesis

1. Propose an active intermediate.
2. Propose a mechanism.
3. Write rate laws.
4. Write rate of formation of product.
5. Write net rate of formation of the active intermediate and use the PSSH.
6. Eliminate the concentration of the active intermediate species in the rate laws by solving the simultaneous equations developed in Steps 4 and 5
Chemical Vapor Deposition

The mechanism of CVD is very similar to a heterogeneous catalytic reaction. The reactant(s) adsorbs on the surface site and then reacts on the surface to form a new surface site. This process may be followed by a desorption step, depending on the particular reaction.

For example:

The growth of germanium films can be accomplished by CVD. A proposed mechanism is:
Gas-phase dissociation:

\[ \text{GeCl}_4 (g) \rightleftharpoons \text{GeCl}_2 (g) + \text{Cl}_2 (g) \]

Adsorption:

\[ \text{GeCl}_2 (g) + \text{S} \rightleftharpoons \text{GeCl}_2 \cdot \text{S} \]

Adsorption:

\[ \text{H}_2 (g) + 2\text{S} \rightleftharpoons \text{2H} \cdot \text{S} \]

Surface reaction:

\[ \text{GeCl}_2 \cdot \text{S} + 2\text{H} \cdot \text{S} \rightleftharpoons \text{Ge} (S) + 2\text{HCl} (g) + 2\text{S} \]
The surface reaction is RDS

\[ r''_{Dep} = k_S f_{GeCl_2} f_H^2 \]

Where
\[ r''_{Dep} = \text{deposition rate per unit surface area, nm/s} \]
\[ k_S = \text{surface specific reaction rate, nm/s} \]
\[ f_{GeCl_2} = \text{fraction of the surface occupied by germanium dichloride} \]
\[ f_H = \text{fraction of the surface covered by hydrogen atom} \]

The difference between developing CVD rate laws and rate laws for catalysis is that the site concentration is replaced by the fractional surface area coverage.

Fractional area balance: \[ f_V + f_{GeCl_2} + f_H = 1 \]
The net rate of GeCl$_2$ adsorption is

$$r_{A GeCl_2} = k_A \left( P_{GeCl_2} f_V - \frac{f_{GeCl_2}}{K_A} \right)$$

Since the surface reaction is rate-limiting, in a manner analogous to catalysis reactions, we have for the adsorption of GeCl$_2$:

$$\frac{r_{A GeCl_2}}{k_A} \approx 0$$

The fractional surface coverage of GeCl$_2$:

$$f_{GeCl_2} = K_A P_{GeCl_2} f_V$$
The dissociative adsorption of hydrogen

\[ r_{AH_2} = k_H \left( P_{H_2} f_V^2 - \frac{f_H^2}{K_H} \right) \]

Since the surface reaction is rate-limiting

\[ \frac{r_{AH_2}}{k_H} \approx 0 \]

Then

\[ f_H = f_V \sqrt{K_H P_{H_2}} \]
Substituting for $f_{GeCl_2}$ and $f_H$ in the rate equation, we obtain:

$$r''_{Dep} = k_S f_{GeCl_2} f_H^2 = f_V^3 k_S K_A P_{GeCl_2} K_H P_{H_2}$$

We solve for $f_V$ in an identical manner to that for $C_V$ in heterogeneous catalysis.

$$f_V + f_V \sqrt{K_H P_{H_2}} + f_V K_A P_{GeCl_2} = 1$$

Rearranging yields

$$f_V = \frac{1}{1 + K_A P_{GeCl_2} + \sqrt{K_H P_{H_2}}}$$
Finally, substituting for $f_V$ in the rate equation

$$r''_{\text{Dep}} = \frac{k_S K_H K_A P_{\text{GeCl}_2} P_{H_2}}{(1 + K_A P_{\text{GeCl}_2} + \sqrt{K_H P_{H_2}})^3}$$

and lumping $K_H$, $K_A$, and $k_S$ into a specific reaction rate $k'$ yields

$$r''_{\text{Dep}} = \frac{k' P_{\text{GeCl}_2} P_{H_2}}{(1 + K_A P_{\text{GeCl}_2} + \sqrt{K_H P_{H_2}})^3}$$
We need to relate the partial pressure of GeCl₂ to the partial pressure of GeCl₄ in order to calculate the conversion of GeCl₄. If we assume that the gas-phase reaction

$$\text{GeCl}_4 (g) \rightleftharpoons \text{GeCl}_2 (g) + \text{Cl}_2 (g)$$

is in equilibrium, we have

$$K_P = \frac{P_{\text{GeCl}_2} P_{\text{Cl}_2}}{P_{\text{GeCl}_4}} \quad P_{\text{GeCl}_2} = \frac{P_{\text{GeCl}_4}}{P_{\text{Cl}_2}} \cdot K_P$$

and if hydrogen is weakly adsorbed ($\sqrt{K_H P_{H_2}} < 1$), we obtain the rate of deposition as

$$r_{\text{Dep}}'' = \frac{k P_{\text{GeCl}_4} P_{H_2} P_{\text{Cl}_2}^2}{\left( P_{\text{Cl}_2} + K_P P_{\text{GeCl}_4} \right)^3}$$
Extended reading:
Surface chemkin: A general formalism and software for analyzing heterogeneous chemical kinetics at a gas-surface interface, International Journal of Chemical Kinetics, DOI: https://doi.org/10.1002/kin.550231205
Catalytic Reaction Engineering

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