Catalysis – continue

Desorption Step is controlling

1. Mass transfer (diffusion) of the reactant(s) (e.g., species A) from the bulk fluid to the external surface of the catalyst pellet
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. Adsorption of reactant A onto the catalyst surface
4. Reaction on the surface of the catalyst (e.g., A B)
5. Desorption of the products (e.g., B) from the surface
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
7. Mass transfer of the products from the external pellet surface to the bulk fluid

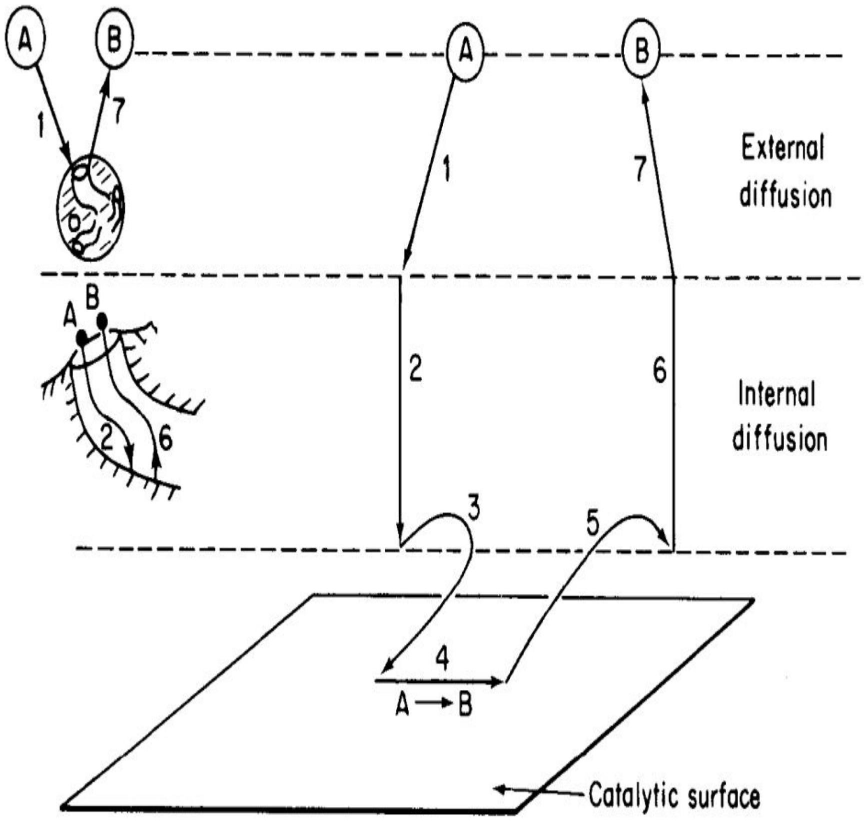


Figure 10-5 Steps in a heterogeneous catalytic reaction.

The Desorption Step

$$A \longrightarrow B + C$$

$$C \bullet S \;\underset{\longleftarrow}{\longrightarrow}\; C + S$$

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

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

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

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

At equilibrium $r_{DC} = o$

This leads to:

$$C_{C*S} = K_C P_C C_v$$

Or in term of concentration:

$$C_{C*S} = K_C C_C C_v$$

Surface reaction Step is controlling

1. Mass transfer (diffusion) of the reactant(s) (e.g., species A) from the bulk fluid to the external surface of the catalyst pellet
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. Adsorption of reactant A onto the catalyst surface
4. Reaction on the surface of the catalyst (e.g., A B)
5. Desorption of the products (e.g., B) from the surface
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
7. Mass transfer of the products from the external pellet surface to the bulk fluid

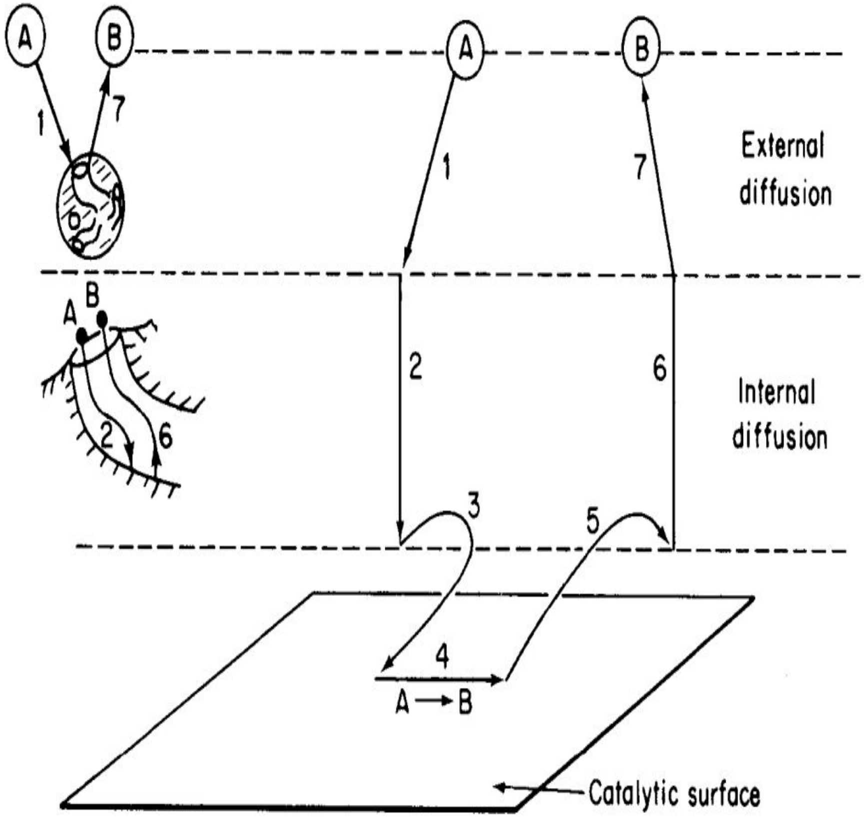
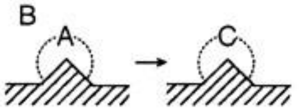


Figure 10-5 Steps in a heterogeneous catalytic reaction.

There are two types for surface reaction controlling step

1. Type I: A is only adsorbed



Eley-Rideal mechanism

For the generic reaction

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

the corresponding surface reaction rate law is

$$r_S = k_S \left(C_{A \cdot S} P_B - \frac{C_{C \cdot S}}{K_S} \right) \qquad (10\text{-}19)$$

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

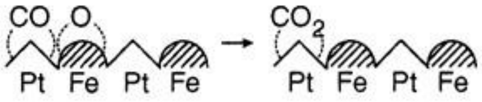
$$k_s = \left(\frac{1}{\text{atm} \cdot \text{s}} \right)$$

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

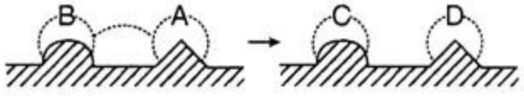
$$K_S = \frac{C_{C*S}}{C_{A*S}\, P_B}$$

There are two types for surface reaction controlling step

1. Type II: Both A and B adsorbed



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

$$r_S = k_S \left(C_{A \cdot S} C_{B \cdot S'} - \frac{C_{C \cdot S'} C_{D \cdot S}}{K_S} \right) \tag{10-18}$$

Langmuir-Hinshelwood kinetics

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

$$K_S = \frac{C_{C*S}\, C_v}{C_{A*S}\, P_{B*S}}$$

Adsorption-Surface reaction-desorption Steps are controlling

1. Mass transfer (diffusion) of the reactant(s) (e.g., species A) from the bulk fluid to the external surface of the catalyst pellet
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. Adsorption of reactant A onto the catalyst surface
4. Reaction on the surface of the catalyst (e.g., A B)
5. Desorption of the products (e.g., B) from the surface
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
7. Mass transfer of the products from the external pellet surface to the bulk fluid

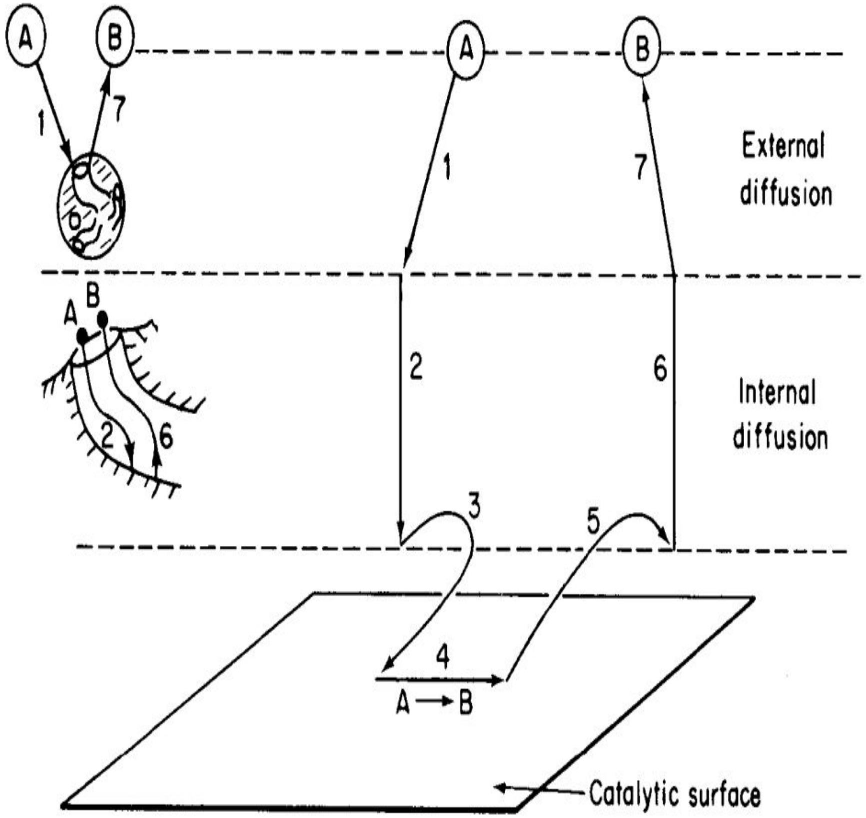


Figure 10-5 Steps in a heterogeneous catalytic reaction.

The following Adsorption-Surface reaction-desorption reaction equation:

$$A + X \overset{K_A}{\Leftrightarrow} A * X \overset{K_S}{\Leftrightarrow} C * X \overset{K_D}{\Leftrightarrow} C + X$$

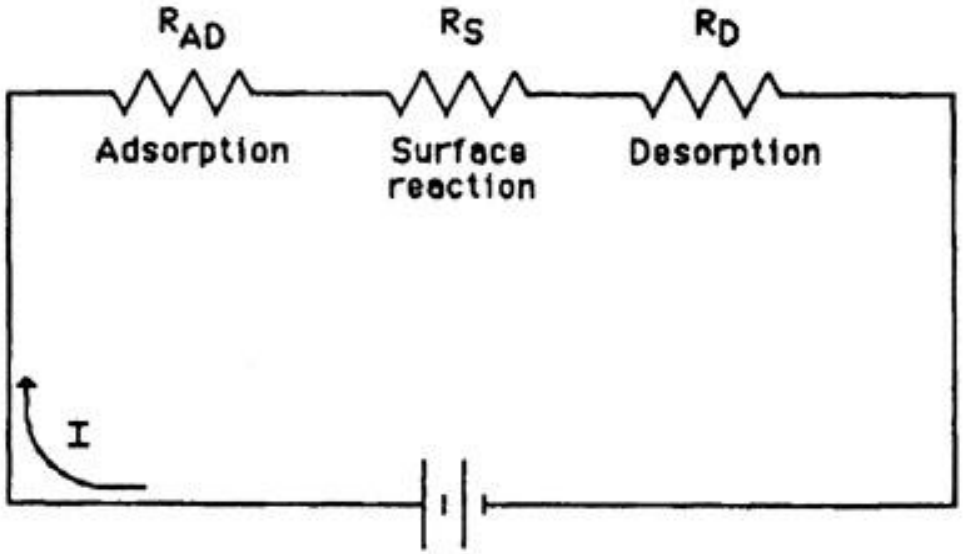
Adsorption Step

Desorption Step

Surface reaction Step

Here, the goal is to have the surface is fully accommodating the reactant A through adsorption, i.e maximum number of active sites are ready for adsorption of A and minimum for desorption of C, why? Because we need to increase the rate of reaction of A to gives C. Here we do have three resistances, Adsorption of A, Surface reaction and desorption of C. We need to figure out which step (intermediate step like we learned in nonelementary reaction) is the slowest, so we can work on this step to be fast. And hence increase the rate of reaction.

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



Electrical analog to heterogeneous reactions

Steps in a Single-Site Catalytic Reactor

Adsorption

$$A + X \leftrightarrow A * X$$
$$B + X \leftrightarrow B * X$$

Surface Reaction

$$A * X + B * X \leftrightarrow C * X + X$$

Desorption

$$C * X \leftrightarrow C + X$$

Which step is the **Rate** Limiting Step (RLS)?

Case 1: assume surface reaction is controlling

From Adsorption of *A* at equilibrium we have $C_{A*X} = K_A C_A C_v$

From Adsorption of *B* at equilibrium we have $C_{B*X} = K_B C_B C_v$

From Desorption of *C* at equilibrium we have $C_{C*X} = K_C C_C C_v$

If surface reaction is controlling, its rate should not equal zero, so it is:

$$-r_{surface} = k_{Sf} C_{A*X}\ C_{B*X} - k_{Sb}\ C_{C*X}$$

or

$$-r_{surface} = k_{Sf}\left(K_A C_A C_v\ \ K_B C_B C_v - \frac{K_C C_C C_v}{K_S}\right)$$

Case 1: Continue

$$-r_{surface} = k_{Sf}\left(K_A C_A C_v \ \ K_B C_B C_v - \frac{K_C C_C C_v}{K_S}\right)$$

But

$$C_T = C_{A*X} + C_{B*X} + C_{C*X} + C_v$$

Vacant sites

Total active site

Adsorbed A & B sites

Desorbed C sites

$$C_T = K_A C_A C_v \ + \ K_B \ C_B C_v \ + K_C C_C C_v + C_v$$

$$C_T = C_v \ \left(K_A C_A \ + \ K_B \ C_B \ + K_C C_C + 1\right)$$

or

$$C_v = \frac{C_T}{\left(K_A C_A \ + \ K_B \ C_B \ + K_C C_C + 1\right)}$$

Case 1: Continue

$$-r_{surface} = k_{Sf}\left(K_A C_A C_v \;\; K_B C_B C_v - \frac{K_C C_C C_v}{K_S}\right)$$

or

$$-r_{surface} = k_{Sf} C_v \left(K_A C_A \;\; K_B C_B - \frac{K_C C_C}{K_S}\right)$$

and

$$C_v = \frac{C_T}{(K_A C_A + K_B C_B + K_C C_C + 1)}$$

Substitute the last equation in the previous one, to yield

$$-r_{surface} = k_{Sf} {C_T}^2 \frac{K_A C_A \;\; K_B C_B - \frac{K_C C_C}{K_S}}{(1 + K_A C_A + K_B C_B + K_C C_C)^2}$$

Case 1: Continue in next class