



CATALYSIS

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- **CATALYSIS** comes from two Greek words, the prefix **CATA-** meaning down and the verb **LYSEIN**, meaning to split or break.
- “A catalyst breaks down the normal forces which inhibit the reactions of molecules”



Catalyst Is a substance which accelerates the rate of approach to equilibrium of a chemical reaction without being substantially consumed in the reaction.

Catalyst is a substance which speeds up a reaction, but is chemically unchanged at the end of the reaction.

Inhibitor Is a substance that decreases the rate of the reaction; it was formerly called a negative catalyst.



1. CRITERIA OF CATALYSIS

1.1 The Catalyst is unchanged chemically at the end of the reaction

The amount of the catalyst should not be changed at the end of the process, unchanged chemically although it frequently changes physically.

Example: Manganese dioxide catalyzes the potassium chlorate decomposition; changes from large crystals to fine powder (Physical change).



1.2 A small amount of catalyst is often sufficient to bring about a considerable extent of reaction

A small amount of catalyst will often cause large quantities of material to react.

Example: Cupric ions (Cu^{2+}) at a concentration of 1g ion in 10^9 liters accelerate the oxidation of sodium sulphite solution by atmospheric oxygen.



1.3 The Catalyst does not affect the position of equilibrium in a reversible reaction

A catalyst does not alter the position of equilibrium for a reversible process. It must affect the direct and reverse reactions to the same extent.

Example: Sulphur trioxide vapor decomposes readily in the presence of platinum, which is also the better catalyst for the combination of sulphur dioxide and oxygen.



1.4 The catalyst is specific in its action

- A good catalyst is selective and permits the formation of only one type of product when reactions may occur along several pathways.

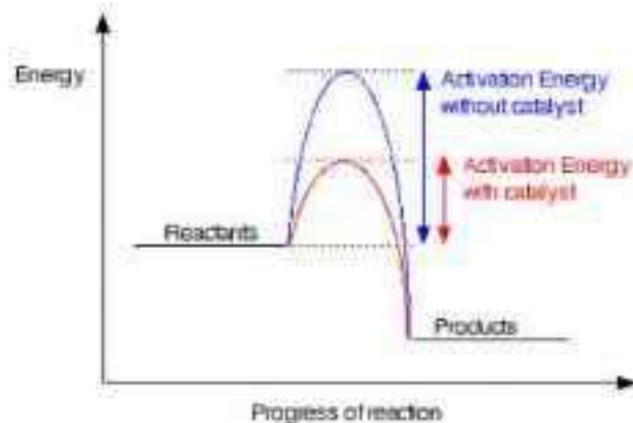


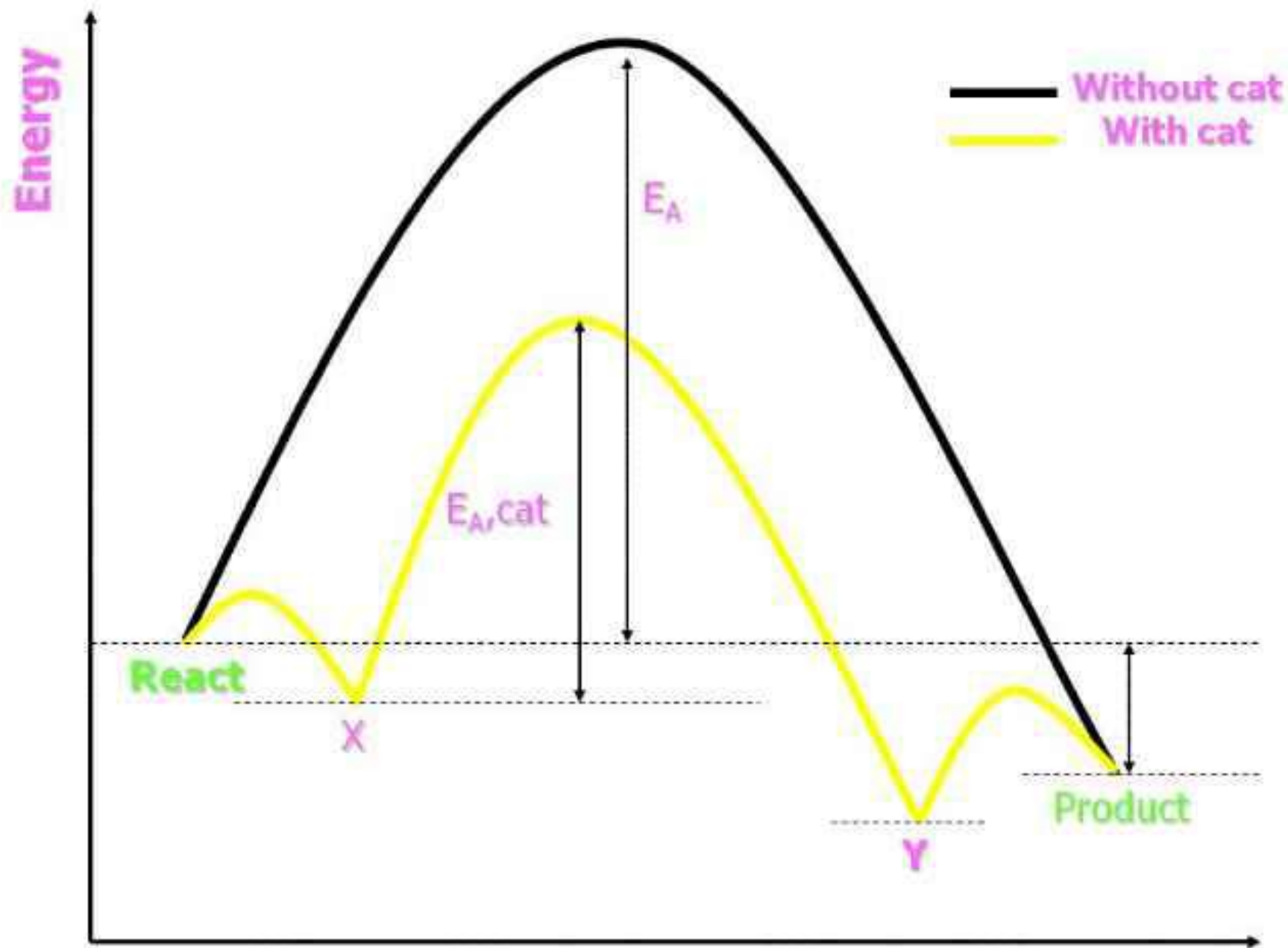


1.5 A catalyst provides an alternative route for the reaction with lower activation energy

"A catalyst provides an alternative route for the reaction with lower activation energy."

It does *not* "lower the activation energy of the reaction"





Classification of Catalytic Systems

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graph TD; A[Classification of Catalytic Systems] --> B[Homogeneous]; A --> C[Heterogeneous]; A --> D[Enzymatic];
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Homogeneous

No phase boundary exists

Heterogeneous

Phase Boundary separates catalyst from the reactants

Enzymatic

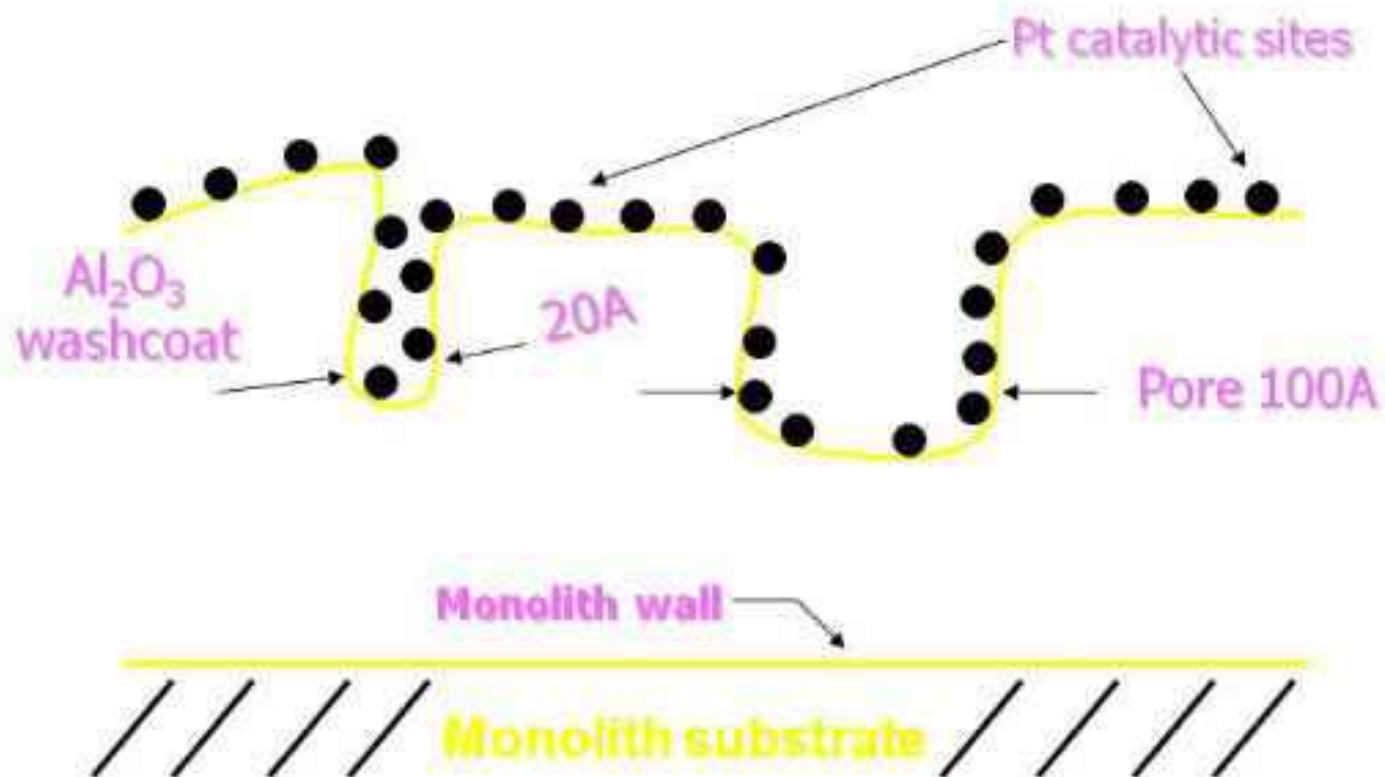
Complex organic molecules, usually protein, which form a lyophilic colloid

1. HETEROGENEOUS CATALYSIS

- Reactants and the catalyst of different phases
- The catalyst is mostly solid

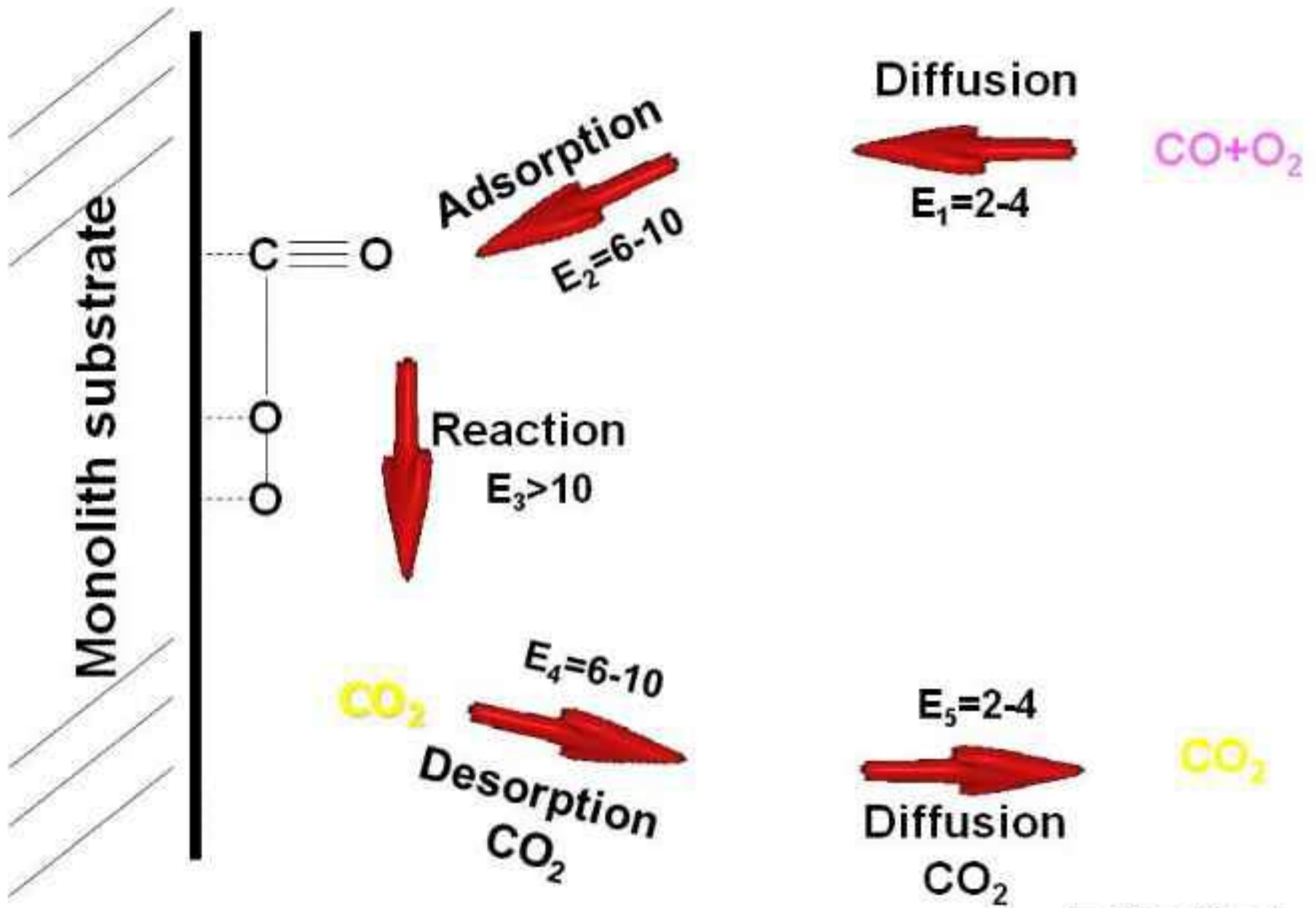
1.1 Catalyst Preparation

- The higher the active surface area of the catalyst, the greater the number of product molecules produced per unit time.
- Transition metal ions or atoms are deposited in the micropores of suitable support (surface area = $100\text{-}400\text{ m}^2/\text{g}$), which are then heated and reduced to produce small metal particles $10\text{-}10^2\text{ \AA}$ in size with virtually all the atoms located on the surface (unity dispersion).
- Additives that are usually electron donors (alkali metals) or electron acceptors (halogens) are adsorbed on the metal or on the oxide to act as bonding modifiers for the coadsorbed reactants.



1.2 Kinetics of Heterogeneous Catalytic reactions

- **Diffusion of the reactants to the surface**
- **Adsorption of one or more of the reactants to the surface**
- **A surface reaction between reactants to give a desired product**
- **Desorption of the products from the catalyst surface**
- **Diffusion from the surface.**



1.2.1 Rates and orders of reactions

1.i. Unimolecular Reactions

They are reactions involving a single reacting substance.

Example: decomposition of ammonia

Langmuir Adsorption isotherm

The relation between the fraction of the surface coverage and pressure is

$$\Theta = \frac{bP}{1+bP}$$

Simply the rate of reaction is given by

$$\text{Rate} = k \Theta$$

$$\text{Rate} = \frac{k b P}{1+bP}$$



Limiting conditions:

1- At high pressure; Rate = k (Zero Order)

2- At low pressure; Rate = k b p (1st Order)

1.ii. Unimolecular Reactions with surface inhibition

If a substance other than the reactant is adsorbed on the surface, with the result that the effective surface area, and therefore the rate, are reduced

Suppose a reactant **A** is adsorbed and an inhibitor **I** is adsorbed also on the surface (competitive adsorption), if the fraction of the surface covered by **A** is Θ_A and fraction covered by **I** is Θ_I

$$\Theta_A = b_A P_A / (1 + b_A P_A + b_I P_I)$$



Limiting conditions:

If the surface is fairly covered by inhibitor I and sparsely covered by the reactant A ; $b P_I \gg 1 + b P_A$, So:

$$\text{Rate} = k b_A p_A / b_I p_I$$

The rate is directly proportional to P_A and inversely proportional to P_I

Questions :

1- Write down the rate equation if the surface is sparsely covered by the inhibitor I?

2- Suppose the decomposition of ammonia over the platinum surface follow a unimolecular adsorption with inhibition by H_2 . Write down the rate of adsorption then rewrite the rate under the limiting conditions?





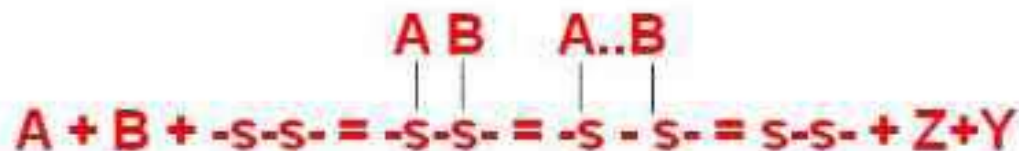
2. Bimolecular Reactions

When a solid surface catalyzes by a bimolecular process, there are two possible mechanisms;

- i- Langmuir-Hinshelwood Mechanism
- ii- Eley-Rideal Mechanism

2.i- Langmuir-Hinshelwood Mechanism

It involves a reaction between two molecules adsorbed on the surface, such as a mechanism may be formulated as follows:

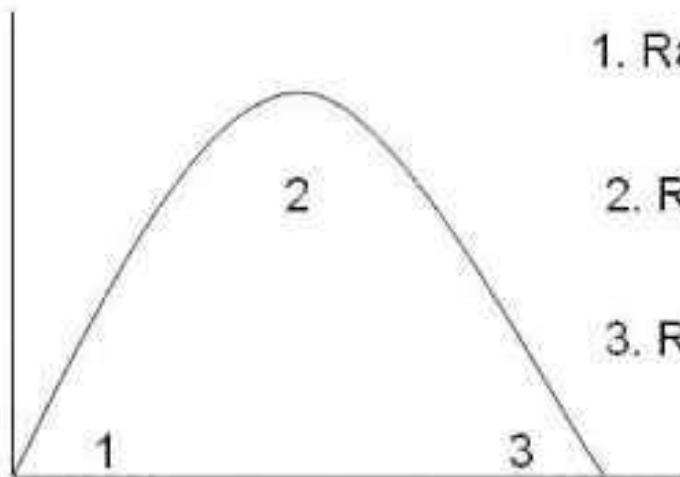




$$\text{Rate} = k \Theta_A \Theta_B$$

$$\text{Rate} = k b_A b_B P_A P_B / (1 + b_A P_A + b_B P_B)^2$$

Rate



1. Rate $\propto P_A$

2. Rate = Equation

3. Rate $\propto 1/P_A$

A is weakly adsorbed and B is strongly adsorbed;

$$\text{Rate} = k b_A P_A / b_B P_B$$

1st order in A and -1 order in B

At very low pressure of A and B;

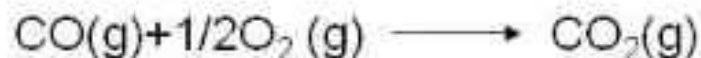
$$\text{Rate} = k b_A b_B P_A P_B$$

2nd order



Example 1: for the oxidation of CO by O₂ on Platinum, consider the rate law obeys **Langmuir-Hinshelwood Mechanism**. Determine the form of the rate law if; (i) the surface is sparsely covered with reactants, (ii) the adsorption of CO is much more extensive than the adsorption of O₂ to the surface.

Solution 1:



The mechanism according to LH is:



$$\text{Rate} = k_3 b_{\text{CO}} b_{\text{O}} P_{\text{CO}} P_{\text{O}} / (1 + b_{\text{O}} P_{\text{O}} + b_{\text{CO}} P_{\text{CO}})^2$$

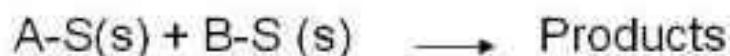
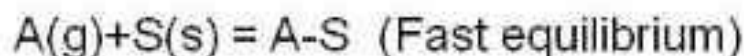
- (i) If the surface is sparsely covered with the reactants; then $b_O P_O + b_{CO} P_{CO}$ neglected and denominator = 1

$$\text{Rate} = k_3 b_{CO} b_O P_{CO} P_O$$

- (ii) If adsorption of CO is much more extensive than adsorption of $O_2(g)$; $b_O P_O + 1$ neglected and the denominator = $(b_{CO} P_{CO})^2$

$$\text{Rate} = k_3 b_O P_O / b_{CO} P_{CO}$$

Question 1: Consider a surface-catalyzed bimolecular reaction between A and B that has a rate law of the form: $\text{rate} = k_3 \theta_A \theta_B$. A mechanism consistent with this reaction is as follows:



Derive expressions for θ_A and θ_B in terms of $[A]$ and $[B]$, k_A and K_B . Use your results to show that the rate law can be written as LH form.



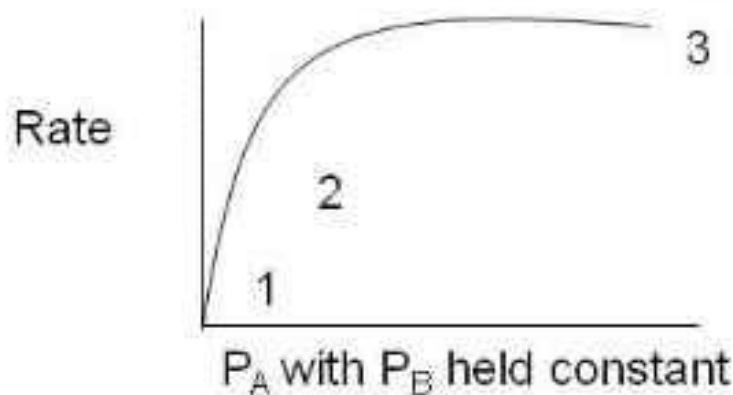
2.II- Eley-Rideal Mechanism



"A" molecule is not adsorbed and "B" is adsorbed; so

$$\text{Rate} = kP_A \theta_B$$

$$\text{Rate} = k b_B P_A P_B / 1 + b_A P_A + b_B P_B$$



1. Rate $\propto P_A$
2. Rate = Equation
3. Rate = Constant

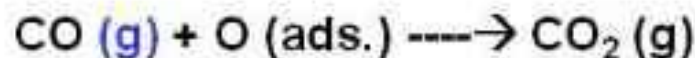
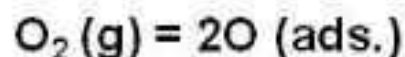


Question2: Write down the limiting conditions then resolve example 1 for oxidation of CO by O₂ applying ER mechanism

Solution:

(I) Answer the first part!

(II) Second part:



ER mechanism supposed that the reaction occurred between one adsorbed and the other in gas phase. So, the rate law is

$$\text{Rate} = k_3 \frac{b_{\text{CO}} b_{\text{O}} P_{\text{CO}} P_{\text{O}}}{1 + b_{\text{O}} P_{\text{O}} + b_{\text{CO}} P_{\text{CO}}}$$



2. HOMOGENEOUS CATALYSIS

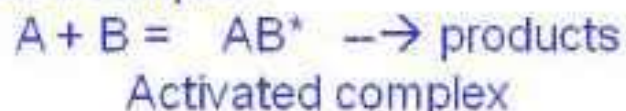
Reactants and the catalyst of the same phases

The catalyst is mostly liquid as reactants

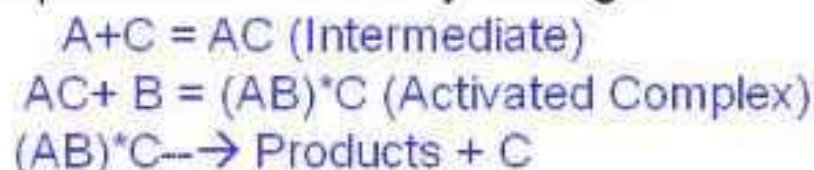
2.1 Activation Process in homogeneous catalysis

In Homogeneous catalytic reactions the catalyst play a different role than that in heterogeneous catalysis

Let us consider a bimolecular non-catalytic reaction proceeding through the formation of an activated complex:



For the same reaction but in presence of a catalyst we get:



2.2. Kinetics of homogeneous catalysis

According to the activated complex theory, the rate of chemical reaction is determined by the rate of dissociation of the activated complex into final products, i.e.

$$d[\text{Products}]/dt = k_4 [(\text{AB})^* \text{C}] \dots \dots \dots (1)$$

Applying the steady state approximation;

The rate of formation of activated complex may be calculated as follows:

$$d[(\text{AB})^* \text{C}]/dt = k_3 [\text{AC}][\text{B}] - k_4 [\text{ABC}] = 0$$

$$\text{Thus } [(\text{AB})^* \text{C}] = k_3/k_4 [\text{AC}][\text{B}] \dots \dots \dots (2)$$

$$\text{And } d[p]/dt = k_3 [\text{AC}][\text{B}] \dots \dots \dots (3)$$

The rate of formation of the intermediate compound AC can also be calculated as follows;

$$d[\text{AC}]/dt = k_1 [\text{A}][\text{C}] - k_2 [\text{AC}] - k_3 [\text{AC}][\text{B}] = 0$$

$$\text{Then } [\text{AC}] = k_1 [\text{A}][\text{C}] / k_2 + k_3 [\text{B}] \text{-----} (4)$$

$$\text{Substitute 4 in 3, we get; } d[\text{P}]/dt = k_1 k_3 [\text{A}][\text{B}][\text{C}] / k_2 + k_3 [\text{B}] \dots \dots \dots (5)$$

From (5), the reaction rate is directly proportional to the concentration of the catalyst, which is in good agreement with the experiments.

Limiting conditions:

- (i) If the rate of dissociation of the intermediate to initial reactants exceeds considerably the rate of the formation of the activated complex, i.e., $k_2 \gg k_3$, then:
- $$d[P]/dt = k_1 k_3 / k_2 [A][B][C] = K [A][B][C]$$

the rate of the reaction is directly proportional to the reactants and the catalyst

The intermediate compound in this case is known as Arrhenius intermediate

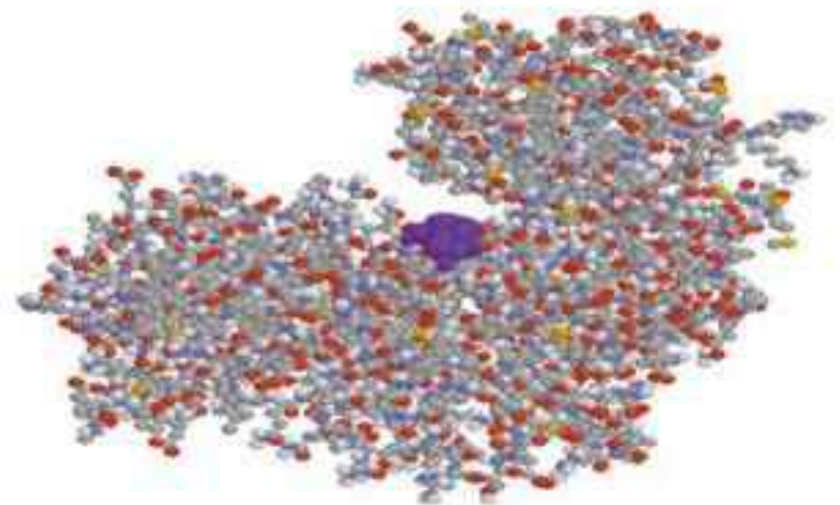
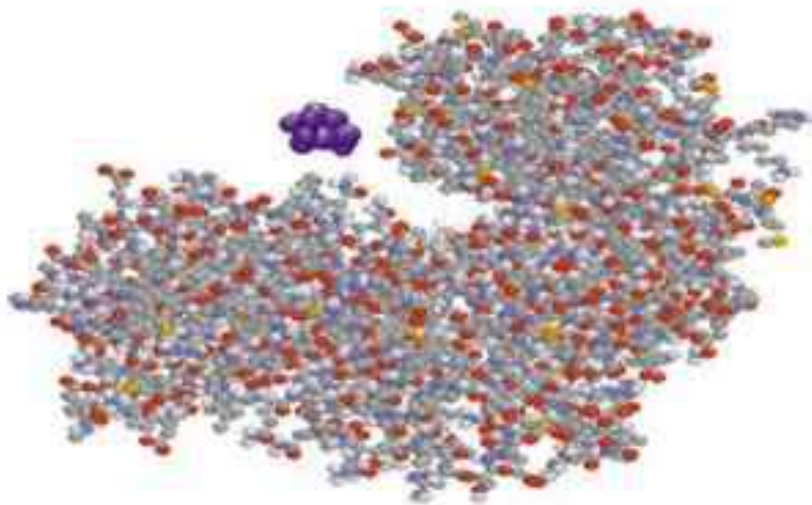
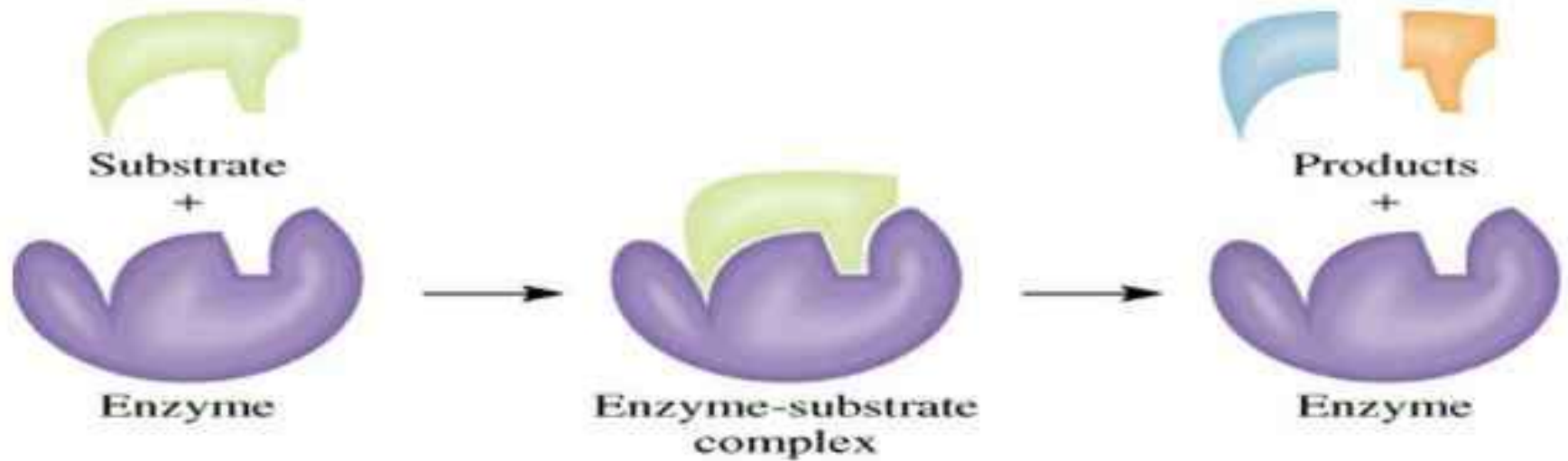
- (ii) If the rate of formation of the activated complex exceeds dissociation of the intermediate, i.e., $k_2 \ll k_3$,

then:

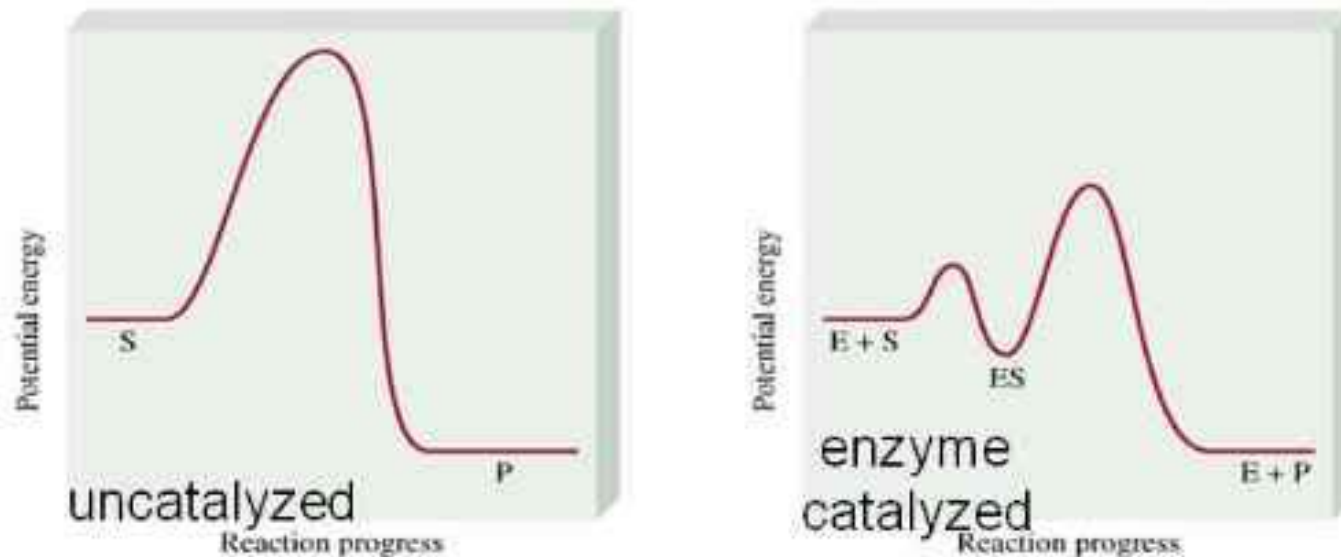
$$d[P]/dt = k_1 [A][C]$$

the rate of the reaction is directly proportional to one of the reactants and the catalyst. The intermediate compound in this case is known as Van't Hoff intermediate

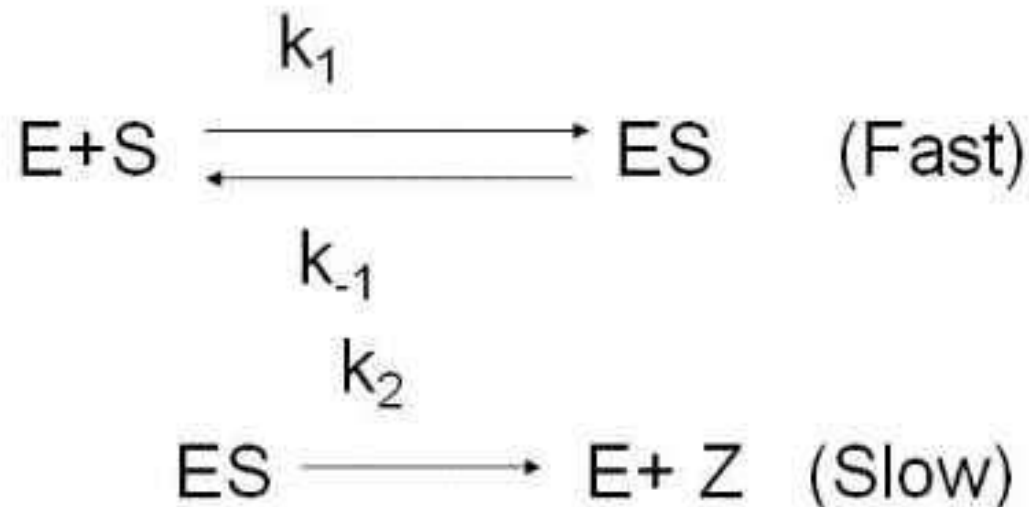
3. ENZYME CATALYSIS



3.1. Kinetics of Enzyme catalysis



Michaelis-Menten mechanism provides useful basic information of the kinetics behaviour observed in many reactions catalyzed by enzyme. Using E and S represent the enzyme and substrate molecules respectively, the mechanism may be written as a sequence of three elementary steps:



Applying steady state approximation, where the substrate concentration is in excess:

$$d[S]/dt = k_1 [E][S] - k_{-1} [ES] - k_2 [ES] = 0$$

$$k_1 [E][S] = k_{-1} [ES] + k_2 [ES]$$

$$[E] = (k_{-1} + k_2)[ES] / k_1 [S]$$

$$\text{Since } [E]_0 = [E] + [ES];$$

Where, $[E]_0$ is the initial enzyme concentration

$[E]$: free enzyme concentration

$[ES]$: usual enzyme concentration

$$\text{So, } [E]_o = [ES] \{ (k_{-1} + k_1) / k_1 [S] + 1 \}$$

$$[ES] = k_1 [E]_o [S] / k_{-1} + k_2 + k_1 [S]$$

$$\text{Since the rate } (R) = k_2 [ES]$$

$$\text{So, } R = k_2 k_1 [E]_o [S] / k_{-1} + k_2 + k_1 [S]$$

$$R = k_2 [E]_o [S] / \{ (k_{-1} + k_2) / k_1 \} + [S]$$

Where; $V = k_2 [E]_o$, called the limiting rate

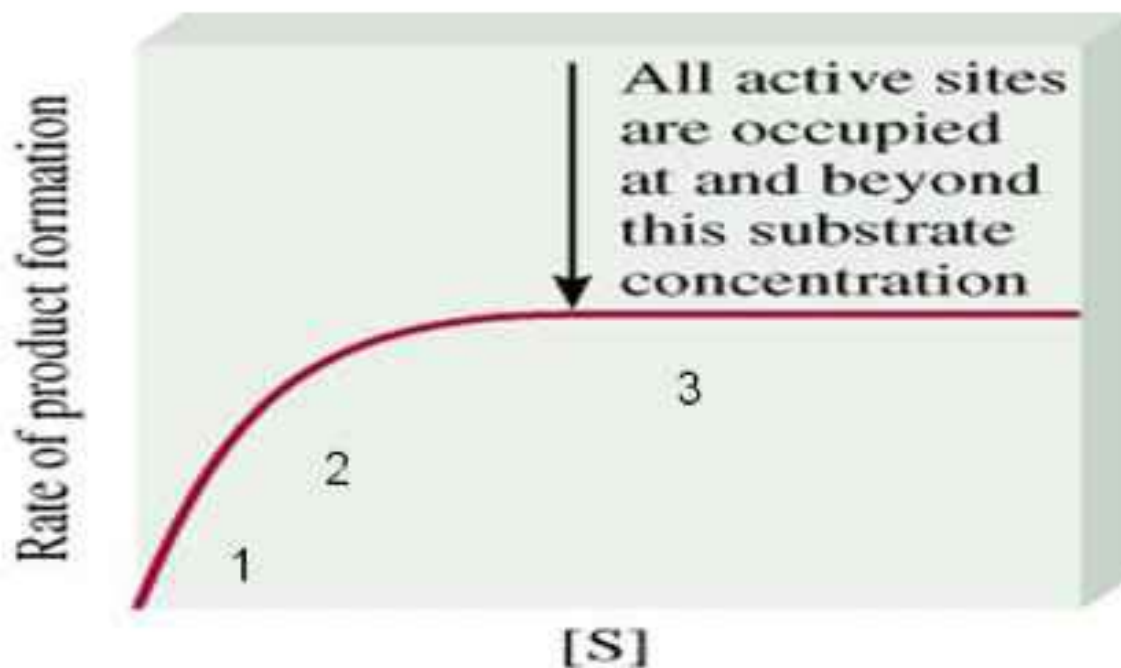
$K_m = (k_{-1} + k_2) / k_1$, named Michaelis constant

$$\text{So, } R = V [S] / K_m + [S]$$

Limiting conditions:

- (i) $[S] \gg K_m$: Rate = $V = k_2 [E]_o$; Zero order; usually we write k_2 as k_c ; which is the catalysis constant
- (ii) $[S] \ll K_m$: Rate = $V[S] / K_m = (k_2 / K_m) [E]_o [S]$; first order to the substrate concentration

(iii) When $[S] = K_m$; Rate = $V[S] / 2 [S] = V/2$



At (1) Rate = $(k_2 / K_m) [E]_o [S]$;

At (2) Rate = $V/2$; At (3) Rate = $k_c [E]_o$

Example

The following data apply to an enzyme catalyzed reaction:

[S] / mol dm ⁻³	Rate, R/ mol dm ⁻³ s ⁻¹
2.5 × 10 ⁻⁴	2.3 × 10 ⁻⁴
5 × 10 ⁻³	7.8 × 10 ⁻⁴

The concentration of the enzyme is 2gdm⁻³ and its molecular weight is 50,000. assume the Michaelis-Menten constant K_m , the limiting rate V , and the rate coefficient k_c

Solution

$$R = V [S] / K_m + [S]$$

$$2.3 \times 10^{-4} = V (2.5 \times 10^{-4}) / K_m + 2.5 \times 10^{-4}$$

$$7.8 \times 10^{-4} = V (5 \times 10^{-3}) / K_m + 5 \times 10^{-3}$$

$$K_m = 7.20 \times 10^{-4} \text{ mol dm}^{-3}; \quad V = 8.92 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

Molar concentration = concentration of enzyme/ molecular weight

$$[E]_0 = 2 \text{ gdm}^{-3} / 50,000 \text{ g mol}^{-1}; \quad [E]_0 = 4 \times 10^{-5} \text{ mol dm}^{-3}$$

$$K_c = V/[E]_0 = 22.3 \text{ s}^{-1}$$