

area of catalyst.

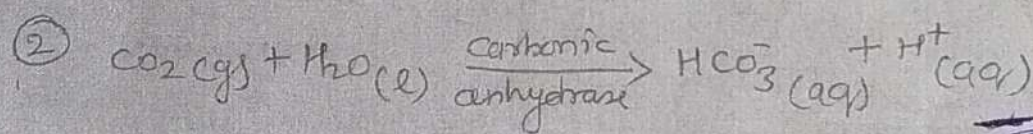
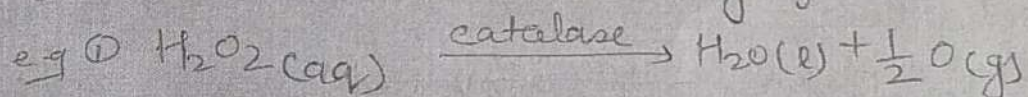
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⇒ These reactions are generally slower than homogeneous catalysis

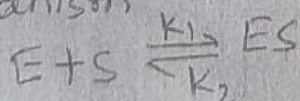
Enzyme catalysis

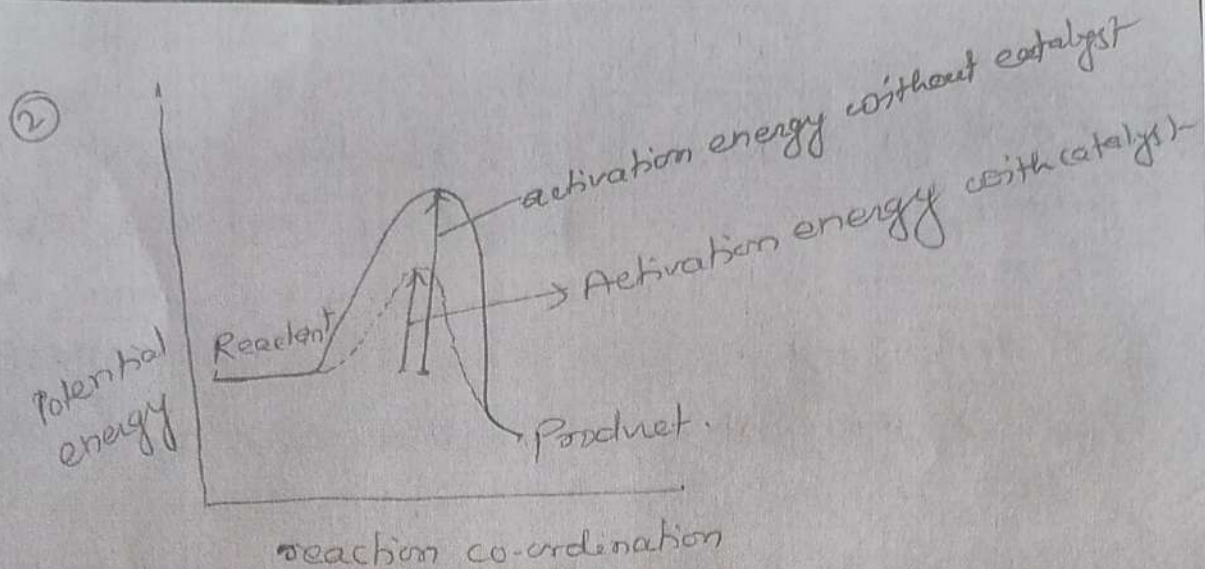
Enzyme are biological homogeneous catalyst. They are large protein molecules. They have large complex structure. Enzyme are very efficient catalyst under very mild conditions in comparison with another type of catalyst. This is because the reduction in activation energy is much greater than that of other catalysts.

The enzymes are highly specific in their action. They catalyse only a single reaction of a single compound. For example, the enzyme amylase catalyses the conversion of starch into glucose but doesn't have any effect on cellulose



~~Acid base catalysis~~ The enzyme-catalyzed kinetics were first described by Michaelis and Menten using the method of steady-state approximation. This approach has provided a convenient alternative to use of integral equation to monitor the elimination of a drug or the formation of the product in enzyme catalyzed reactions. Michaelis and Menten showed that the conversion of substrate S to the product P by enzyme E can be described by following mechanism





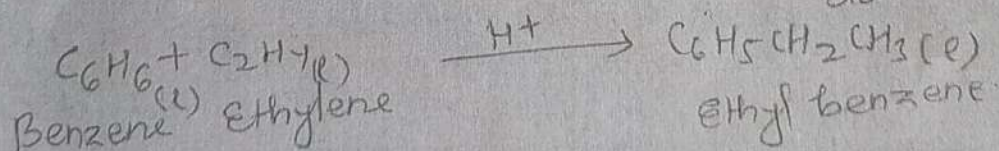
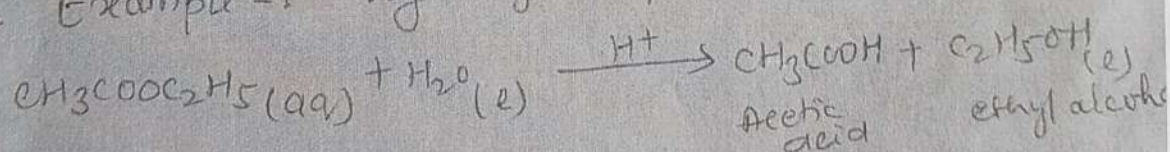
⇒ A catalyst does not affect the energies of the reactants and products. Hence the heat of reaction is ^{the} same for catalysed and uncatalysed reaction.

⇒ A catalyst increases the rate of reaction but they don't initiate the reaction.

Homogeneous catalysis

A homogeneous catalysis is one in which the catalyst and the reactants exist in the same phase. A homogeneous catalyst dissolves in the gas phase or solution and acts uniformly throughout.

e.g. ⇒ Example - 1 hydrolysis of ester



Characteristics of homogeneous catalysis

- The catalyst and reactant form a single phase
- The catalyst dissolves into the gas phase or solution
- The reaction occurs in the gas phase or

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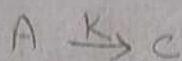
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Acid-Base catalyses

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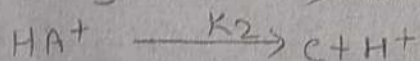
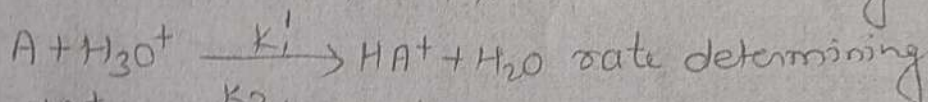
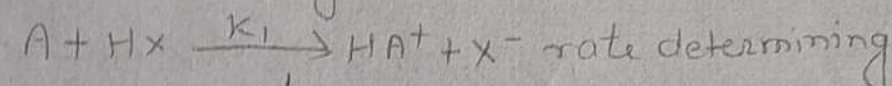
Acid-base catalysis consists of general acid-base catalysis where the catalytic action derives from the whole and part of acid or base molecule, and specific acid-base catalysis where the catalytic action is attributed specifically to H^+ or OH^- .

The catalytic action of an acid or base can be easily understood in terms of the reaction intermediate. For general acid catalysis involving a weak acid HX , ~~to~~ to alter the reaction rate, the catalyst must enter into the rate determining step. Consider the following reaction in an aqueous solution



The rate of noncatalyzed reaction is $d[C]/dt = k[A]$.

The weak acid may catalyze the reaction through either the H^+ or conjugated base X^- . If the acid catalysis is due to the formation of the intermediate HA^+ , the following reaction steps can be written to account for all the acid-catalyzed reactions:



In this case the reaction is catalyzed by HX and by H_3O^+ and the overall rate equation is

$$\frac{d[C]}{dt} = k[A] + k_1[A][HX] + k_1'[A][H_3O^+] \rightarrow$$

The first ~~and~~ second and third terms indicate noncatalysed, HX -catalysed and H^+ catalysed reaction respectively. Equation 1 illustrated the proton transfer by the acid is rate determining.

In case where the catalytic action comes from the X^- , the rate-determining step involves the subtraction of proton from HA^+ by the bases HA^+ by the base X^- and H_2O , as shown

$ES \xrightarrow{k_3} P + E$ rate determining

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where the rate-determining step is conversion of the enzyme-substrate complex to the product. It follows that

$$dP/dt = k_3[ES]$$

The steady-state condition is such that $d[ES]/dt = 0$

$$[ES] = \frac{k_1[E][S]}{k_1 + k_3}$$

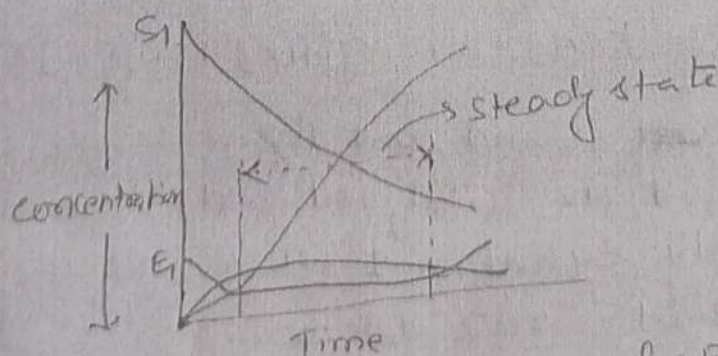
and

$$\frac{d[P]}{dt} = \frac{k_1 k_3 [E][S]}{k_2 + k_3}$$

If one defines the quantity of $(k_2 + k_3)/k_1$ to be K_m (the Michaelis-Menten constant) and total enzyme concentration is E_0 that is $[E] = E_0 - [ES]$, the following equation is obtained and is recognized as the Michaelis-Menten equation

$$\frac{d[P]}{dt} = \frac{k_3 E_0 [S]}{(K_m + [S])}$$

It should be mentioned that as k_3 is involved in the slow rate determining step, k_2 is likely greater than k_3 , and the Michaelis-Menten constant is then regarded as the dissociation constant of the substrate-enzyme complex with a larger value of K_m indicating a lesser enzymatic reaction



concentration-time curves for $E + S \rightarrow [ES] \rightarrow P + E$

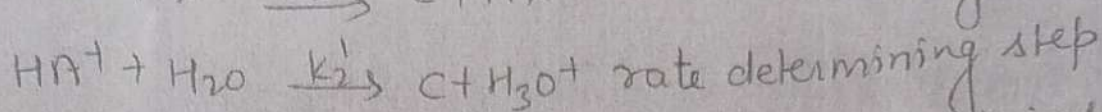
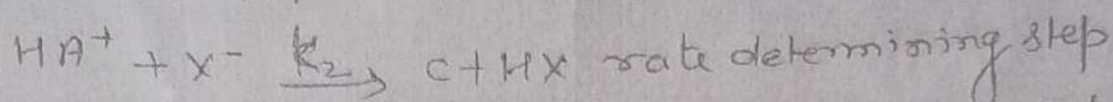
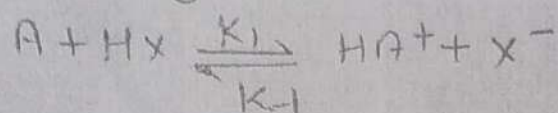
If steady state condition defined as velocity, then the equation may be written as

$$V = \frac{V_m [S]}{K_m + [S]}$$

$$V_m = k_3 E_0$$

in following equations

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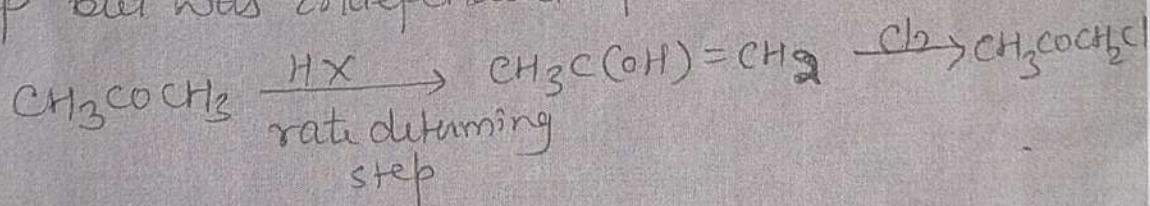


The overall rate equation can thus be obtained as

$$d[C]/dt = k[A] + k_2[HA^+][X^-] + k_2'[HA^+] \rightarrow (2)$$

where first term represents the uncatalysed process, the second term X^- catalysed reaction and third term water acting as a base. Because the water concentration is always in excess, it is considered a constant and is incorporated into rate constant in eq. 2

The mechanism of the general acid-base catalysis describe above may be seen from the reaction of acetone with chlorine, which shows that the rate of ~~reaction~~ chlorination at moderate pH values was enhanced by both acids and base through the formation of the enol intermediate as rate determining step but was independent of concentration of chlorine



Catalyst

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A catalyst is defined as a substance which when added to the reacting system increases the rate of reaction without itself being consumed in the reaction and the phenomenon is called catalysis.

e.g.: \Rightarrow Thermal decomposition of KClO_3 is a very slow process. But this decomposition can be carried out even at a lower temperature by heating KClO_3 with MnO_2 powder. Here MnO_2 acts as a catalyst.

Characteristics of catalyst: \Rightarrow

- It seems that the catalyst does not take part in the reaction but actually it forms a complex with reactant/ reactants which further regenerates into product/ products and catalyst. ~~Then~~
- ^{Formation of} Reactant/ Reactants - catalyst complex then after completion catalyst complex turned into product/ products + catalyst
- Thus catalyst is recovered at the end of the reaction
- In reversible reactions, the catalyst increases the rate of both the forward reaction and backward reaction and the backward reaction. Thus equilibrium is not influenced by the presence of a catalyst.
- An extremely small quantity of catalyst causes a considerable increase in the rate of reaction.
- The activation energy of catalysed reaction is always lower than that of the same reaction when it is uncatalysed.

$$V = \frac{V_{\text{max}}}{K_m + [S]}$$

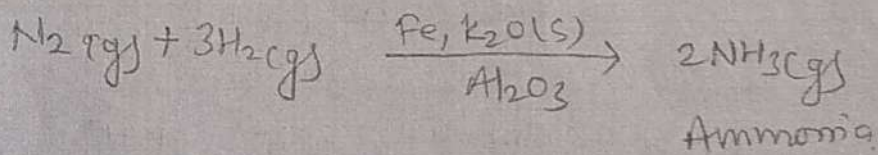
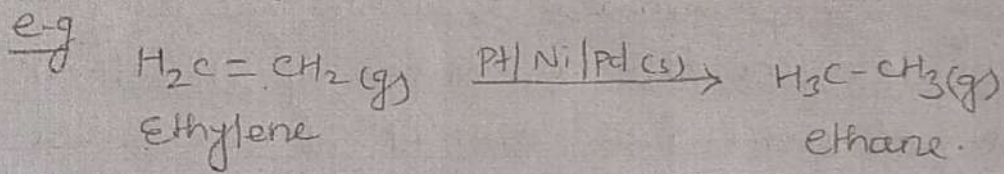
liquid phase.

- ⇒ The catalyst is often involved in ^③ the chemical reaction
- ⇒ The catalyst cannot be easily separated from the products of the reaction
- ⇒ The rate of reaction does not depend on the surface area of catalyst
- ⇒ These reactions are generally faster than heterogeneous

Heterogeneous catalysis \Rightarrow

A catalyst which exists in a different phase from the reactants is known as heterogeneous catalyst and the catalysis ~~is~~ known as heterogeneous catalysis.

Generally, the heterogeneous catalysts are in a solid state, while the reactants are in the liquid or gaseous state.



Characteristics

- ⇒ The catalyst and the reactants form different phases
- ⇒ The catalyst does not dissolve into reacting mixture.
- ⇒ The reaction does not occur in the gas phase or liquid phase but takes place on the surface of the catalyst
- ⇒ The catalyst is not involved in the chemical reaction. It absorbs the reactants on its surface.
- ⇒ it can be easily separated from products of the reaction
- ⇒ The rate of reaction depends on the surface