

Catalysis

Md Khairul Islam (Ph.D.)

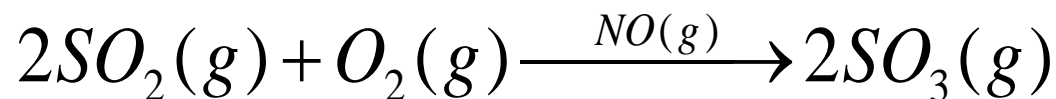
Applied Chemistry & Chemical Engineering
Rajshahi University

Catalyst & catalysis

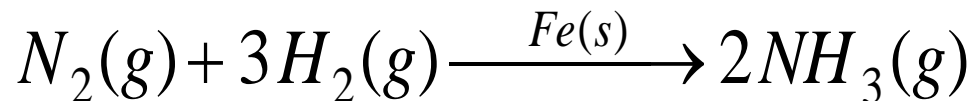
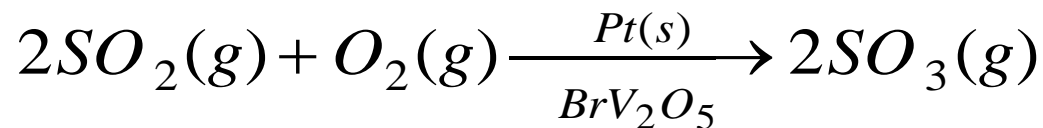
- A **catalyst** is defined as a substance which alters the rate of a chemical reaction, itself remaining chemically unchanged at the end of the reaction. The process is called **Catalysis**.

Types of catalysis

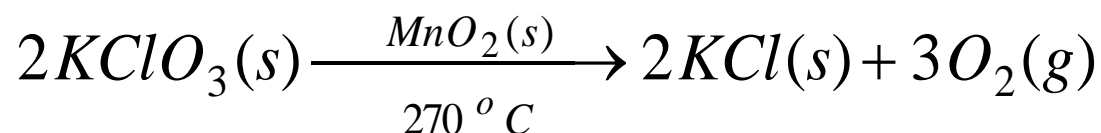
- Homogeneous catalysis: When the reactants and the catalyst are in the same phase (*i.e.* solid, liquid or gas). The catalysis is said to be **homogeneous**. The following are some of the examples of homogeneous catalysis. For examples



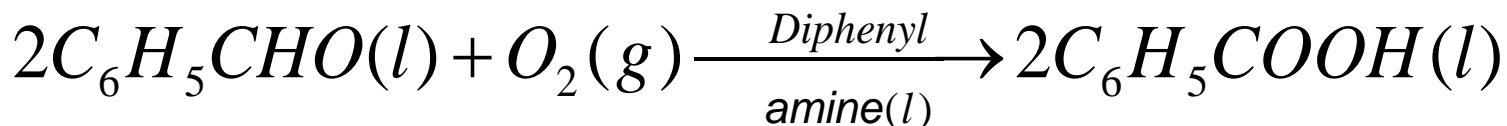
- Heterogeneous catalysis: The catalytic process in which the reactants and the catalyst are in different phases is known as **heterogeneous catalysis**. Some of the examples of heterogeneous catalysis are given below.



➤ Positive catalysis: When the rate of the reaction is accelerated by the foreign substance, it is said to be a **positive catalyst** and phenomenon as **positive catalysis**. Some examples of positive catalysis are given below



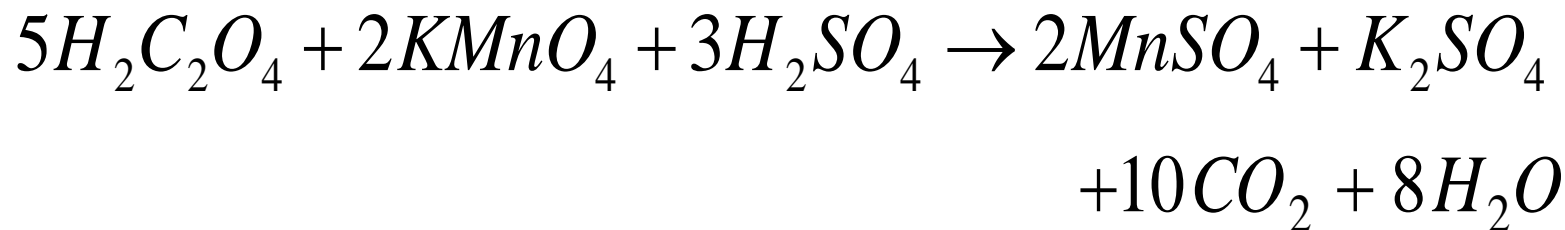
➤ Negative catalysis: There are certain, substance which, when added to the reaction mixture, retard the reaction rate instead of increasing it. These are called **negative catalyst** or **inhibitors** and the phenomenon is known as **negative catalysis**. Some examples are as follows.



Contd.

➤ Auto-catalysis: In certain reactions, one of the product acts as a catalyst. In the initial stages the reaction is slow but as soon as the products come into existences the reaction rate increases. This type of phenomenon is known as auto-catalysis. Some examples are as follows

- The rate of oxidation of oxalic acid by acidified potassium permanganate increases as the reaction progresses. This acceleration is due to the presence of ions which are formed during reaction. Thus ions act as auto-catalyst.

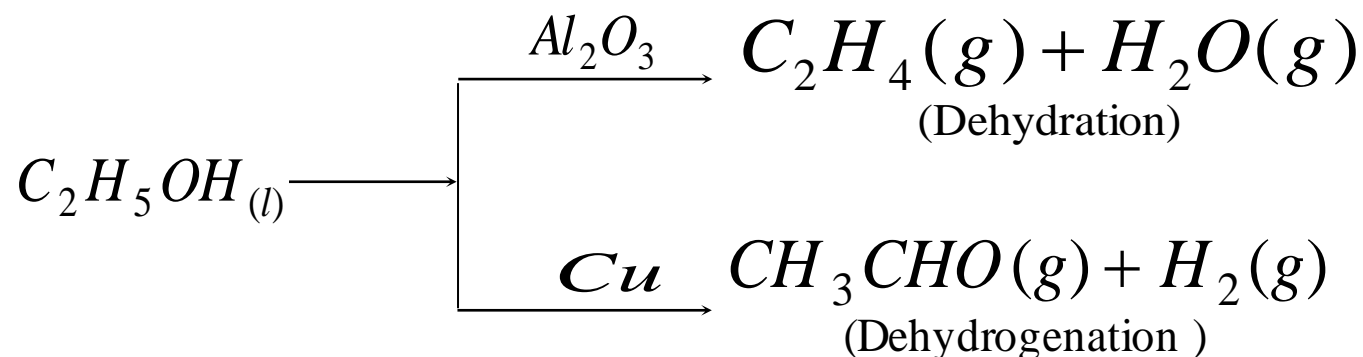


Characteristics of catalysis

- A catalyst remains unchanged in mass and chemical composition at the end of the reaction.
- A small quantity of the catalyst is generally sufficient to catalyses almost unlimited reactions
- The catalyst can not initiate the reaction: The function of the catalyst is to alter the speed of the reaction rather than to start it.
- The catalyst can not change the position of equilibrium: The catalyst catalyze both forward and backward reactions to the same extent in a reversible reaction and thus have no effect on the equilibrium constant.

Contd.

- The catalyst is generally specific in nature: A substance, which acts as a catalyst for a particular reaction, fails to catalyse the other reaction, different catalysts for the same reactant may form different products.



- Change of temperature alters the rate of a catalytic reaction as it would do for the same reaction without a catalyst.

Catalyst Promoter

Substances which themselves are not catalysts, but when mixed in small quantities with the catalysts increase their efficiency are called as promoters or activators. For example, in Haber's process of ammonia production, traces of molybdenum increases the activity of finely divided iron catalyst.

Mechanism of catalyst promoter

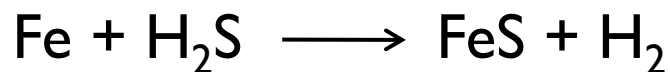
- Change of Lattice Space: The lattice spacing of the catalyst is changed thus enhancing the spacing between the catalyst particles. The adsorbed molecules of the reactant are further weakened and cleaved. This makes the reaction go faster.
- Increase in peaks and cracks: Promoters increase the peaks and cracks on the surface of the catalyst thereby increasing the concentration of reactant molecules and hence the rate of reaction.

Catalyst Poisons

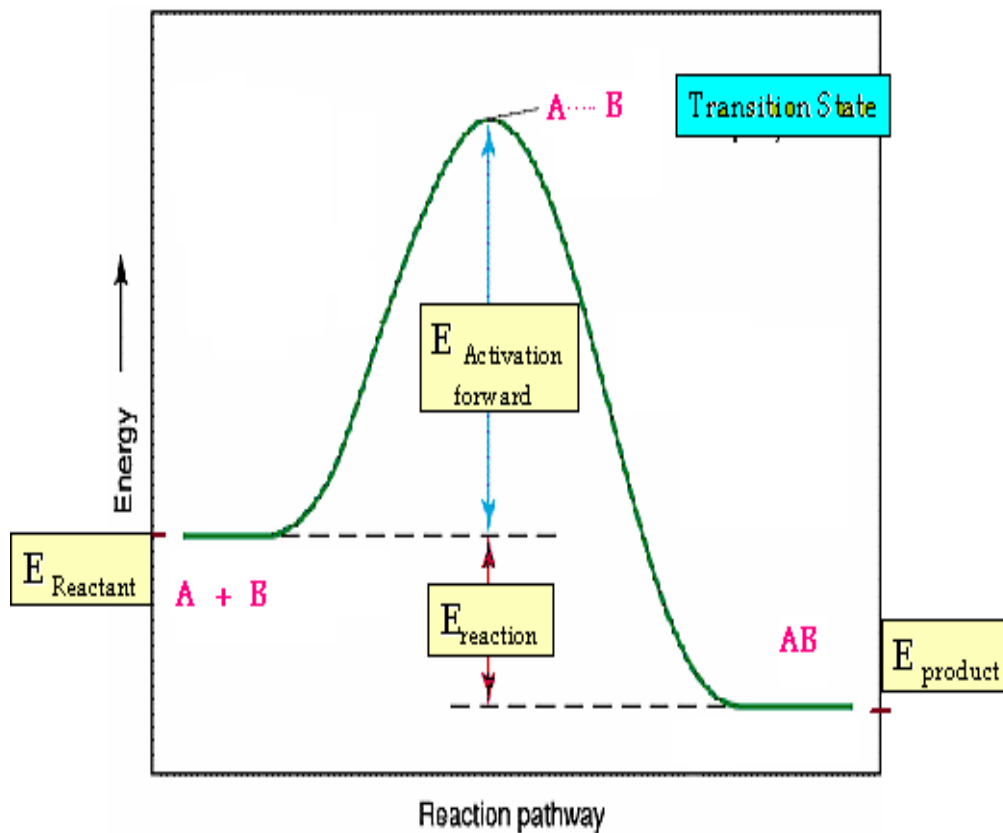
Substances which destroy the activity of the catalyst by their presence are known as **catalytic poisons**. For example, the presence of traces of arsenious oxide in the reacting gases reduces the activity of platinized asbestos which is used as catalyst in contact process for the manufacture of sulphuric acid.

Mechanism of Catalytic Poisoning

- The poison is adsorbed on the catalyst surface in preference to the reactants.
- The catalyst may combine chemically with the impurity.



Kinetic Vs. Thermodynamic

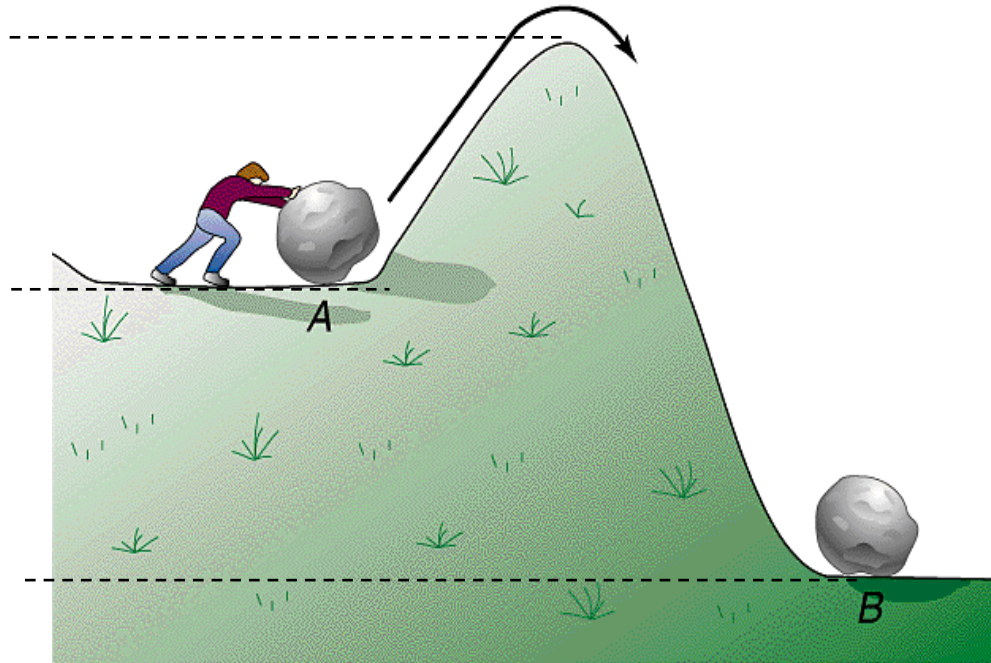


Reaction path for conversion of A + B into AB

Activation Energy

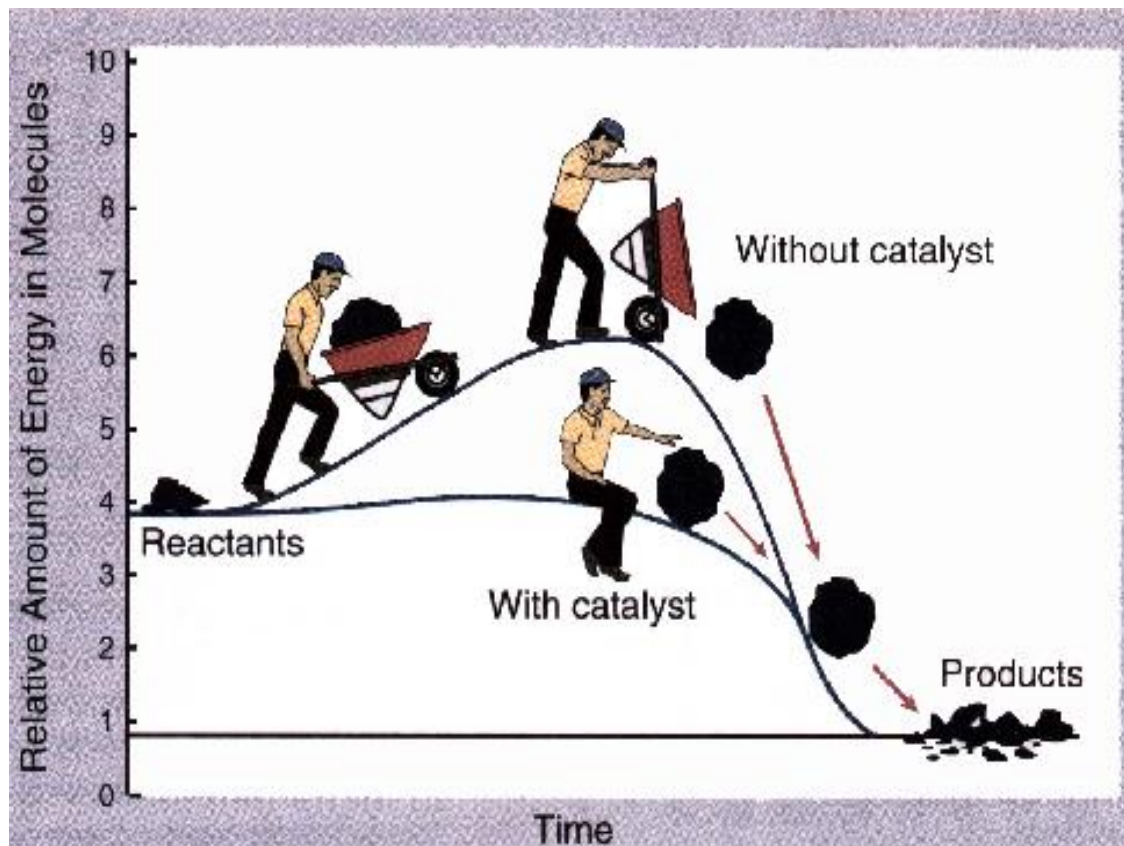
The energy required to overcome the reaction barrier.
Usually given a symbol E_a .

The Activation Energy (E_a) determines how fast a reaction occurs, the *higher* Activation barrier, *the slower the reaction rate*. *The lower the Activation barrier, the faster the reaction*



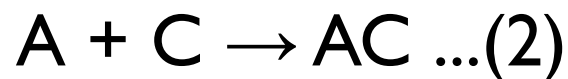
Activation Energy

A catalyst lowers the activation energy of the reaction by providing a new pathway (mechanism). Catalyst lowers the activation energy for both forward and reverse reactions.



Intermediate Compound Formation Theory

In homogeneous catalysis, catalyst form an intermediate compound (highly reactive) with one of the reactants. The highly reactive intermediate compound then reacts with the second reactant to yield the product, releasing the catalyst. taking the general reaction



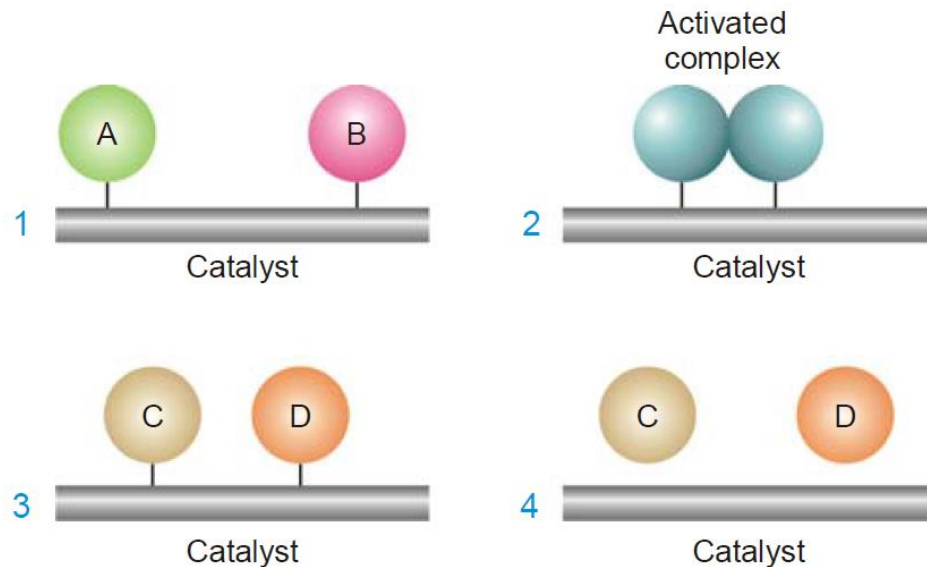
Intermediate



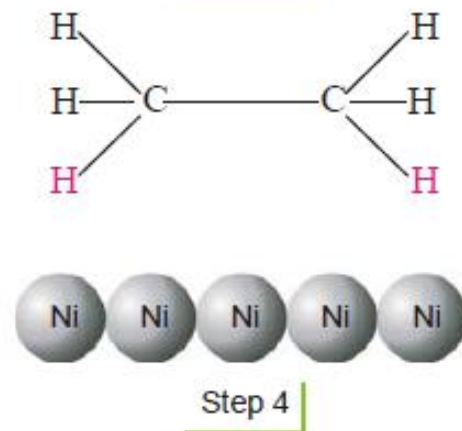
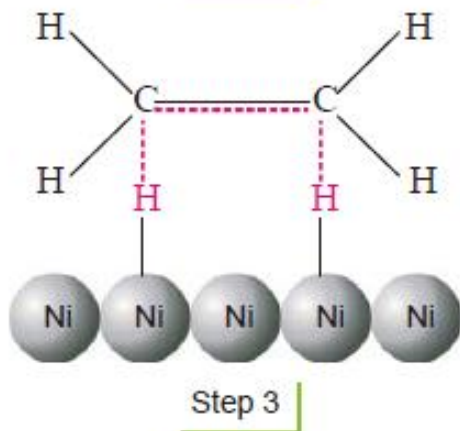
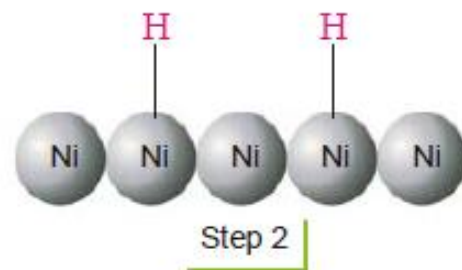
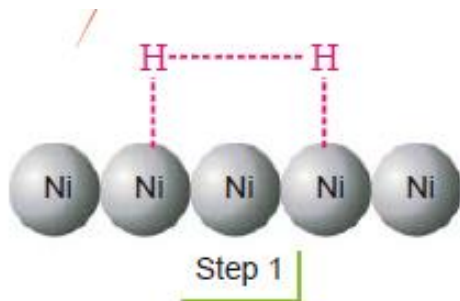
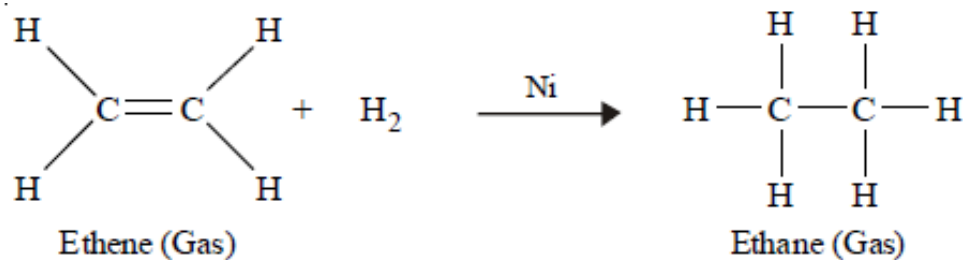
The activation energies of the reactions (2) and (3) are lower than that of the reaction (1).

The Adsorption Theory (Mechanism of heterogeneous catalysis)

- Four steps can be put forward for heterogeneous catalysis.
 - Step 1. Adsorption of Reactant molecules
 - Step 2. Formation of Activated complex
 - Step 3. Decomposition of Activated complex
 - Step 4. Desorption of Products

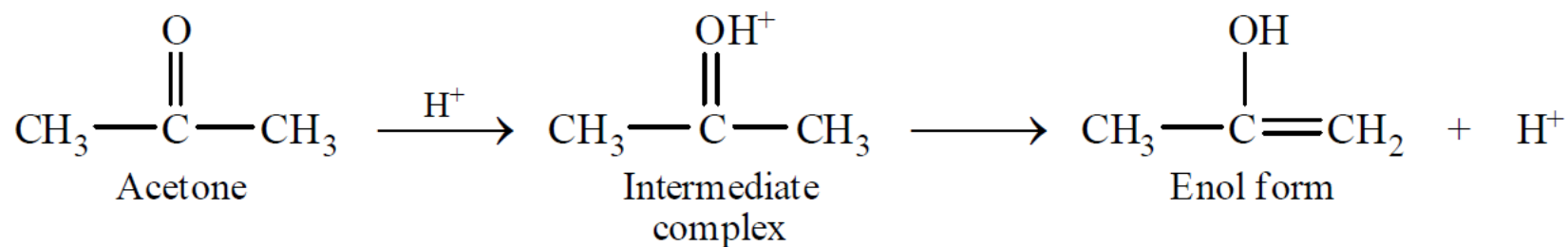


Hydrogenation of Ethylene

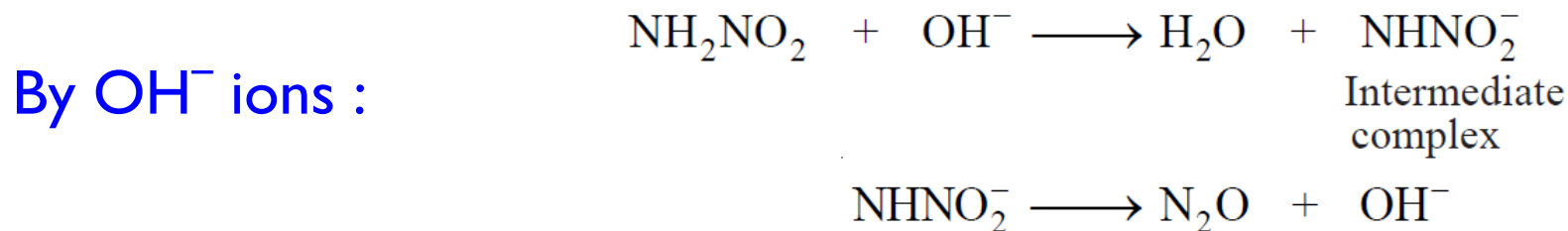


Mechanisms of catalysis

In **acid catalysis**, the H^+ (donated by Bronsted acid) forms an intermediate complex with the reactant, which then reacts to give back the proton. For example, the mechanism of keto-enol tautomerism of acetone is :



In **base catalysis**, the OH^- ion (or any Bronsted base) accepts a proton from the reactant to form an *intermediate complex* which then reacts or decomposes to regenerate the OH^- . For example, the decomposition of nitramide:



Characteristics of Acid-base catalysis

- Very often-used mechanism in enzyme reactions, e.g., hydrolysis of ester/ peptide bonds, phosphate group reactions, addition to carbonyl groups, etc.
- Enzyme *avoids unstable charged intermediates in reaction* (which would have high free energies) by:
 - donating a proton (act as a *general acid*), or
 - accepting a proton (abstract a proton, act as a *general base*)
- If a group *donates* a proton (acts as a *general acid*) in chemical mechanism, it has to get *a proton (a different one!) back* (act as a *general base*) by end of catalytic cycle, and vice versa
- Protein functional groups that can function as general acid/base catalysts:
 - e.g. His imidazole, α -amino group, α -carboxyl group, thiol of Cys, R group carboxyls of Glu, Asp, aromatic OH of Tyr, etc

Enzymes

- Enzymes are biological catalysts.
- Most enzymes are protein molecules with large molecular masses (10,000 to 10^6 amu).
- Enzymes have very specific shapes.
- Most enzymes catalyze very specific reactions.
- Substrates undergo reaction at the active site of an enzyme.
- A substrate locks into an enzyme and a fast reaction occurs.
- The products then move away from the enzyme.

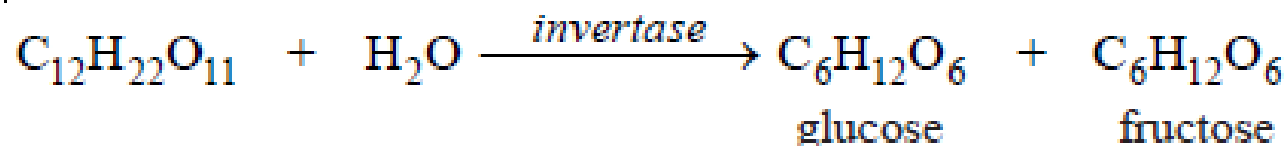
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- Only substrates that fit into the enzyme lock can be involved in the reaction.
- If a molecule binds tightly to an enzyme so that another substrate cannot displace it, then the active site is blocked and the catalyst is inhibited (enzyme inhibitors).
- The number of events (turnover number) catalyzed is large for enzymes (10^3 - 10^7 per second).

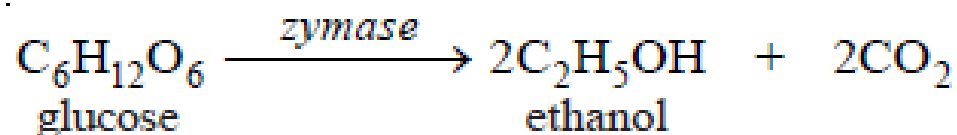
Examples of enzymes catalysis

Some common examples of the biochemical reactions catalysed by enzymes are :

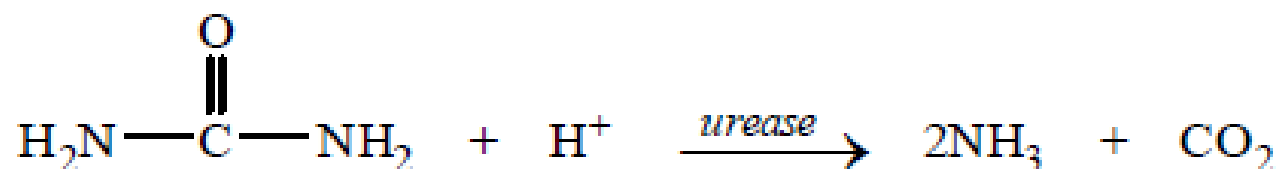
(1) Inversion of cane sugar ($C_{12}H_{22}O_{11}$) by *Invertase* present in yeast,



(2) Conversion of glucose into ethanol by *Zymase* present in yeast,



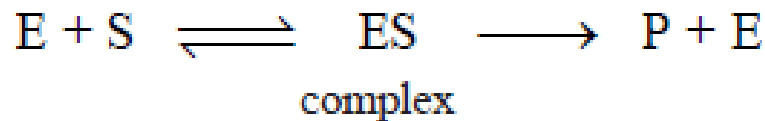
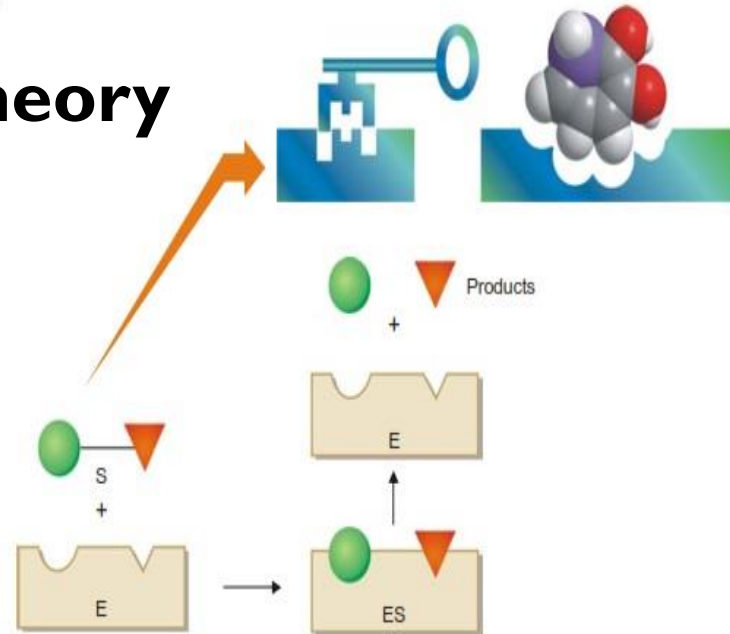
(3) Hydrolysis of urea ($H_2N-CO-NH_2$) by *Urease* present in soya bean,



Mechanism of enzyme catalysis

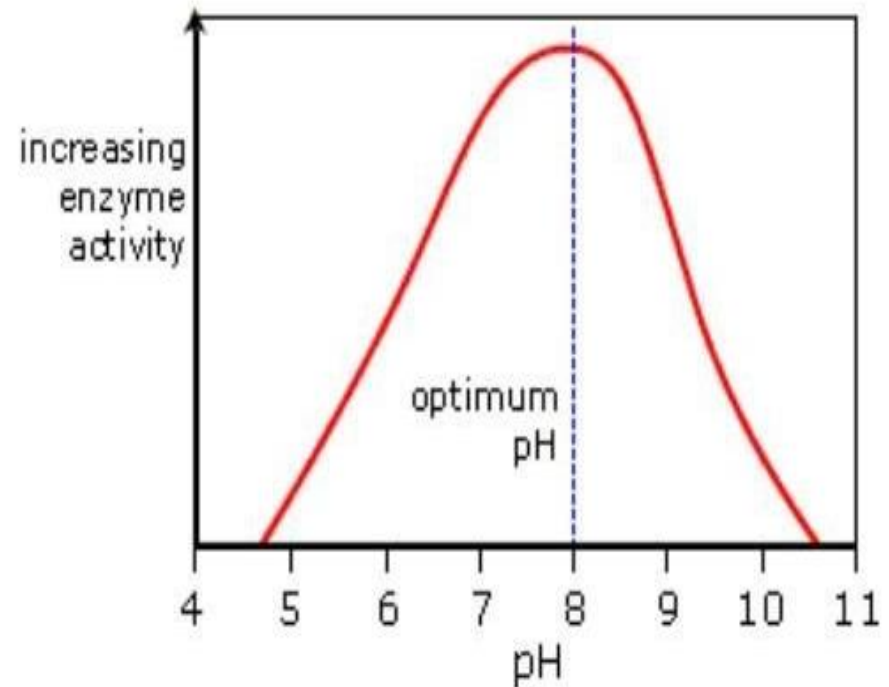
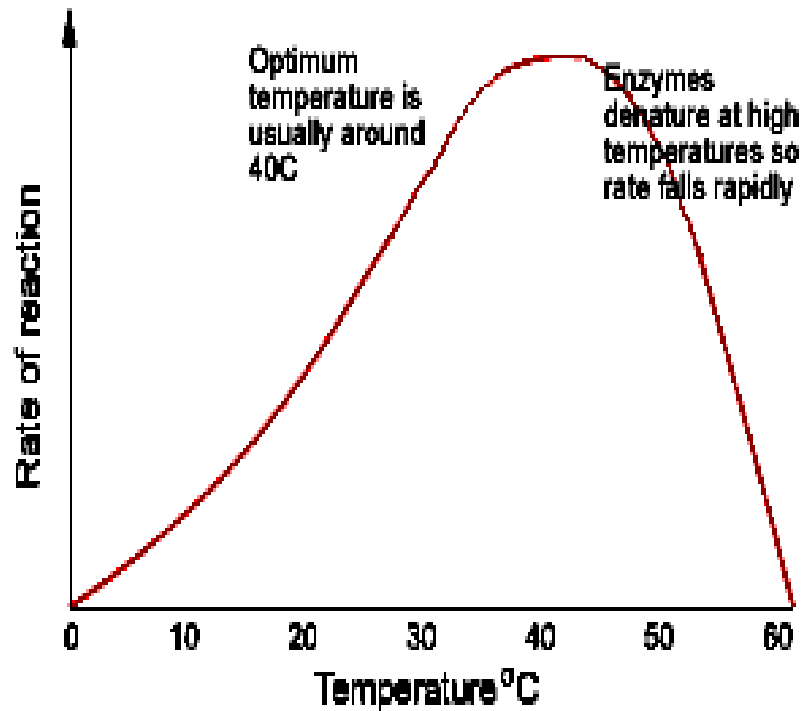
Michaelis and Menten theory

Active sites (cavities of enzyme molecule with functional groups) act as lock and substrate acts as key.



where E = enzyme; S = substrate (reactant); ES = activated complex; P = products.

Effect of temperature and pH on enzyme activity

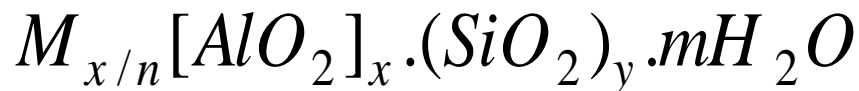


Activity and Selectivity

- Activity: Activity is the ability of catalysts to accelerate chemical reaction, the degree of acceleration can be as high as times in certain reactions
- Selectivity: Is the ability of catalysts to direct reaction to yield particular products (excluding other).
- Stability: The number of reactions performed by each active site before it decays or becomes inactive.

Zeolite (Shape selective catalysis)

Zeolite are alumino–silicates of the general formula,



where, M may be simple cation, n is the charge on the simple cation, m is the number of molecules of water of crystallization.

The zeolite catalyst ZSM-5 converts alcohols to gasoline (petrol) by dehydrating the alcohol