Gibb's Free energy:

The Gibbs free energy of a system at any moment is time is defined as the enthalpy of the system minus the product of the temprature times the entropy of the system

$$G = H - TS$$

G = Gibbs free energy ($KJ \, mol^{-1}$)
H = heat of combustion, ethalpy ($KJ \, mol^{-1}$)
T = Temprature (Kelvin)
S = entropy ($J°K^{-1}$)

The change in the Gibbs free energy of the system that occurs during a reaction is therefore equal to the change in the enthalpy of the system minus the change in the product of the temprature times the entropy of the system

$$\Delta G = \Delta H - \Delta(TS)$$

If the reaction is run at constant temprature. this equation can written as follows

$$\Delta G = \Delta H - T\Delta S$$

If ΔG is less than O ($\Delta G < O$) for any reaction, reaction will be favorable or spontaneous and if $\Delta G > O$ reaction will be unfavorable or non-spontaneous.

Spontaneous chemical reactions:

A spontaneous reaction is a reaction that favors the formation of products at the conditions under which the reaction is occuring. The entropy of the system increases during a combustion reaction. The combination of energy decreases and entropy increases dictates that combustion reactions are spontaneous reactions.

In other words entropy can be difined as for a ~~ve~~ reversible change taking place at a fixed temprature (T), the change in entropy (ΔS) is equal to heat energy absorbed or evolved divided by the temprature T. That is

$$\Delta S = \frac{q}{T}$$

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If heat is absorbed, then ΔS is positive and there will be increase in entropy. If heat is evolved ΔS is negative and there is a decrease in entropy. The unit of entropy is calories per degree per mole i.e. $cal \, mol^{-1} k^{-1}$ ~~en~~ and in SI unit it is Joules per mole per degree i.e $J mol^{-1} k^{-1}$.

Enthalpy

The total heat content of a system at constant pressure is equivalent to the internal energy E plus the PV energy. This is called enthalpy of the system and is represented by the symbol H.

$$H = E + PV$$

Where E = internal energy
P = Pressure
V = volume

If ΔH be the difference of enthalpy of a system in final state (H_2) and in the initial state (H_1).

$$\Delta H = H_2 - H_1$$

$$\Delta H = (E_2 + P_2 V_2) - (E_1 + P_1 V_1)$$

$$\Delta H = (E_2 - E_1) + (P_2 V_2 - P_1 V_1)$$

$$\Delta H = \Delta E + \Delta PV \quad \text{if P is constant while gas is expanding}$$

$$\boxed{\Delta H = \Delta E + P\Delta V}$$

Factors affecting the extent of gas-solid adserption:

The extent to which adsorption will happen on a solid surface depends on following factors.

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(1.) Nature of adsorbent: ⇒

The adsorption of the gas depends on the nature of the adsorbent. A gas can be adsorbed on different adsorbent surfaces in different amounts. e.g Hydrogen is weakly adsorbed on the alumina surface whereas it is strongly adsorbed on the nickel surface under certain conditions.

(2.) Surface Area:

Adsorption being a surface phenomenon, the extent of adsorption depends on the surface area. Increase in the surface area of the adsorbent, increases the total amount of gas adsorbed. So finely divided solids and some porous substances are good adsorbents.

(3) Nature of the gas:

In general, if a gas is more liquefiable it will be more easily absorbed. for example like NH_3, HCl, Cl_2, CO_2 which can be liquefied easily are more readily adsorbed on the solids surface, rather than permanent gases like O_2, H_2 etc

(4) Heats of Adsorption:

Heat of adsorption is defined as the energy liberated when 1gm mole of a gas is adsorbed on the solid surface. In Physical adsorption, gas molecules concentrate on the solid surface. Thus it is similar to the condensation of a gas to liquid. Therefore, adsorption like condensation is an exothermic process. when the temprature increases the kinetic energy of the gas molecules also increases which results is more number of collisions between the molecules

and the gas.

(5.) Effect of Pressure !

On the solid surface, there is a fixed number of adsorption sites where gas molecules can be adsorbed. Initially when the pressure has increased the rate of adsorption increases due to an increase in the gas molecules striking on the surface. Thus, an increase in the pressure increases the rate of adsorption linearly. But after sometime, it will reach a point when the pressure has no effect on the rate of adsorption as the number of adsorption sites is fixed and no more adsorption can happen in those sites. Hence, at that point, the extent of adsorption will be independent of the pressure.

(6.) Effect of temprature:

Physical adsorption occurs rapidly at low temprature and chemisorption like most chemical changes, generally with temprature. Thus a rise of temprature can often cause physical adsorption to change to chemisorption. Nitrogen for example is physically adsorbed on iron at 463 K but chemisorbed to form a nitride at 773 K.

(1) Explain the Zeroth law of Thermodynamics: **19** ①

Ans: The term zeroth law was coined by Ralph H. Fowler.
The Zeroth law of thermodynamics tells us the
concept of temprature. The law states that if two
bodies are each in thermal equilibrium with third
One, then they are in thermal equilibrium with each
Other. A Thermal equilibrium is a system whose macroscopic
properties like pressure, temprature, volume etc are not
changing in time.

2. what is Phase rule or Gibbs phase rule.

Ans: In 1875 Josiah Williard Gibbs published a general principle
governing system in thermodynamic equillibrium called
the Phase rule in a paper titled " on the Equillibrium
of Heterogeneous substances.

    It can mathematically represented as

$$P + F = C + 2$$

where
P = The number of Phases of material
F = The number of degrees of freedom
C = The number of component of a system
2 = represents two variables (Pressure & temprature)

Phase: A region of material that is chemically uniform,
Physically distinct and mechanically seperable.

component: Minimum number of independent species
necesary to define the composition of all Phases
of the system.

Degree of freedom:

The number of intensive variables that are independant of each other or in other words the number of thermo-dynamics variables which can be specified independantly without changing the phase in equillibrium.
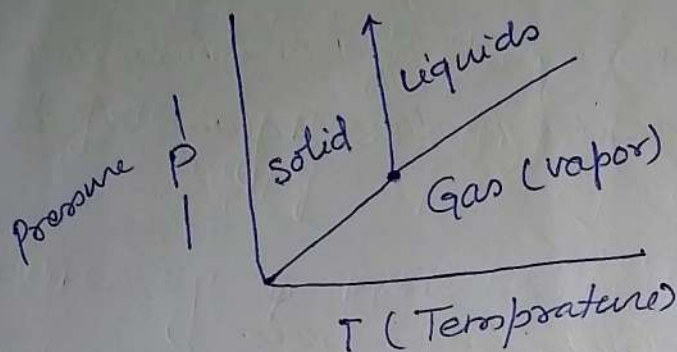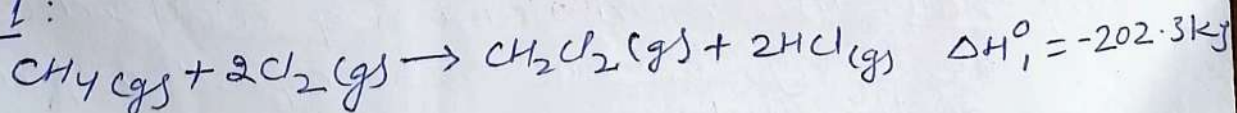

③ Define Hess's law

Ans: Hess's law of heat summation states that for a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation is the sum of enthalpy changes for the individual steps. or in other words the change in enthalpy in a chemical reaction, at a constant pressure is not dependent on the process, and only dependent on the initial and final states of the chemical reaction. Hess's law can be seen as an application of the principle of conservation of energy

e.g consider the following two routes for preparation of methylene chloride (CH_2Cl_2) from the reaction between methane (CH_4) and chlorine (Cl_2)
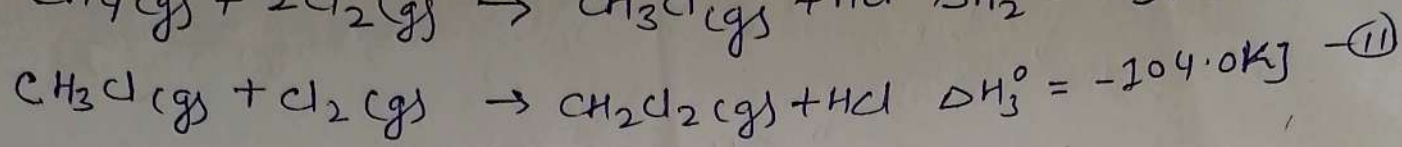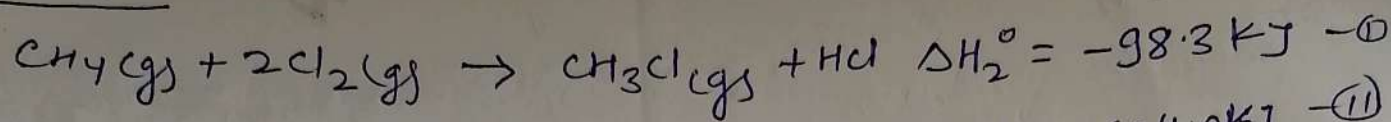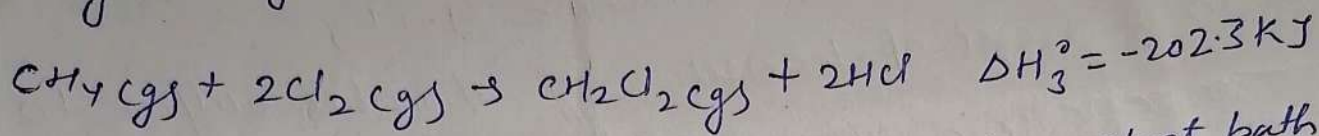
Route I:
$$CH_4\,(g) + 2Cl_2\,(g) \rightarrow CH_2Cl_2\,(g) + 2HCl\,(g) \qquad \Delta H^\circ_1 = -202.3\,kJ$$

$$CH_4 (g) + 2Cl_2 (g) \rightarrow CH_3Cl (g) + HCl \quad \Delta H_2^{\circ} = -98.3 \, KJ \quad —①$$

$$CH_3Cl (g) + Cl_2 (g) \rightarrow CH_2Cl_2 (g) + HCl \quad \Delta H_3^{\circ} = -104.0 KJ \quad —①①$$

Adding change in enthalpy of both step

$$CH_4 (g) + 2Cl_2 (g) \rightarrow CH_2Cl_2 (g) + 2HCl \quad \Delta H_3^{\circ} = -202.3 KJ$$

Thus it can be clearly seen that no matter what path we follow, the total enthalpy change in the reaction is always the same

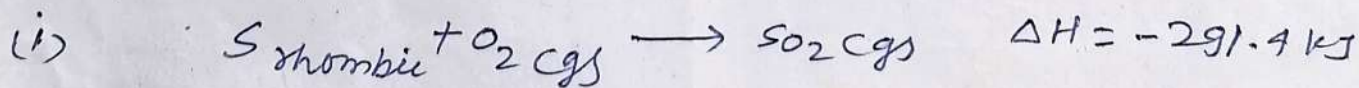$$\Delta H_1^{\circ} = \Delta H_2^{\circ} + \Delta H_3^{2} = -202.3 \, kJ$$

Application of Hen's law

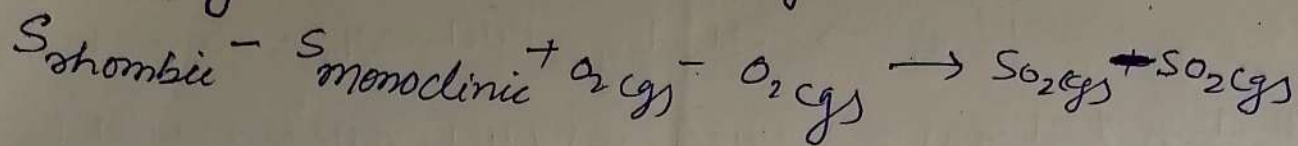(1) Determination of heat of formation of substance which otherwise cannot be measured experimentaly :

Substances like methane, CO_2, CO, benzene etc cannot be prepared by uniting their elements. Therefore it is not possible to measure the heats of formation of such compounds directly. These can be determined indirectly by using Hess's law.

② Determination of Heat Transition

The heat of transition of one allotropic form to another can also be calculated with the help of Hess's law. for example the enthalpy of transition from monoclinic sulfur to rhombic sulfur can be calculated for their heats of combustion which are

(i) $\quad S_{rhombic} + O_2 (g) \longrightarrow SO_2 (g) \quad \Delta H = -291.4 \, kJ$

(ii) $\quad S_{monoclinic} + O_2 (g) \rightarrow SO_2 (g) \quad \Delta H = -295.4 \, kJ$

Substracting eq. ① from (i) we get **22** ④

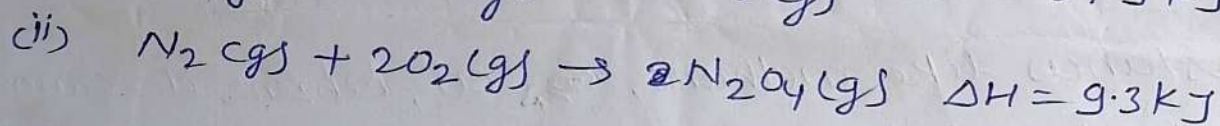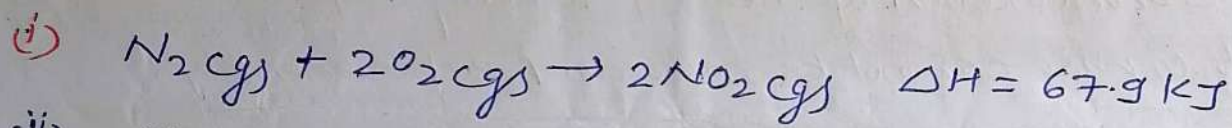$$S_{rhombic} - S_{monoclinic} + O_{2(g)} - O_{2(g)} \rightarrow SO_{2(g)} + SO_{2(g)}$$
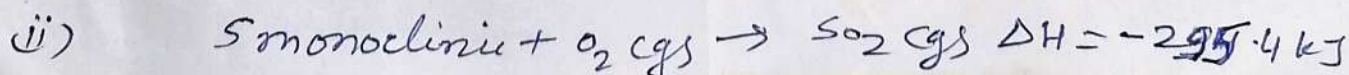
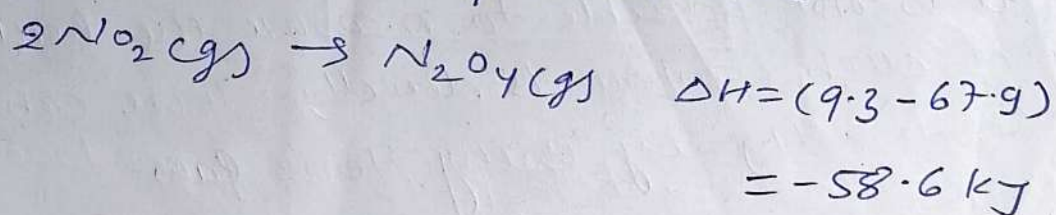$$\Delta H = -291.4 - (-295.4)$$

$$\Delta H = 4.0 \, kJ$$

Thus heat of transition of rhombic sulfur to monoclinic sulfur is 4.0 kJ

(3.) **Determination of heats of various reactions:**

By using Hess's law we can calculate the heats or enthalpies of many reactions which otherwise cannot be measured directly. for example, from the following equations the enthalpy of dimerization of NO_2 can be calculated

(i) $N_{2(g)} + 2O_{2(g)} \rightarrow 2NO_{2(g)}$ $\Delta H = 67.9 \, kJ$

(ii) $N_{2(g)} + 2O_{2(g)} \rightarrow 2N_2O_4(g)$ $\Delta H = 9.3 \, kJ$

Substracting eq. ① from eq. II we have

$$2NO_{2(g)} \rightarrow N_2O_4(g) \quad \Delta H = (9.3 - 67.9)$$

$$= -58.6 \, kJ$$

Thus the heat of dimerization of NO_2 is $-58.6 \, kJ$

Catalyst

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.

*. A catalyst may increase or decrease the rate of reaction.

⇒ which increases rate of reaction is called Positive catalyst and process is called Positive catalysis or simply catalysis

⇒ A catalyst retards the rate of reaction is called negative catalyst and process is called negative catalysis.

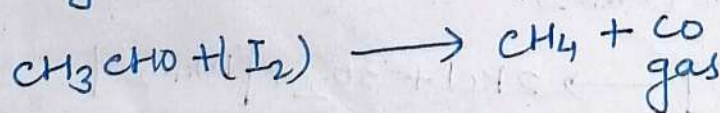## Types of catalysis

There are two main types of catalysis

(a) Homogeneous catalysis

(b) Heterogeneous Catalysis

(c) Enzyme catalysis

(a) Homogeneous catalysis:

In homogeneous catalysis, the catalyst is in the same phase as the reactants and is evenly distributed throughout. This type of catalysis can occur in gas phase or the liquid (solution) Phase.

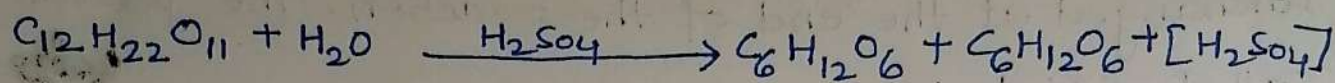### Example of Homogeneous Catalysis in Gas Phase

(a.) Decomposition of acetaldehyde (CH_3CHO) with iodine(I_2) catalyst

$$CH_3CHO + (I_2) \longrightarrow CH_4 + CO$$
$$\text{gas}$$

(b) Example of homogeneous Catalysis in solution Phase: ②

Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H_2SO_4} C_6H_{12}O_6 + C_6H_{12}O_6 + [H_2SO_4]$$
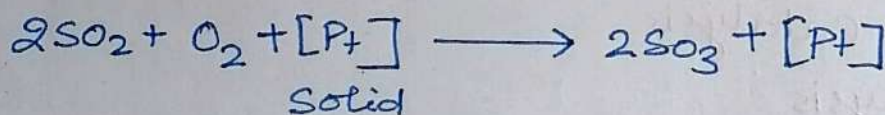
Heterogeneous catalysis.

The catalysis in which the catalyst is in a different Physical Phase from the reactant is termed Heterogeneous catalysis. In this catalysis reactants are in the gas phase while the catalyst is a solid. This process is also called contact catalysis since the reaction occurs by contact of reactant with the catalyst surface.

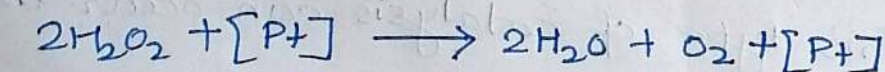**(1) Example of heterogeneous catalysis with gaseous reactant**

Combination of sulphur dioxide (SO_2) and oxygen in the presence of finely divided platinum or Vanadium pentoxide, V_2O_5

$$2SO_2 + O_2 + \underset{\text{Solid}}{[Pt]} \longrightarrow 2SO_3 + [Pt]$$

(2.) Heterogeneous catalysis with liquid reactants

The decomposition of aqueous solution of hydrogen peroxide (H_2O_2) is catalyzed by manganese dioxide (MnO_2) or Platinum in colloidal form
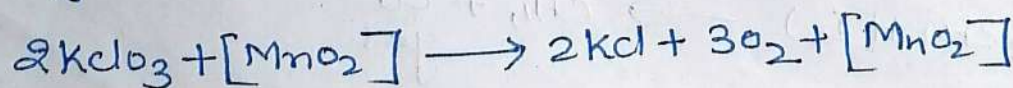
$$\underset{\text{liquid}}{2H_2O_2} + \underset{\text{solid}}{[Pt]} \longrightarrow 2H_2O + O_2 + [Pt]$$

(3.) Heterogeneous catalysis with solid reactants

The decomposition of potassium chlorate ($KClO_3$) is catalyzed by manganese dioxide (MnO_2).
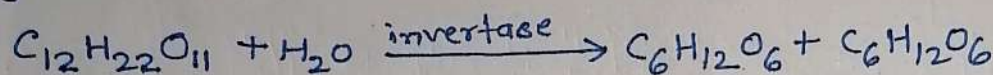
$$2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2 + [MnO_2]$$

Enzyme Catalysis

Enzymes are protein molecules which act as catalyst to speed up organic reactions in living cells. The catalysis brought about by enzymes is know as Enzyme catalysis or biocatalysis.

e.g:

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

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

(b) conversion of glucose into ethanol by Zymase present in yeast

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$
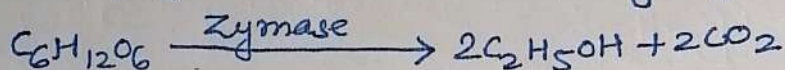
Mechanism of Enzyme catalysis

The long chains of the enzyme (protein) molecules are coiled on each other to make a rigid colloidal particle with cavities on its surface. These cavities which are of characteristic shape and abound in active groups (NH_2, $COOH$, SH, OH) are termed Active centers. The molecules of Substrate which have complementary shape, fit into these cavities just as key fits into lock (Lock-and-key theory). By virtue of the presence of active groups, the enzyme forms an activated complex with the substrate which at once decomposes to yield the product.

Michaelis and Menten proposed the following mechanism for enzyme catalysis

$$E + S \rightleftharpoons ES \longrightarrow P + E$$
$$\text{Complex}$$
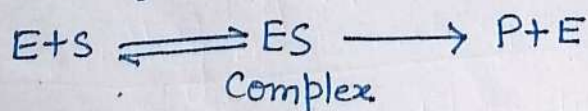
where E = enzyme, S = Substrate (Reactant) ES = Activated complex
P = Product
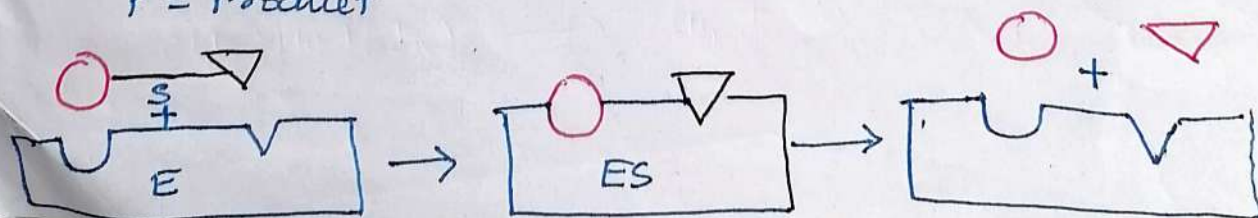
Characteristics of Enzyme catalysis

In general; enzyme behave like inorganic heterogeneou s catalyst. However, they are unique in their efficiency and high degree of specificity. Some more important features of enzyme catalysis are listed below
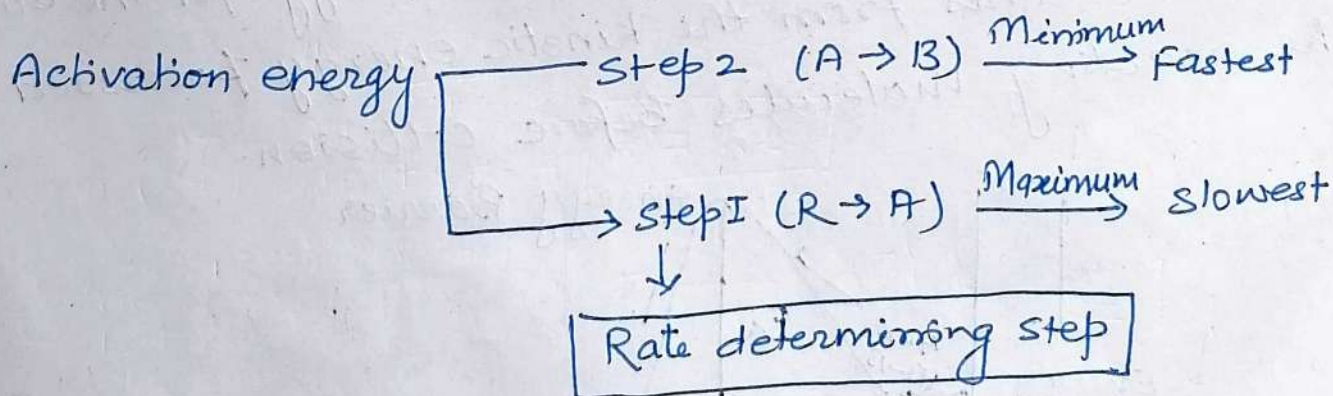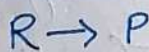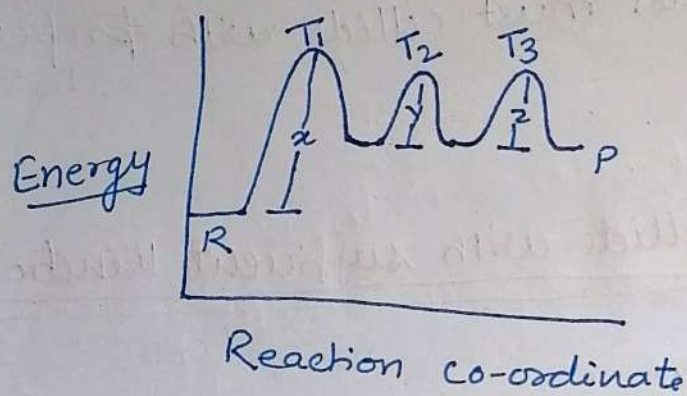
~~Elorade~~

(i)

Complex reaction:

Complex reaction proceed in a series of steps instead of a single and rate all over reaction is in accordance with stoichiometric equation for that reaction or such reaction occur in several steps where each step is elementary. Which molecularity is not defined but molecularity of each step can be defined and it's rate depends on slowest step of the reaction

Energy

Reaction co-ordinate

$R \longrightarrow P$

$R \longrightarrow A \longrightarrow$ 1st step
$A \longrightarrow B \longrightarrow$ 2nd step
$B \longrightarrow P \longrightarrow$ 3rd step
___

$R \longrightarrow P$

Activation energy — Step 2 $(A \rightarrow B)$ $\xrightarrow{\text{Minimum}}$ fastest

$\longrightarrow$ Step I $(R \rightarrow A)$ $\xrightarrow{\text{Maximum}}$ slowest

$\downarrow$

Rate determining step

Theories of chemical kinetic

A/c to this theory a chemical reaction takes place only by collision between the reacting molecules. The two main conditions for a collision between the reacting molecules to be productive are:
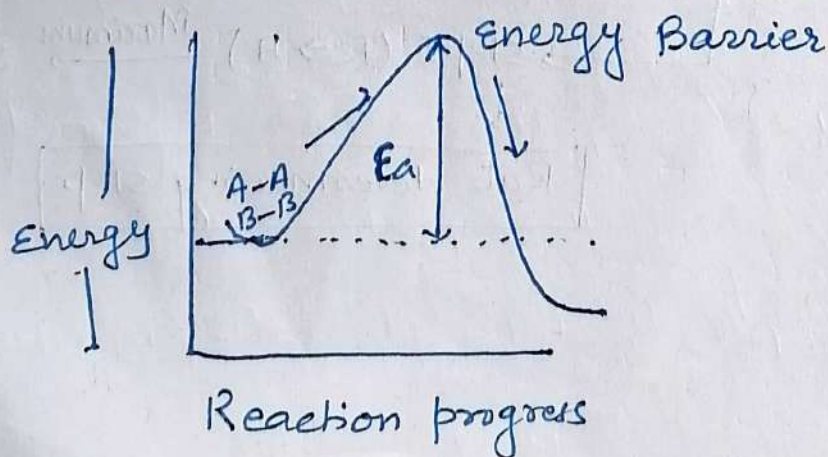
(1.) The colliding molecules must posses sufficient kinetic energy to cause a reaction

(2.) The reacting molecules must collide with proper orientation.

(1.) The molecule must collide with sufficient kinetic energy

Let us consider a reaction

$$A-A + B-B \longrightarrow 2A-B$$
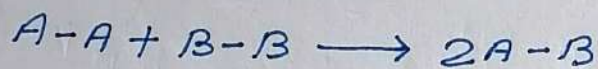
A chemical reaction occurs by breaking bonds between the atoms of the reacting molecules as forming new bonds in product molecules. The energy for the breaking of bonds comes from the kinetic energy possessed by the reacting molecules before collision.

The figure shows the activation energy. Ea that is the minimum energy necessary to cause a reaction between the colliding molecules. Only the molecules colliding with kinetic energies greater than Ea are able to get over the barrier and react and whoes kinetic energy less than Ea fail to surmount the barrier and this type of collisions are unproductive.

(2.) <u>The molecule must collide with correct orientation ⇒</u>

The reactant molecules must collide with favorable orientation. The correct orientation is that which ensure direct contact between the atoms involved in the breaking and forming of bond i.e only the molecule colliding with kinetic energy greater than Ea (activation energys) and with correct orientation can cause reaction. Let's suppose

$$A + B \rightarrow C + D$$

Then the reaction rate of elementary process is given by the expression

$$rate = f \times P \times Z$$

f = fraction of molecule which process sufficient energy to react, P = Probable fraction of collision with effective orientations and Z = collision frequency.