

Thermodynamics

Thermodynamics: Thermo = heat; dynamics = motion.

Thermodynamics means that branch of science which deals with the conversion of heat into mechanical work and vice versa. Ex: electrical energy, chemical energy, radiant energy.

Thermodynamics is also defined as that "***branch of science which deals with the quantitative relationships between heat and other forms of energy***".

Thermodynamics is based on three generalizations, called as

- i) First law of thermodynamics,
- ii) Second law of thermodynamics,
- iii) Third law of thermodynamics.

Thermodynamics find applications in chemistry, physics and in engineering.

Applications in chemistry:

- (i) Most of the important laws of physical chemistry such as colligative properties, Raoult's law of lowering of vapour pressure, Van't Hoff law of dilute solutions, expressions for elevation in boiling point and depression in freezing point, distribution law, phase rule, law of chemical equilibrium and law of thermo-chemistry can be deduced from the laws of thermodynamics.
- (ii) Thermodynamics help us in predicting the feasibility of a particular process (physical or chemical), i.e., whether the process can occur or not under a given set of conditions of temperature, pressure and concentration etc.
- (iii) Thermodynamics also helps in determining the extent to which a reaction would proceed before attainment of equilibrium and thus it may predict the yield of products.
- (iv) Thermodynamics is applicable equally in physics and engineering.

Limitations of thermodynamics:

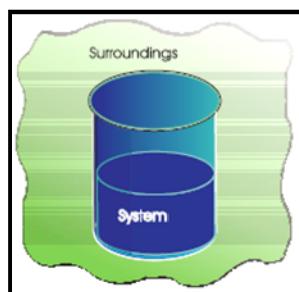
- (i) The laws of thermodynamics are applicable to any matter in bulk, i.e. assemblage of large number of molecules (macroscopic systems), and not to individual molecules or atoms. Thus thermodynamics is independent of atomic and molecular structure of matter, i.e., it ignores the internal structure of atoms and molecules
- (ii) Although thermodynamics predicts about the feasibility, direction and extent of a given process under a given set of conditions, it does not tell anything about the rate at which a given process may proceed, i.e., it provides no information regarding the time taken to reach the equilibrium or the state of completion.
- (iii) It concerns itself only with the initial and final states of a system and gives no information about the path taken (mechanism) by a process.

Terms used in thermodynamics:

System: A system is defined as a specified part of universe or specified portion of the matter which is under experimental investigation.

Surroundings: The part of the universe other than the system is known as surroundings.

Boundary: The wall that separates the system from the surroundings is called boundary. The boundary may be real or imaginary.



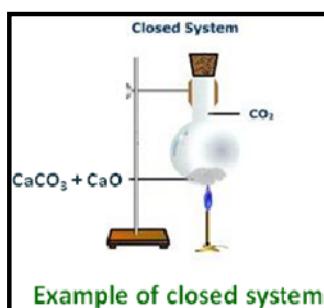
Types of thermodynamic systems:

Open system: The system in which energy and matter both can be exchanged with the surroundings. Ex: Boiling water in open vessel.



Closed system: The system in which only energy can be exchanged with the surroundings.

Ex: calcinations of CaCO_3 taken in a sealed tube.



Isolated system: The system in which neither energy nor matter can be exchanged with the surroundings.

Ex: a reaction carried out in a closed and well insulated container (such as thermos flask).



Homogeneous systems: A system is said to be homogeneous if it is uniform throughout, i.e., it consists of only one phase. Ex: A solution of sugar in water, a pure solid, airs (a mixture of several gases).

Heterogeneous systems: A system is said to be heterogeneous if it is not uniform throughout in its characteristics, i.e., it consists two or more phases.

Ex: system consisting of water and oil, a saturated solution of sugar in water.

Work (W): The displacement of system with the application of force.

If F = magnitude of force; I = the displacement of the point of application in the direction in which the force acts,

Then $W = F I$.

i) Electrical work = charge X potential
 $= Q \times V$

ii) Gravitational work = $(mg) h$

Where m = mass of body; g = acceleration due to gravity, h = height moved.

iii) **Pressure – volume work:** the work done when the gas expands or contracts against the external pressure (generally atmospheric pressure).

$$w = P_{ext} (V_2 - V_1) = P_{ext} \Delta V$$

Where V_1 = initial volume, V_2 = final volume.

Work done on the system, $w = +$ ve (since $V_2 > V_1$)

Work done by the system, $w = -$ ve (since $V_2 < V_1$)

Units of Heat and Work:

Heat (Q): The quantity of heat required to raise the temperature of one gram of water by 1 °C. The unit of heat is calorie (cal). SI unit of heat is joule (J).

$$1 \text{ joule} = 0.2390 \text{ cal}$$

$$1 \text{ joule} = 10^7 \text{ erg}$$

$$1 \text{ calorie} = 4.184 \text{ J}$$

$$1 \text{ kcal} = 4.184 \text{ kJ}$$

$$\mathbf{1 \text{ litre-atm} = 101.3 \text{ J} = 1.013 \times 10^9 \text{ erg} = 24.206 \text{ cal.}}$$

Work and heat are interrelated, $W \propto Q$ or $W = JQ$.

Thermodynamic properties: These are of two types.

a) **Extensive properties:** properties of a system which depend on the total amount of the material present in the system.

Ex: mass (m); volume (v); internal energy (E); heat content (H); Gibbs energy (G); entropy (S); heat capacity (C) etc.

b) **Intensive properties:** properties of a system which are independent of the amount of the material present in the system.

Ex: Density (ρ); pressure (P); temperature (T); boiling point (B.P); freezing point (F.P); vapour pressure (V.P); specific heat (s); surface tension (σ); viscosity (η) etc.

Q. What is meant by state of a system? Explain.

State of the system: it may be defined as the condition of existence of the system when its macroscopic properties have definite values.

The macroscopic properties of a system, which change with the change in the state of the system, are called state variables or state functions. Or a measurable property required to describe the state of a system is called state variable.

Commonly used variables to define the state of a particular system are temperature (T), pressure (P), volume (V) and chemical composition (n).

Ex: H_2O .

H_2O can exist in 3 physical states, i.e., ice, water and steam depending upon the conditions of temperature and pressure.

At 1 atm pressure, H_2O is:

Solid, if temperature is below 0 °C.

Liquid, if temperature is between 0 to 100 °C.

Gas, if temperature is above 100 °C.

Therefore, in order to define the physical state of water, we need specification of its conditions of temperature and pressure.

Again, consider H_2O (l) at two temperatures, 25 °C and 50 °C respectively, both at 1 atm pressure. Although physical state of the 2 samples is same, yet their macroscopic properties like energy, viscosity, surface tension etc. are different. Hence the thermodynamic state of two samples is different.

The values of state functions depend only upon the state of the system but do not depend upon how that state is achieved.

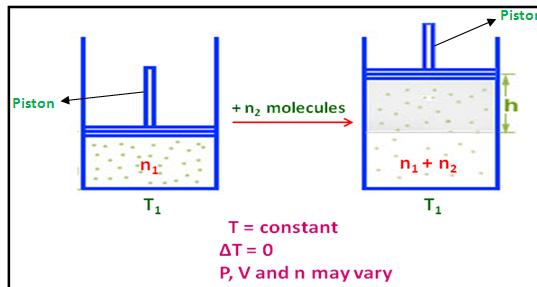
Consider 1 mole of CO_2 at N.T.P., its volume will be 22.4 liters irrespective of the method through which the given sample of CO_2 is obtained.

Similarly, the values of other state variables are also fixed for this particular system of CO_2 at N.T.P. some common state functions are volume, pressure, temperature, internal energy, enthalpy, entropy and free energy.

Q) Write short notes on thermodynamic processes.

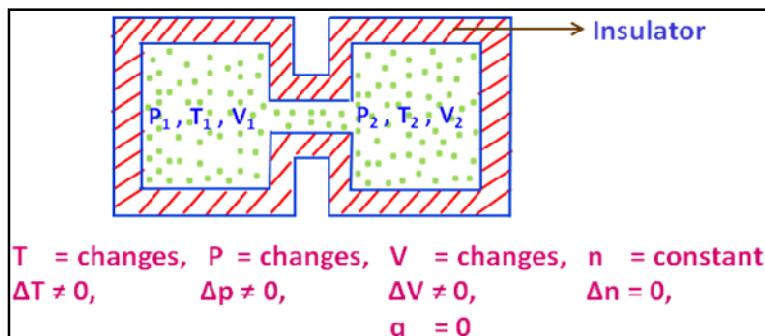
Isothermal process: Isothermal process is that in which the temperature of the system remains constant.

Ex: Expansion or compression of a gas at constant temperature.



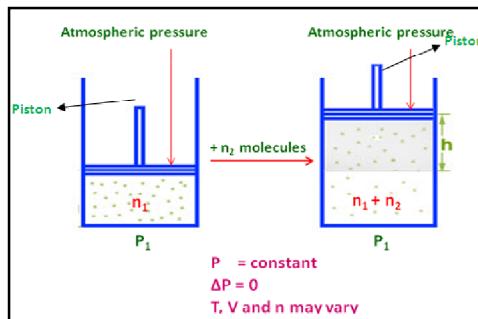
Adiabatic process: Adiabatic process is where there is no exchange of energy and matter between the system and its surroundings.

Ex: Joule-Thomson expansion of air takes place under adiabatic conditions.



Isobaric process: Isobaric process is when the pressure on the system remains constant during any operation.

Ex: A gas contained in a vessel fitted with a frictionless piston. It expands at constant atmospheric pressure.



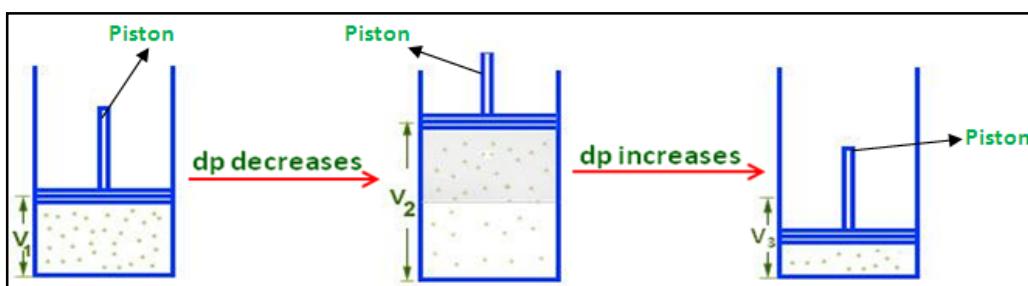
Isochoric process: isochoric process is that in which the volume of the system does not change.

Ex: reactions carried out in a closed vessel of a definite volume.

Cyclic process is one when the system returns to its initial state after having undergone a series of changes.

Reversible process occurs when a process is carried out infinitesimally slowly so that the system and the surroundings are always in equilibrium. And infinitesimally slowly when the constraint applied on the system is reversed, the equilibrium also is shifted in the reverse direction.

Example: Irreversible process is that which is carried out rapidly so that the system does not return to its initial state.



Internal energy (E): The total energy contained in a system or substance is called its internal energy or intrinsic energy. It is a state function.

$$E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}} + \dots$$

Let ΔE be the difference of energy of the initial (E_{in}) and the final state (E_f), then

$$\Delta E = E_f - E_{\text{in}}$$

ΔE is positive if $E_f > E_{\text{in}}$ and negative if $E_f < E_{\text{in}}$

A system may transfer energy to or from the surroundings as heat or Work or both.

Characteristics of internal energy

- (i) Internal energy of a system is an extensive property.
- (ii) Internal energy is a state property.
- (iii) The change in the internal energy does not depend on the path by which the final state is reached.
- (iv) There is no change in internal energy in a cyclic process.

First law of thermodynamics:

- (i) Energy cannot be created or destroyed but it can be converted from one form to another.
- (ii) The total energy of the universe is constant.
- (iii) Whenever a quantity of one kind of energy disappears, an exactly equivalent quantity of energy in some other form must appear.
- (iv) It is impossible to construct a perpetual motion machine which could produce work without consuming energy.
- (v) The total energy of an isolated system remains constant though it may change from one form to another.

When a system is changed from initial state to the final state, it undergoes a change in the internal energy from E_{in} to E_f .

$$\text{Thus, } \Delta E = E_f - E_{in}$$

The change in internal energy can be brought about in two ways:

- (i) Either by allowing the heat to flow into the system (absorption) or out of the system (evolution).
- (ii) By doing work on the system or the work done by the system.

Consider a system whose internal energy is E_1 . If the system is supplied q amount of heat, the internal energy of the system will become $E_1 + q$. now if work w is also done on the system, the final internal energy becomes E_2 .

$$\text{Thus, } E_2 = E_1 + q + w$$

$$E_2 - E_1 = q + w$$

$$\Delta E = q + w$$

Where, q = heat absorbed and w = **work done on the system**.

If, q = heat absorbed and w = **work done by the system**, then the relationship becomes

$$\Delta E = q + (-w) = q - w$$

This is the mathematical statement of the first law of thermodynamics.

The First law of thermodynamics may also be stated as:

"It is impossible to construct a mobile or perpetual machine that can work without consumption of any fuel energy."

Enthalpy (H): it is defined as the sum of the internal energy of the system and the product of its pressure and volume of the gaseous system.

$$H = E + PV$$

Where, E = internal energy, P = pressure and V = volume of the gaseous system.

Enthalpy is also called heat content.

Enthalpy change: every substance have a definite value of enthalpy in a particular state, i.e., Enthalpy is a state function. The absolute value of enthalpy cannot be measured but change in enthalpy can be determined by

$$\Delta H = H_{\text{products}} - H_{\text{reactants}} = H_p - H_r$$

Where, H_p = enthalpy of products and H_r = enthalpy of reactants ΔH = change in enthalpy.

If a reaction is carried out at constant temperature and pressure the heat exchanged (evolved or absorbed) by the system with the surroundings is equal to change in enthalphy. i.e., $H = E$.

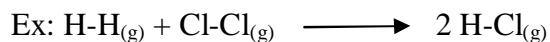
Explanation of the energy evolved or absorbed in chemical reaction:

In chemical reactions, the bonds in the reactants are broken and new bonds are formed in the reactions. Then energy is required to break the bonds. Similarly energy is released when the new bonds are formed.

Therefore, net energy change = [energy required to break the bonds of reactants (A)] – [energy in new bond formation for products (B)]

If, $A > B$ then $\Delta H = + \text{ve}$ (endothermic)

$A < B$ then $\Delta H = - \text{ve}$ (exothermic)



The energy required to break one mole of hydrogen = 437 KJ

The energy required to break one mole of chlorine = 244 KJ

The energy released for the formation of one mole of HCl = 433 KJ

Therefore, enthalpy change = $(437+244) - (2 \times 433) = -185 \text{ KJ}$.

i.e., an exothermic change takes place.

The amount of heat exchanged with the surroundings for a reaction at constant pressure (ΔH) is different from that exchanged at constant volume (ΔE) and at constant temperature. The energy changes for reactions at constant pressure, includes energy contributions due to expansion or contraction against atmospheric pressure *i.e.*, the volume of the reacting system changes. If the volume increases, the system expands against the atmospheric pressure and energy is required for this expansion. Therefore, a part of energy will be used for the expansion. Thus the amount of heat exchanged at constant pressure (ΔH) would be less than the amount of heat exchanged at constant volume (ΔE). *i.e.*, if the expansion or the compression processes do not take place. This is applicable to gaseous systems more than the systems containing the liquids or solids only.

Relationship between ΔH and ΔE :

Consider a reaction $A \longrightarrow B$

At constant pressure 'P', let H_A be the total enthalpy of the reactants and H_B be the total enthalpy of the products so that change in enthalpy,

$$\Delta H = [H_B - H_A]$$

But $H = \{E + PV\}$ by definition for gaseous systems

Let E_A and V_A be the internal energy and volume of the reactants and E_B and V_B corresponding values for the products. Therefore

$$H_A = [E_A + PV_A] \text{ and } H_B = [E_B + PV_B]$$

$$\Delta H = \{H_B - H_A\}$$

$$\Delta H = (E_B + PV_B) - (E_A + PV_A)$$

$$\text{Or } \Delta H = (E_B - E_A) + P(V_B - V_A)$$

$$\text{Or } \Delta H = \Delta E + P\Delta V$$

Where ΔE is the change in internal energy and ΔV is the change in volume of the system

Heat capacity:

Heat capacity gives a measure of the quantity of heat absorbed by a system. It is defined as “**the amount heat required to raising the temperature of the system through 1 °C**”.

Specific heat (C):

“**The quantity of heat required to raise the temperature of unit mass of the substance through 1 °C is defined as the heat of the substance.**”

If ‘q’ is the heat required by the system to raise its temperature from T_1 to T_2 , then

$$q \propto \Delta T \implies q = C \Delta T, \text{ where } C \text{ is proportionality constant.}$$

$$C = \frac{q}{(T_2 - T_1)} \text{ or } \frac{q}{\Delta T}$$

Heat capacity is a path function i.e. it depends on the conditions of measurement and so the conditions such as constant volume or constant pressure have to be specified to define the path for calculating the heat capacity of a system.

The heat capacity at constant volume is represented by C_v and that at constant pressure is represented by C_p .

Significance of C_v and C_p :

We know that

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

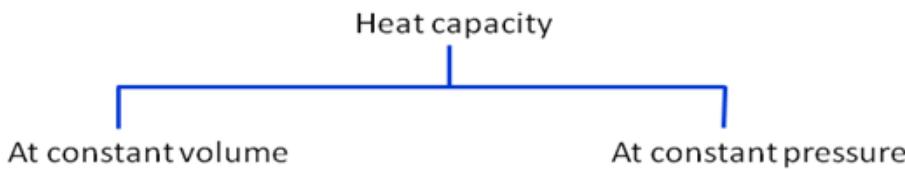
But from first law of thermodynamics

$$q = \Delta E + W$$

$$q = \Delta E + P\Delta V$$

$$\text{and } C = \frac{q}{\Delta T}$$

$$\therefore C = \frac{\Delta E + P\Delta V}{\Delta T}$$



$$\Delta V = 0$$

$$\text{Therefore } C_v = \frac{q_v}{\Delta T}$$

$$= \frac{(\Delta E + 0)}{\Delta T}$$

$$= \frac{\Delta E}{\Delta T}$$

$$\Delta V \neq 0$$

$$C_p = \frac{q_p}{\Delta T}$$

$$= \frac{(\Delta E + P\Delta V)}{\Delta T}$$

$$\text{Therefore } C_p = \frac{\Delta H}{\Delta T}$$

$$(\therefore \Delta H = \Delta E + P\Delta V)$$

Thus, heat capacity at constant volume represents the rate of increase of internal energy of the system with temperature, while the heat capacity at constant pressure represents the rate of increase of enthalpy of the system with temperature.

Molar heat capacities:

The heat capacities of 1 mole of a gaseous system at constant volume and at constant pressure are called molar heat capacities.

The Ratio C_p/C_v :

The ratio of molar heat capacities at constant pressure to that at constant volume is represented by gamma (γ). The value of γ gives information about the atomicity of gases

$$\frac{C_p}{C_v} = \gamma$$

For monoatomic gases $\gamma = 1.67$

For diatomic gases $\gamma = 1.40$

For triatomic gases $\gamma = 1.30$

Relationship between C_p and C_v :

When the temperature of 1 mole of ideal gas is to be raised through one degree Kelvin (1 K) the gas is heated at constant volume. The gas under this condition does no external work and the heat supplied increases the internal energy of the gas. When the gas is heated at constant pressure, there will be an increase in its volume. The gas will expand and do some external work. Extra heat must be supplied to the gas to enable it to perform this external work. Thus, heat capacity at constant pressure (C_p) is larger than that at constant volume (C_v). The difference between the two i.e., $(C_p - C_v)$, gives the work done by 1 mole of the gas when it is heated through one degree. This represents the work done per mole per degree rise in temperature, i.e., R the universal gas constant. Thus,

$$C_p - C_v = R$$

The above conclusion can be arrived at mathematically as follows

$$C_p - C_v = \left[\frac{\Delta H}{\Delta T} - \frac{\Delta E}{\Delta T} \right] \quad \text{----- (i)}$$

$$\text{Also } H = E + PV$$

$$\text{For an ideal gas, } PV = RT$$

$$\text{Therefore } H = E + RT$$

$$\text{Differentiation with respect to } T, \frac{\Delta H}{\Delta T} - \frac{\Delta E}{\Delta T} + R$$

$$\text{or } \left[\frac{\Delta H}{\Delta T} - \frac{\Delta E}{\Delta T} \right] = R \quad \text{----- (ii)}$$

$$\text{Comparing (i) and (ii)} \quad C_p - C_v = R \quad \text{For 1 mole of ideal gas}$$

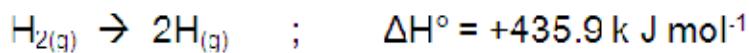
The above relation is also called Meyer's relationship.

It can also be written as $[C_p - C_v] = R = 1.99 \text{ cal K}^{-1} \text{ mol}^{-1} = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$.

Enthalpy of Bond dissociation:

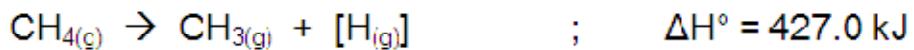
It is defined as "*The amount of energy required breaking one mole of bonds of a particular type in a molecule in the gaseous state*"

It is expressed in terms of kJ mol^{-1} or Cals mol^{-1} or k Cal mol^{-1} . For example, the bond dissociation energy of H – H bond in H_2 molecule is +439.9 kJ mol^{-1}



In polyatomic molecules, the bond energies vary depending on the environment in the molecule. For example

The bond dissociation energies for step wise dissociation of CH_4 molecules are



The energy for each step is different due to the reason that in each step of dissociation, different fragments of methane involved. In such cases, for normal purposes the average bond energies are considered.

The average bond dissociation energy in methane is $\frac{1}{4}$ of the total energy required to break one mole of $\text{CH}_{4(g)}$ into $\text{C}_{(g)} + 4[\text{H}_{(g)}]$

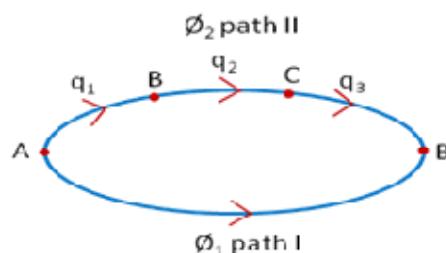
$$\begin{aligned}\text{C – H bond dissociation energy} &= \frac{(427.0+418.4+460.2+343.1)}{4} \\ &= +\frac{1648.7}{4} \\ &= +412.2 \text{ kJ}\end{aligned}$$

Hess's Law:

This law states that, “the heat change in a particular reaction remains the same whether it takes place in one step or several steps”.

Illustration of Hess's law:

Let us suppose that “A” is changed to “D” in a chemical reaction. Let us assume that the reaction takes place in two different paths



In path I “A” changes to “D” directly in a single step.



In path II “A” changes to “D” in three consecutive steps as shown below



The total heat change in the path shown in II is $-\emptyset_2$

$$\text{i.e., } \emptyset_2 = [q_1 + q_2 + q_3]$$

Therefore as per Hess's law

- \emptyset_1 , the heat change in path (I) must be equal to total change in path (II), - \emptyset_2

$$\text{Therefore } \emptyset_1 = [q_1 + q_2 + q_3] = \emptyset_2$$

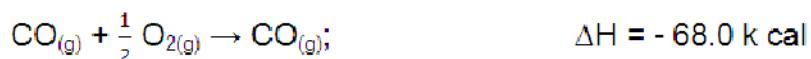
Examples:

(i) Formation of carbondioxide from carbon:

First method: carbon is directly converted into $\text{CO}_{2(\text{g})}$



Second method: carbon is first converted into $\text{CO}_{(\text{g})}$ and then $\text{CO}_{(\text{g})}$ into $\text{CO}_{2(\text{g})}$, i.e., conversion has been carried out into two steps

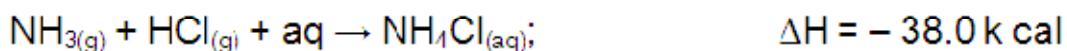


Sum of the enthalpy changes in the two steps = $- 26.0 - 68.0 = - 94.0 \text{ k cal}$

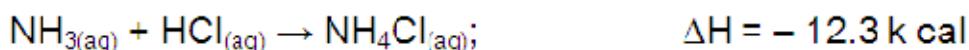
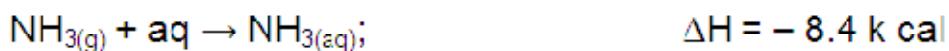
Total enthalpy change in $\text{C}_{(\text{s})}$ to $\text{CO}_{2(\text{g})}$ by either process is the same; i.e., $\Delta H = - 94.0 \text{ k cal}$

(ii) Formation of ammonium chloride from ammonia and hydrochloric acid:

First method:



Second method:



Applications of Hess's law:

a. Determination of heat formation:

"In the determination of heat of formation of intermediate compounds which are unstable or which cannot be isolated."

Ex: Heat of formation (ΔH) of CO.



The heat of formation of $CO_{(g)}$ is given by



This is given by

$$\begin{aligned}\Delta H \text{ of CO formation} &= \{(\Delta H_1) - (\Delta H_2)\} \\ &= -393.52 - (-283.02) \\ &= -110.50 \text{ kJ}\end{aligned}$$

b. Determination of heat of transition:

The heat of transition of allotropic modifications of substances such as diamond to graphite, rhombic sulphur to monoclinic sulphur, yellow phosphorous to red phosphorous etc. can be determined by using Hess's law.

Ex: Heat of transition of diamond to graphite:



The conversion that is required is



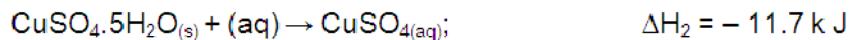
This can be obtained by subtracting the second equation from the first one



c. Determination of heat of hydration:

The heat of hydration of a substance is calculated using Hess's law.

Ex: Heat of hydration copper sulphate:



The process of hydration can be expressed as

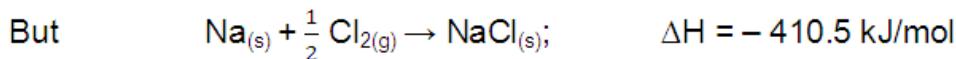
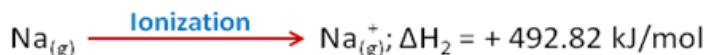
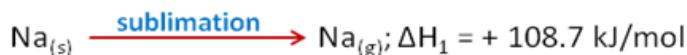
According to Hess's law

$$\Delta H = [\Delta H_1 + \Delta H_2]$$

$$= -66.5 - 11.7$$

$$= -78.2 \text{ kJ/mol}$$

d. In the calculation of lattice energy (U) of NaCl:



By the application of Hess's law of constant heat summarization, we have

$$\Delta H = [\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5]$$

$$\Delta H_5 = \{\Delta H - (\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4)\}$$

$$= -410.5 - (108.7 + 492.82 + 119.55 - 361.57)$$

$$= -770 \text{ kJ}$$

$$\Delta H_5 = -U = -770 \text{ kJ mol}^{-1}$$

Entropy (S):

“Entropy is thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system.”

It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state. The change entropy from an initial to a final state of a system is denoted by ΔS .

Entropy is a state function depends only on the initial and final states of the system.

$$\Delta S = [S_{\text{final}} - S_{\text{initial}}]$$

When $S_{\text{final}} > S_{\text{initial}}$, ΔS is positive.

For a chemical reaction,

$$\Delta S = [S_{\text{products}} - S_{\text{reactants}}]$$

The greater the disorder of molecules in a system, the higher is the entropy. The entropy change, ΔS between any two states is given by the equation,

$$\Delta S = \left[\frac{q \text{ cal s mol}^{-1}}{T} \right]$$

(q = heat absorbed by the system isothermally and at “ T ” during the state change)

Units of entropy are Joule $K^{-1} M^{-1}$ (or) cal $K^{-1} M^{-1}$.

Spontaneity in terms of entropy change:

- 1) For a spontaneous process in an isolated system, the change in entropy is positive, i.e., $\Delta S > 0$.
- 2) If a system is not isolated, the entropy changes of both the system and surroundings are to be taken into account because system and surroundings together constitute the system. Thus, the total entropy change (ΔS_{total}) is the sum of the changes in entropy of the system (ΔS_{system}) and the surroundings ($\Delta S_{\text{surroundings}}$).

$$\Delta S_{\text{total}} = [\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}]$$

For a spontaneous process, ΔS_{total} must be positive, i.e.,

$$\Delta S_{\text{total}} = [\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}] > 0.$$

ΔS_{total} is also termed as $\Delta S_{\text{universe}}$

At equilibrium for an isolated system, $\Delta S = 0$.

For a non-spontaneous process, ΔS_{total} is negative, i.e., $\Delta S_{\text{total}} < 0$.

Gibbs Free energy (G):

It is defined as “the thermodynamic quantity of the system, the decrease in whose value during a process is equal to useful work done by the system.”

$$\Delta G = W_{\text{system}}$$

$$G = H - TS \longrightarrow (1)$$

Where, H = enthalpy, T = absolute temperature, S = entropy

$$\text{We know that, } H = [E + PV] \longrightarrow (2)$$

From equations (1) and (2)

$$G = [E + PV - TS]$$

Free energy change, at constant temperature and pressure, can be given as

$$\Delta G = [\Delta E + P\Delta V - T\Delta S]$$

$$\Delta G = \Delta H - T\Delta S \longrightarrow (3)$$

(Gibbs – Helmholtz equation)

$$\text{Since } \Delta H = [\Delta E + P\Delta V]$$

Gibbs – Helmholtz equation is used to discuss the driving force, i.e., the overall criterion of spontaneity.

Free energy change and spontaneity:

Let us consider a system which is not isolated from its surroundings. In this case, total entropy change can be calculated as,

$$\Delta S_{\text{total}} = [\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}] \longrightarrow (1)$$

Let us consider a process at constant temperature and pressure. Let q_p amount of heat be given by the system to the surroundings.

$$(q_p)_{\text{surroundings}} = (-q_p)_{\text{system}} = -\Delta H_{\text{system}}$$

$$\Delta S_{\text{surroundings}} = \frac{(q_p)_{\text{surroundings}}}{T} = \frac{-\Delta H_{\text{system}}}{T} \longrightarrow (2)$$

From (1) and (2)

$$\Delta S_{\text{total}} = \left[\Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T} \right]$$

$$T \Delta S_{\text{total}} = [T\Delta S_{\text{system}} - \Delta H_{\text{system}}]$$

$$-T \Delta S_{\text{total}} = [\Delta H_{\text{system}} - T\Delta S_{\text{system}}]$$

According to Gibbs-Helmholtz equation

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

$$\text{Therefore } \Delta G_{\text{system}} = -T\Delta S$$

For spontaneous process $\Delta S > 0$

Hence $\Delta G = \text{-ve}$ for spontaneous process

For spontaneous process $T\Delta S_{\text{total}}$ should be positive or ΔG should be negative.

Conclusions from the above are

ΔG_{system} = negative for spontaneous reaction ($\Delta G < 0$)

ΔG_{system} = positive for non-spontaneous reaction ($\Delta G > 0$)

ΔG_{system} = zero for equilibrium reaction ($\Delta G = 0$)

Important formulas in Thermodynamics:

First law of thermodynamics:

$$\Delta E = q + w \text{ (Where } w = \text{work done on the system).}$$

$$\Delta E = q - w \text{ (Where } w = \text{work done by the system)}$$

Pressure – volume work:

$$w = -P_{ext} \Delta V \text{ (Where } w = \text{work done by the system)}$$

$$w = P_{ext} \Delta V \text{ (Where } w = \text{work done on the system)}$$

Entropy change:

$$\Delta S = \left[\frac{q \text{ cals mol}^{-1}}{T} \right]$$

$$\Delta S_{\text{total}} = [\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}]$$

Enthalpy:

$$\text{Enthalpy: } H = E + PV$$

$$\text{Change in enthalpy: } \Delta H = \Delta E + P\Delta V$$

$$\text{Gibbs free energy: } G = H - TS$$

$$\text{Gibbs – Helmholtz equation: } \Delta G = \Delta H - T\Delta S$$

Chemical Equilibrium

The state of equilibrium is a state in which the measurable properties of the system do not undergo any noticeable change under a particular set of conditions.

Chemical reactions can be classified as irreversible and reversible reactions:

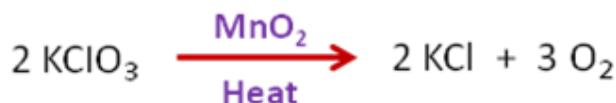
Irreversible reactions:

The chemical reactions which proceed in such a way that reactants are completely converted into products, i.e. the reactions which move in one direction, i.e. forward direction only are called irreversible reactions. In such reactions, products do not react together to produce reactants again, i.e. the reaction does not move in backward direction.

Ex:



1. Thermal decomposition of potassium chlorate



2. Precipitation reactions

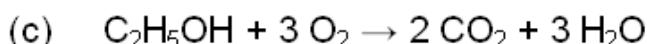
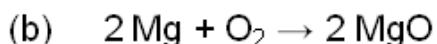


3. Neutralization reactions



Strong acid Strong base

4. Redox and combustion reaction

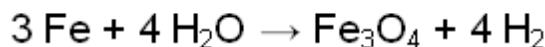


Reversible reactions:

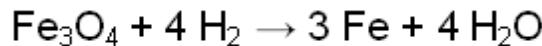
The chemical reactions which take place in both directions under similar conditions are called reversible process. In such reactions, the products also react with each other and produce reactants again.

Ex:

Forward reaction:



Backward reaction



Therefore



Some more examples:



Dynamic natured quilibrium:

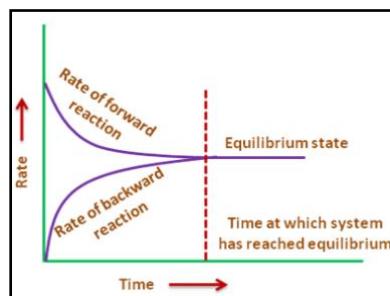
The stage of the reversible reaction at which the concentrations of the reactants and products do not change with time is called the **equilibrium state**.

The most important characteristic property of a reversible reactions is that it always attains state of chemical equilibrium,

Let us consider a general reversible reaction in a closed vessel



In the initial state only A and B are present; both react with each other, i.e rate of forward reaction is maximum as only the concentrations of A and B are involved (at the beginning, the concentrations of products C and D are nil.). As soon as the products C and D are produced, the backward reaction starts functioning. By the expiry of time, the rate of forward reaction decreases as the concentration of A and B decreases while the rate of backward reaction increases as the concentration of products C and D increase. Ultimately, a stage comes when the rate of forward reaction becomes equal to rate of backward reaction. This state is called the **equilibrium state**.



At equilibrium state,

Rate of forward reaction = Rate of backward reaction.

Therefore, chemical equilibrium in a reversible reaction is the state at which both forward and backward reactions or two opposing reactions occur at the same speed.

This state will continue indefinitely if the conditions such as temperature and concentration are not changed. At the state of equilibrium, the concentrations of reactants and products in the reaction mixture attain a constant value and the concentrations do not change with time.

Main characteristics of chemical equilibrium:

- 1) The measurable equilibrium can be attained only if the system is closed. If the system is not closed, some of the products may escape from the container and therefore, the backward reaction will not take place.
Consequently, it will not be possible to attain the equilibrium.
- 2) The measurable properties of the system become constant at equilibrium and remain unchanged with time so long as the external factors remain the same.
- 3) A catalyst does not alter the equilibrium point.
- 4) The equilibrium can be approached from either direction.

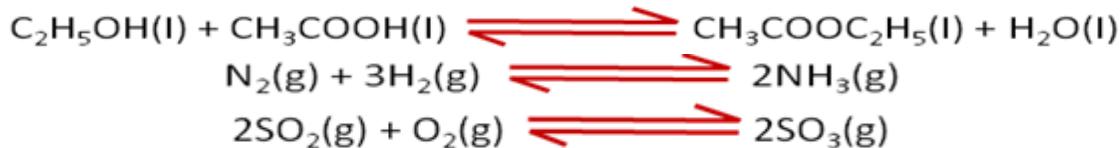
Types of Equilibrium:

The equilibrium between different chemical species present in the same or different phases is called chemical equilibrium. There are two types of chemical equilibrium.

Ex:

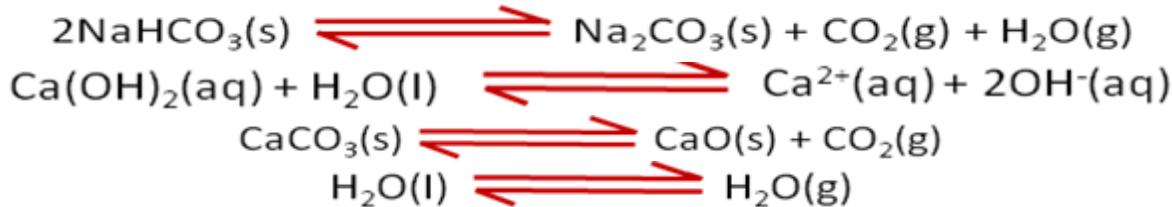
1. Homogeneous equilibrium:

The reactions, in which all the reactants and the products are in the same phase, are called homogeneous equilibrium reactions.



2. Heterogeneous equilibrium:

The reactions, in which all the reactants and the products are in different phase, are called heterogeneous equilibrium reactions.



Equilibrium constant:

Consider a reversible reaction,



Then according to the law of mass action,

Rate of the forward reaction, $r_f = k_f [A]^a [B]^b$

or Rate of the forward reaction, $r_f = k_f [A]^a [B]^b$

Similarly,

Rate of the forward reaction = Rate of the backward reaction

So, at equilibrium

$$k_f [A]^a [B]^b = k_b [C]^c [D]^d$$

$$\frac{k_f}{k_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

But, $\frac{k_f}{k_b}$ = Equilibrium constant, K

$$\text{So, } K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The above equation is the law of chemical equilibrium.

This law states,

'For a reversible reaction at equilibrium, **the ratio of the product of the active masses of the products to the product of the active masses of the reactants each raised to a power equal to the corresponding stoichiometric coefficient in the balanced chemical equation at a constant temperature is constant**. This constant is called equilibrium constant'.

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Further, if the reaction is a homogeneous gas phase reaction then the molar concentration of a substance is directly proportional to its partial pressure 'p' at constant temperature. In that case, the equilibrium constant is expressed in terms of partial pressure of the reactants and products. Such an equilibrium constant is denoted by K_p .

Then similar to the above equation,

$$K_p = \frac{(p_C^c) \times (p_D^d)}{(p_A^a) \times (p_B^b)}$$

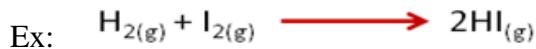
K_c and K_p are different forms of the equilibrium constant of a reaction.

Units of equilibrium constant:

The unit of equilibrium constant (K) of a reaction depends upon the number of moles of the reactants and products involved in the reaction.

Case 1:

When the total number of moles of products is equal to the total number of moles of reactants (except for pure liquids, solids and solvent present in large amounts).



Equilibrium constant is given by,

$$K = \frac{[\text{HI}_{(\text{g})}]^2}{[\text{H}_{2(\text{g})}][\text{I}_{2(\text{g})}]}$$

$$\text{Units of } K = \frac{\left(\frac{\text{mol}}{\text{L}}\right)\left(\frac{\text{mol}}{\text{L}}\right)}{\left(\frac{\text{mol}}{\text{L}}\right)\left(\frac{\text{mol}}{\text{L}}\right)} = \text{No units}$$

Case 2:

When the total number moles of the products is greater than the total number of moles of the reactants (except for pure liquids, solids and the solvent in excess).

Ex:



Equilibrium constant is,

$$K = \frac{[\text{NO}_{2(\text{g})}]^2}{[\text{N}_2\text{O}_{4(\text{g})}]}$$

$$\text{So, Units of } K = \frac{(\text{mol/L})^2}{\frac{\text{mol}}{\text{L}}} = \text{mol/L}$$

For a general reaction



Equilibrium constant is,

$$K = \frac{[\text{X}][\text{Y}][\text{Z}]}{[\text{A}]}$$

$$\text{So, Units of } K = \frac{(\text{mol/L})(\text{mol/L})(\text{mol/L}) \dots \dots}{(\text{mol/L})} = (\text{mol/L})^n$$

Case 3:

When the total number of moles of the products is less than the total number of moles of reactants (except for pure liquids, solids and the solvent in excess).

In such cases, the equilibrium constant has the unit = $(\text{mol/L})^{-n}$

Where, n may be 1, 2,.....

Ex: 1)



Equilibrium constant is,

$$K = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3}$$

So,

$$\text{Unit of } K \text{ is } \frac{(\text{mol/L})^2}{(\text{mol/L})(\text{mol/L})^3} = \frac{1}{(\text{mol/L})^2} = \text{mol/L}^{-2} \text{ or L}^2 \text{ mol}^{-2}$$

2)



Equilibrium constant is,

$$K = \frac{[\text{Fe}(\text{SCN})^{2+}(\text{aq})]}{[\text{Fe}^{3+}(\text{aq})][\text{SCN}^-(\text{aq})]}$$

$$\text{So, Unit of } K \text{ is } \frac{\left(\frac{\text{mol}}{\text{L}}\right)}{\left(\frac{\text{mol}}{\text{L}}\right)\left(\frac{\text{mol}}{\text{L}}\right)} = \frac{1}{\left(\frac{\text{mol}}{\text{L}}\right)^2} = \left(\frac{\text{mol}}{\text{L}}\right)^{-1} \text{ or L mol}^{-1}$$

Therefore from above results

$$n = \{[\text{total number of moles of products}] - [\text{total number of moles of reactants}]\}$$

While counting the number moles, the number of moles of pure liquids, solids and of the solvent in excess are not considered.

The units of equilibrium constant are given by

$$\text{Unit of } K = (\text{mol/L})^n$$

Relationship between K_c and K_p :

In a reaction, $aA + bB = cC + dD$

We can write

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b}$$

Assuming the gaseous components to behave ideally,

$$P_i V_i = n_i RT \quad \text{or} \quad P_i = \frac{n_i}{V_i} RT = C_i RT = [i] RT$$

Where (i) is the molar concentration of the species 'i'.

$$\text{Then } K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} = \frac{[C]^c (RT)^c \times [D]^d (RT)^d}{[A]^a (RT)^a \times [B]^b (RT)^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \times (RT)^{\overline{c+d-a+b}}$$

If $\overline{c+d} - \overline{a+b} = \Delta n$,

$$\Delta n = [(\text{Number of moles of gaseous products}) - (\text{Number of moles of gaseous reactants})]$$

Thus, n is equal to the difference in the number of gaseous moles of products and the number of gaseous moles of reactants, the above equation can be rewritten as

$$K_p = K_c (RT)^{\Delta n}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}}$$

Factors effecting equilibrium:

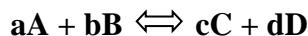
The state of equilibrium of a reversible chemical reaction is mainly influenced by the following factors.

- a) Concentration
- b) Temperature
- c) Pressure
- d) Catalyst

a. Effect of concentration on equilibrium:

If a system is at equilibrium and the concentration of one of the species involved in the reaction is increased, the system will readjust so as to decrease the concentration of that species. Thus, the reaction will proceed in such a manner so as to consume some of the increased concentration. Similarly if the concentration of some substance is decreased, the reaction will proceed so as to make up the loss in the concentration.

To illustrate this, let us consider the reaction



At equilibrium, the concentration of A, B, C and D are constant. If at equilibrium a small amount of the substance 'A' is added to this reaction, then according to the Le Chatelier's principle, the equilibrium shifts in a direction so as to undo the effect of the increased concentration of 'A'. In other words the reaction proceeds in the direction, which decreases the concentration of 'A'. Thus, with an increase in the concentration of any one of the

reactants such as 'A', the equilibrium will shift towards right, (products side) by making more 'A' to react with B, to form more products.

On the other hand, when the concentration of C (or any other product) is increased, the reaction will shift towards left (reactants side).

Increase in the conc. of any of the 'reactants'	 Shifts the equilibrium towards	Forward direction
Decrease in the conc. of any of the 'reactants'	 Shifts the equilibrium towards	Backward direction
Increase in the conc. of any of the 'products'	 Shifts the equilibrium towards	Backward direction
Decrease in the conc. of any of the 'products'	 Shifts the equilibrium towards	Forward direction

Thus, according to Le Chatelier's principle in general, an increase in the concentration of any of the substances on one side of the equilibrium shifts the equilibrium to produce more of the substances on the other side of it.

Factor	Reactant	Direction in which equilibrium shifted	product	Direction in which equilibrium shifted
concentration	Increase	Forward	Increase	Backward
	Decrease	Backward	Decrease	Forward

b. Effect of temperature on equilibrium:

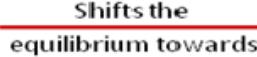
According to the Le Chatelier's principle, when the temperature is raised or heat is supplied to a system in equilibrium, the system should move in a direction so that the added heat is absorbed. Thus, an increase in the temperature of a chemical system at equilibrium, favours an endothermic reaction i.e., a reaction that proceeds with the absorption of heat.

On the other hand, if temperature of the system is decreased under constant pressure and volume conditions, the equilibrium will shift in such a way so as to produce some heat. A decrease in the temperature of a system at equilibrium, favours an exothermic reaction i.e., the reaction, which proceeds with the evolution of heat.

Ex:



Increase in temperature  Shifts the equilibrium towards

Increase in temperature  Shifts the equilibrium towards

Decrease in temperature $\xrightarrow{\text{Shifts the equilibrium towards}}$ Forward direction

Decrease in temperature $\xrightarrow{\text{Shifts the equilibrium towards}}$ Backward direction

Factor	Exothermic	Direction in which equilibrium shifted	Endothermic	Direction in which equilibrium shifted
temperature	Increase	Backward	Increase	Forward
	Decrease	Forward	Decrease	Backward

c. Effect of pressure on equilibrium:

The effect of pressure has no significant effect on the following equilibrium.

- The equilibrium involving only solids are not affected by a change of pressure. Because no change in volume results due to change in pressure in solids.
- The equilibrium involving liquids and/or gases, where the number of molecules before and after the attainment of equilibrium remain the same, (where $n = 0$), the reactions are not affected by a change of pressure

Examples:



1mol 1mol 2 mol (No change in the number of moles of gaseous substances)



1mol 1mol 2 mol (No change in the number of moles of gaseous substances)

Where $n = 0$

- In gaseous reactions where there is a change in the number of molecules in going from reactants to products or vice-versa, pressure plays an important role.

Ex:



1mol 2 mol ($\Delta n = + 1$) (Number of moles increases)



1mol 3mol 2 mol ($\Delta n = - 2$ Number of moles decreases)

Therefore,

Increase in pressure **Shifts the equilibrium towards** Decrease in volume
 (lesser number of gaseous molecules)

Factor	Increase in pressure	Direction in which equilibrium shifted	Decrease in pressure	Direction in which equilibrium shifted
Pressure	No. of moles of reactants = No. of moles of products	No shift	No. of moles of reactants = No. of moles of products	No shift
	No. of moles of reactants > products	Forward	No. of moles of reactants > products	Backward
	No. of moles of reactants < products	Backward	No. of moles of reactants < products	Forward

d. Effect of catalyst on equilibrium:

Catalyst has no effect upon the equilibrium state of the reactants and products. In fact, a catalyst accelerates the forward and backward reactions to the same extent and therefore simply helps in the attainment of the equilibrium state faster.

Le Chatelier's principle:

It is stated as '**If a system at equilibrium is subjected to a change in one or more variables such as, pressure, temperature and/or concentration, then the equilibrium shifts in such a way so as to undo the effect of the change**'.

The Le Chatelier's principle is also called the principle of mobile equilibrium'. It is very useful in predicting qualitatively, the effect of change in the reaction variables on a system at equilibrium.

Application of Le Chatelier's principle

Liquid – vapour system

Equilibrium between a liquid and its vapours can be represented by the equation.



The effect of change in temperature and pressure on this equilibrium is as follows.

An increase in pressure on a system where a liquid – vapour equilibrium exists:

According to the Le Chatelier's principle, this will make the system move in a direction of lower volume. An increase in pressure on the system will result in the condensation of vapours to give liquid, since, liquids have lower volume as compared to vapours. The equilibrium will shift towards left. On the other hand, if the pressure is decreased, more and more liquid will get converted into vapours.

The effect of increase in temperature where a liquid – vapour equilibrium exists:

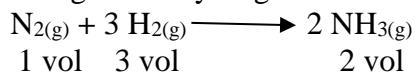
According to the Le Chatelier's principles, this will make the reaction move in a direction which absorbs heat i.e., the endothermic process will be favored. As vaporization (liquid - vapours) is an endothermic process, a rise in temperature will favour the process of vaporization i.e. more liquid would get converted into vapours.

As a result of these effects an increase in temperature and decrease in pressure, shall favor this process **Liquid \rightleftharpoons Vapour** to proceed in the forward direction.

Ex: During the preparation of carbonated drinks such as Cola or beer, a large amount of CO₂ is dissolved in the solution under high pressure. When these bottles are opened, the pressure decreases and the dissolved CO₂ escape out.

Manufacture of Ammonia (NH₃) (Haber's Process):

Ammonia can be synthesized by nitrogen and hydrogen in accordance with the reaction.



The equilibrium constant of this reaction may be written as,

$$K_c = \frac{[\text{NH}_{3(\text{g})}]^2}{[\text{N}_{2(\text{g})}][\text{H}_{2(\text{g})}]^3} \text{ or } K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

The characteristics of the reaction are:

Firstly, the reaction proceeds with a decrease in volume. Therefore, an increase in pressure should favor the forward reaction. The equilibrium between nitrogen, hydrogen and ammonia at 200 °C has been studied at different pressures and the following data has been obtained.

Pressure/atom	1	100	300	1000
NH ₃ (%)	15.3	81.5	90.0	99.3

The most favorable pressure range for the production of ammonia is found to be 200 – 900 atm.

Secondly, the reaction is exothermic; therefore the Le Chatelier's principle predicts lower temperature to be favourable for the forward reaction.

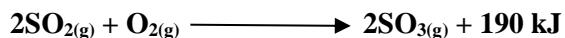
Temp./°C	200	400	600	700
NH ₃ (%)	90.0	47.7	13.8	7.3

Since at low temperature, the reactions tend to be slow due to kinetic effects, an optimum temperature (450 °C) should give the most favorable results.

Thirdly, the use of a suitable catalyst should accelerate the reaction in the forward direction. The catalyst used is iron.

Manufacture of Sulphur trioxide (SO₃) (Contact process):

During the manufacture of sulphuric acid (contact process), SO₃ is prepared by the oxidation of SO₂ in accordance with the reaction,



This reaction proceeds with a decrease in volume. Therefore, high pressure will favor the forward reaction.

Secondly, the reaction is exothermic, hence low temperature will be favorable for higher yield.

Thirdly, if the reaction is carried out under excess of oxygen, the equilibrium shifts in a direction so as to give larger amount of SO₃, due to the effect of increased concentration of one of the reactants. The optimum conditions for the reaction between SO_{2(g)} and O_{2(g)} are: a pressure of 1.5 – 1.7 atm and temperature 420 °C – 450 °C.

Q) Write the relationship between K_p and K_c for the following reactions.



Acids & Bases

- Acids are taste sour, corrosive to metals, change blue litmus to red and become lose acidic nature when mixed with bases.
- Bases feel slippery, change red litmus to blue and become lose basic nature when mixed with acids.

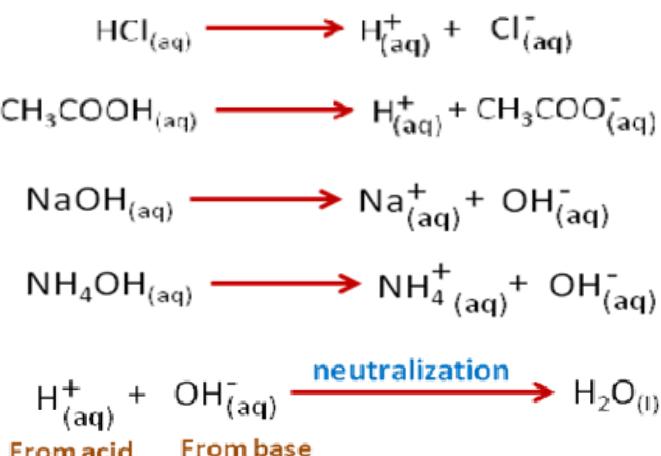
Several theories were proposed to explain the acids and bases.

1. Arrhenius concept of acids and bases:

According to this theory,

An acid is a hydrogen-containing compound, which gives free hydrogen ions (H^+) when dissolved in water. i.e., in aqueous solutions.

A base is a hydroxyl group containing compound which gives free hydroxyl ions (OH^-) when dissolved in water i.e., in aqueous solutions.



Limitations:

- This concept is only applicable to the acid – base behavior in the aqueous medium. It does not provide any explanation to the acid - base behavior in the absence of water.
- This concept defines acids and bases as compounds containing hydrogen and hydroxyl groups respectively.
- However, there are many compounds, which act as an acids even when there is no hydrogen.



Similarly there are many bases, which do not contain hydroxyl group.

Ex:



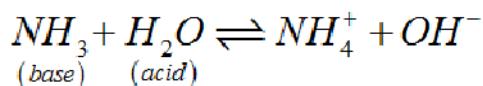
2. Bronsted-Lowry concept (the proton donor-acceptor concept):

According to this theory,

An acid is a substance (molecule or ion) that can donate protons, i.e., a hydrogen ion, H^+ , to some other substance and a base is a substance (molecule or ion) that can accept a proton from an acid.

In short, an acid is a proton donor and a base is a proton acceptor.

Ex:



When an acid loses one proton, the residual part of it has a tendency to regain a proton. Therefore, it behaves as a base



The acid and base which differ by one proton are known as a conjugate pair or conjugate acid-base pair.



The acid base pairs are



The reaction can be written as



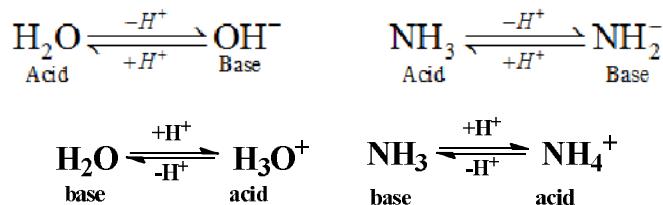
Thus according to this theory, every acid has its conjugate base and every base has its conjugate acid. It is further observed that strong acids have weak conjugate bases while weak acids have strong conjugate bases.



Reactants			Products			
Acid 1	Base 2	\rightleftharpoons	Acid 2	Base 1	Conjugate pair 1	Conjugate pair 2
H ₂ O	NH ₃		NH ₄ ⁺	OH ⁻	H ₂ O; OH ⁻	NH ₄ ⁺ ; NH ₃
HCN	H ₂ O		H ₃ O ⁺	CN ⁻	HCN; CN ⁻	H ₃ O ⁺ ; H ₂ O
HF	CH ₃ COOH		CH ₃ COOH ₂ ⁺	F ⁻	HF; F ⁻	CH ₃ COOH ₂ ⁺ ; CH ₃ COOH
CH ₃ COOH	NH ₃		NH ₄ ⁺	CH ₃ COO ⁻	CH ₃ COOH; CH ₃ COO ⁻	NH ₄ ⁺ ; NH ₃
NH ₃	NH ₃		NH ₄ ⁺	NH ₂ ⁻	NH ₃ ; NH ₂ ⁻	NH ₄ ⁺ ; NH ₃
H ₂ O	H ₂ O		H ₃ O ⁺	OH ⁻	H ₂ O; OH ⁻	H ₃ O ⁺ ; H ₂ O
HCO₃⁻	H ₂ O		H ₃ O ⁺	CO ₃ ²⁻	HCO₃⁻ ; CO ₃ ²⁻	H ₃ O ⁺ ; H ₂ O
NH₄⁺	H ₂ O		H ₃ O	NH ₃	NH₄⁺ ; NH ₃	H ₃ O; H ₂ O

There are certain molecules which can have dual character of an acid and a base. These are called amphiprotic or amphoteric.

Ex: NH₃, H₂O, CH₃COOH etc.



The strength of an acid depends upon its tendency to lose its proton and the strength of the base depends upon its tendency to gain the proton

In aqueous solutions, the strength of all those acids which are stronger than H₃O⁺ tends to have identical values. This tendency may change in different solvents. Similarly bases stronger than OH⁻ in aqueous solutions have almost identical strengths. This influence of the solvent is known as leveling effect.

Acid	Conjugate base
HClO_4 (Perchloric acid)	ClO_4^- (Perchlorate ion)
H_2SO_4 (Sulphuric acid)	HSO_4^- (Hydrogen sulphate ion)
HCl (Hydrogen chloride)	Cl^- (Chloride ion)
HNO_3 (Nitric acid)	NO_3^- (Nitrate ion)
H_3O^+ (Hydronium ion)	H_2O (Water)
HSO_4^- (Hydrogen sulphate ion)	SO_4^{2-} (Sulphate ion)
H_3PO_4 (Ortho – phosphoric acid)	H_2PO_4^- (Dihydrogen phosphate ion)
CH_3COOH (Acetic acid)	CH_3COO^- (Acetate ion)
H_2CO_3 (Carbonic acid)	HCO_3^- (Hydrogen carbonate ion)
H_2S (Hydrogen sulphide)	HS^- (Hydrosulphide ion)
NH_4^+ (Ammonium ion)	NH_3 (Ammonia)
HCN (Hydrogen cyanide)	CN^- (Cyanide ion)
$\text{C}_6\text{H}_5\text{OH}$ (Phenol)	$\text{C}_6\text{H}_5\text{O}^-$ (Phenoxyde ion)
H_2O (Water)	OH^- (Hydroxide ion)
$\text{C}_2\text{H}_5\text{OH}$ (Ethyl alcohol)	$\text{C}_2\text{H}_5\text{O}^-$ (Ethoxide ion)
NH_3 (Ammonia)	NH_2^- (Amide ion)
CH_4 (Methane)	CH_3^- (Methide ion)

Increasing order of acid strength

Increasing order of basic strength

The strength of an acid also depends upon the solvent. The acids HClO_4 , H_2SO_4 , HCl and HNO_3 which have nearly the same strength in water will be in the order of $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$ in acetic acid, since, the proton accepting tendency of acetic acid is much weaker than water. So, the real strength of acids can be judged by solvents.

On the basis of proton interaction, solvents can be classified into 4 types.

a. Protophilic solvents:

Solvents having greater tendency to accept protons than to donate are called protophilic solvents i.e., water, alcohol, liquid ammonia etc.

b. Protogenic solvents:

Solvents having the tendency to produce protons than to accept are called protogenic solvents i.e., water, liquid HCl, glacial CH_3COOH etc.

c. Amphiprotic solvents:

Solvents which act both as protophilic or protogenic, e.g., H_2O , NH_3 and $\text{C}_2\text{H}_5\text{OH}$ etc.

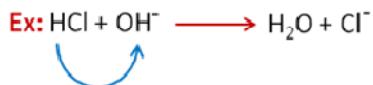
d. Aprotic solvents:

Solvents which neither donate nor accept protons, e.g., benzene (C_6H_6), carbon tetrachloride (CCl_4), carbon disulphide (CS_2) etc.

HCl acts as acid in H₂O, stronger acid in NH₃, weak acid in CH₃COOH, neutral in C₆H₆ and a weak base in HF.



A reaction in which proton transfer takes place from an acid to a base is known as neutralization



3. Lewis concept of acids and bases

According to this theory,

An acid is any species which can accept a pair of electrons forming coordinate bond and a base is a species, which can donate a pair of electrons towards the formation of a coordinate covalent bond. Thus, a Lewis acid is an electrophile, and a Lewis base is a nucleophile.

Ex:



Lewis acids:

- a. All molecules possessing an atom with incomplete octet of electrons or Lewis acids.

Ex: BF₃, AlCl₃.

- b. All cations are Lewis acids.

Ex: Ag⁺, Cu²⁺, Fe³⁺ etc. are Lewis acids.

- c. All molecules in which the central atom can acquire more than eight valence electrons.
i.e., expand its octet.

Ex: SiCl₄, SiF₄ etc., are Lewis acids.

- d. Molecules with multiple bonds between atoms of different electronegativities.

Ex: CO₂, SO₂ etc. are Lewis acids.



Lewis bases:

- a. All anions are Lewis bases e.g., OH⁻, CN⁻, CH₃COO⁻ etc.
- b. All molecules having lone pairs of electrons

Ex: NH₃, H₂O, CO and amines etc. are Lewis bases.

It may be noted that all Bronsted bases are also Lewis bases, but all Bronsted acids are not Lewis acids.

Lewis Acid-Base Reaction:

Whenever a Lewis acid reacts with a Lewis base, a coordinate covalent bond is formed.

Ex:



Limitations:

- a. It fails to account for the relative strength of acids and bases, as it is not based on ionization.
- b. An acid-base reaction being an electron-transfer reaction, should be quite fast. However, many Lewis acid-base reactions are slow.

Ionic equilibrium:

Ionic equilibrium is a condition at which the rate of dissociation of unionized molecules is equal to the rate of combination of the ions.

Ex:

Electrolytes: The compounds which give ions either in the molten state or in solution are called electrolytes. In the solid state they may be bad conductors, but they become good conductors either in the molten state or in aqueous or a polar solvent solution.

There are 2 types of electrolytes

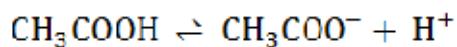
1. **Strong electrolytes:** These are totally ionized when dissolved in a polar medium like water and they act as good conductors of electricity.

Ex: HNO₃, NaOH, KOH, HCl etc. their degrees of ionization are high and almost unity.

2. **Weak electrolytes:** These are ionized to negligible extent when dissolved in polar solvents like water and they act as poor conductors of electricity.

Ex: CH₃COOH, NH₄OH, H₃PO₄, H₃BO₃ etc.

Equilibrium between ions and unionized molecules is established in solution



Concept of pH

pH: It is defined as the negative logarithm of hydrogen ion concentration to the base 10.

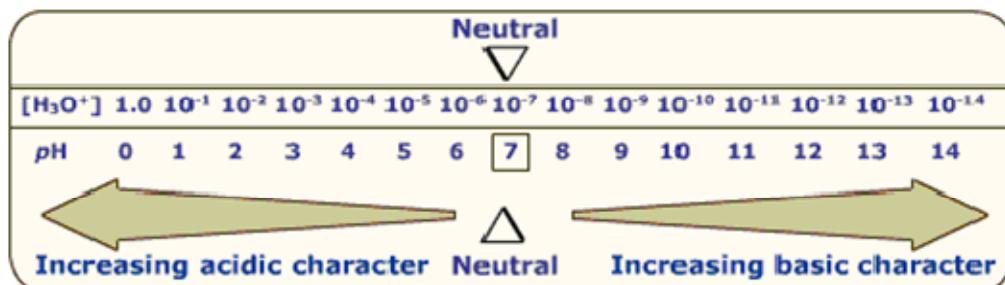
$$\text{pH} = -\log[\text{H}^+]$$

The pH scale has a range from 0 to 14 in aqueous solutions.

For acidic solutions $\text{pH} < 7$

For basic solutions $\text{pH} > 7$

For neutral solutions $\text{pH} = 7$



pH between 0 to 2 are strongly acidic

pH between 2 to 4 are moderately acidic

pH between 4 to 7 are weakly acidic

pH between 7 to 10 are weakly basic

pH between 10 to 12 are moderately basic

pH between 12 to 14 are strongly basic.

$[\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14}$ in aqueous solutions

$\text{pH} + \text{pOH} = 14.0$ in all aqueous solutions

Problems

1) What is the pH of the following solution?

- a. 10^{-3} M HCl
- b. 0.0001 M NaOH
- c. 0.0001 M H_2SO_4

2) Calculate the pH of the following solutions assuming complete dissociation

- a. 0.365 g L⁻¹ HCl solution
- b. 0.001 M Ba(OH)₂ solution

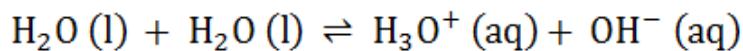
P5.Q) What is the pH of a solution containing 0.63g of HNO₃ in 100ml of solution

P6.Q) Find the pOH and pH of 0.2N Ba(OH)₂

P7.Q) Calculate the pH of an aqueous solution having 2g of NaOH per 500ml of it

Ionic product of water:

Pure water being a weak electrolyte undergoes self ionization to a small extent as follows:



$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

The equilibrium constant for this reaction is:

The concentration of unionized water, [H₂O], is taken as constant because the degree of ionization of water is very small. So we can write this equation as:

$$K \times [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\text{or } K \times \text{constant} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\text{i.e. } K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (\text{Where } K_w = K. \text{ constant})$$

Where K_w is a constant and is known as the **ionic product of water** whose value is **1.008 × 10⁻¹⁴ mol² L⁻²** at 298 K. In pure water the concentration of H₃O⁺ and OH⁻ are equal and so we can write,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

If, $K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1.008 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$ then, _____ (1)

$$[\text{H}_3\text{O}^+] [\text{OH}^-] = 1.008 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+]^2 = 1.008 \times 10^{-14} = [\text{OH}^-]^2$$

$$\text{or } [\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{1.008 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ mol L}^{-1}$$

Thus in pure water $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ mol L}^{-1}$ at 298 K

Salt hydrolysis

Pure water is a weak electrolyte and is neutral in nature i.e. H^+ ion concentration is exactly equal to OH^- ion concentration,

$$[\text{H}^+] = [\text{OH}^-]$$

When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic.

When $[\text{H}^+] > [\text{OH}^-]$, the solution becomes acidic and when $[\text{H}^+] < [\text{OH}^-]$, the solution acquires basic nature. This is exactly the change which occurs during the phenomenon known as **Salt Hydrolysis**.

It is defined as “**A reaction which cation or anion or both of a salt react with water to produce acidity or alkalinity in the solution.**”

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations of weak base origin get hydrolyzed. These react with water to produce H^+ ions.

Thus, the solution acquires acidic



In other salts, anions derived from weak acids get hydrolyzed. These react with water to produce OH⁻ ions. Thus, the solution becomes basic.



The process of hydrolysis is actually the reverse of neutralization.



If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both acid and the base are equally strong equally weak the solution is generally neutral in nature.

As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

1. Salt of a strong acid and a weak base
Ex: FeCl₃, CuCl₂, AlCl₃, NH₄Cl, CuSO₄ etc.
2. Salt of a strong base and a weak acid.
Ex: CH₃COONa, NaCN, NaHCO₃, Na₂CO₃ etc.
3. Salt of a weak acid and a weak base.
Ex: CH₃COONH₄, (NH₄)₂CO₃, NH₄HCO₃ etc.
4. Salt of a strong acid and a strong base.
Ex: NaCl, K₂SO₄, NaNO₃, NaBr etc.

Nature of a salt of a strong acid and a weak base:

The solution of such a salt is acidic in nature. The cation of the salt which has come from weak base gets hydrolyzed. It reacts with water to form a weak base and H⁺ ions.



Consider, for example, NH₄Cl. It ionizes in water completely into NH₄⁺ and Cl⁻ ions. NH₄⁺ ions react with water to form a weak base (NH₄OH) and H⁺ ions are present in excess in the solution.



Thus, H⁺ ion concentration increases and the solution becomes acidic.

Salt of weak acid and a strong base:

The solution of such salt is basic in nature. The anion of the salt is hydrolyzed. It reacts with water to form a weak acid and OH⁻ ions.



Ex:

Consider, for example, the salt CH₃COONa. It ionizes in water completely to give CH₃COO⁻ and Na⁺ ions. CH₃COO⁻ ions react with water to form a weak acid, CH₃COOH and OH⁻ ions are released into water.

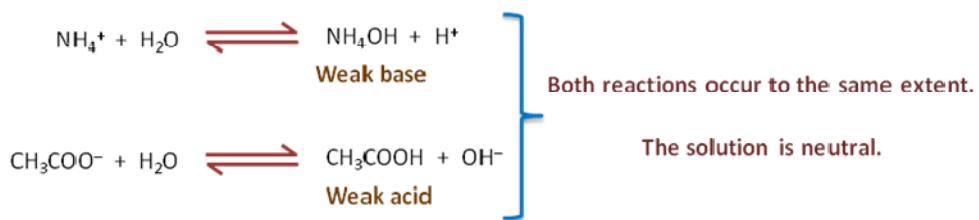
Thus OH⁻ ion concentration increases in the solution. Hence the solution becomes alkaline.



Salt of a weak acid and a weak base:

Maximum hydrolysis occurs in the case of such a salt as both the cation and anion are hydrolyzed and react with water to produce H⁺ and OH⁻. The solution may be neutral alkaline; if the two hydrolysis reactions take place with slightly different rates.

Consider, for example, the salt CH₃COONH₄. It gives CH₃COO⁻ and NH₄⁺ ions in solution. Both react with water.





$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]}$$

Salts of a strong acid and a strong base:

These salts do not hydrolyze. In aqueous solutions they give cations and anions.

Ex: NaCl gives Na^+ and Cl^-

The cations and the anions do not undergo any hydrolysis. Hence there is no change in the concentration of $[\text{H}^+]$ and $[\text{OH}^-]$ and therefore the solution is neutral.

$$\text{i.e. } \text{pH} = 7.0$$

$$[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$$

Hydrolysis at a glance

Salt	NaCl [Strong acid + Strong base]	CH_3COONa [Weak acid + Strong base]	NH_4Cl [Strong acid + Weak base]	$\text{CH}_3\text{COONH}_4$ [Weak acid + Weak base]
Nature	Neutral	Acidic	Basic	*

In case of salt of weak acid and weak base, nature of medium after hydrolysis is decided in the following manner.

- i. If $K_a = K_b$, the medium will be neutral
- ii. If $K_a > K_b$, the medium will be acidic
- iii. If $K_a < K_b$, the medium will be basic

The degree of hydrolysis of a salt of weak acid and weak base is unaffected by dilution because there is no concentration term in the expression of degree of hydrolysis.

Relation between Hydrolysis constant and degree of hydrolysis of a salt of strong acid and a weak base:

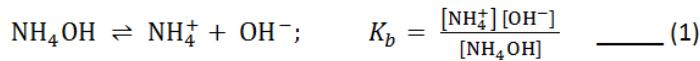
Applying law of mass action.

$$K = \frac{[\text{H}^+][\text{NH}_4\text{OH}]}{[\text{NH}_4^+][\text{H}_2\text{O}]} = \frac{\text{C}_x \text{C}_x}{\text{C}(1-x)} = \frac{x^2 \text{C}}{(1-x)}$$

$$K[\text{H}_2\text{O}] = K_h = \text{hydrolysis constant}$$

$$= \frac{[\text{H}^+] [\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

Where, C is concentration of salt and x the degree of hydrolysis. Other equilibria which exist in solution and the corresponding equilibrium constant are



From (1) and (2)

$$\frac{K_w}{K_b} = \frac{[\text{H}^+] [\text{NH}_4\text{OH}]}{[\text{NH}_4^+]} = K_h \quad (3)$$

Rearranging the equation (3) we get,

$$[\text{H}^+] = \frac{K_w \times [\text{NH}_4^+]}{K_b \times [\text{NH}_4\text{OH}]} = \frac{K_w}{K_b} \cdot \frac{[\text{salt}]}{[\text{base}]}$$

Taking logarithms on both sides

$$\log^{[\text{H}^+]} = \log^{K_w} - \log^{K_b} + \log^{\frac{[\text{salt}]}{[\text{base}]}}$$

i.e. $-P^H = -P^{K_w} + P^{K_b} + \log^{\frac{[\text{salt}]}{[\text{base}]}} \quad (4)$

$$(P^{K_w} - P^H) = P^{K_b} + \log^{\frac{[\text{salt}]}{[\text{base}]}}$$

$\therefore P^{OH} = P^{K_b} + \log^{\frac{[\text{salt}]}{[\text{base}]}} \quad (5)$

The extent to which hydrolysis proceeds is expressed as degree of hydrolysis and is defined as the fraction of the total amount of the salt that is hydrolyzed when the equilibrium has been attained. It is generally expressed as h or x or α .

$$h = \frac{\text{Amount of salt hydrolysed}}{\text{Total salt taken}}$$

Considering again equation (i) and substituting the values of $[\text{H}^+]$; $[\text{NH}_4\text{OH}]$ and $[\text{NH}_4^+]$, we get,

$$K_h = \frac{x^2 C}{(1-x)}$$

Where x is very small $(1-h) \longrightarrow 1$

$$x^2 = K_h(1/C)$$

$$x = \sqrt{\frac{K_h}{C}}$$

$$= \sqrt{\frac{K_w \times C}{K_b \times C}}$$

$$[H^+] = x \times C$$

$$= \sqrt{\frac{K_w \times C}{K_h}}$$

$$\log[H^+] = \frac{1}{2} \log K_w + \frac{1}{2} \log C - \frac{1}{2} \log K_b$$

$$P^H = \frac{1}{2} P^{K_w} - \frac{1}{2} \log C - \frac{1}{2} P^{K_b}$$

$$P^H = \frac{1}{2} [P^{K_w} - P^{K_b} - \log C] \quad \text{_____ (6)}$$

Quantitative values of Hydrolysis at a Glance

Salt	Degree	Hydrolysis constant	P ^H
NaCl [strong acid + strong base]	No hydrolysis	—	7
CH ₃ COONa [Weak acid+ strong base]	$x = \sqrt{\frac{K_w}{C K_a}}$	$K_h = \frac{K_w}{K_a}$	$P^H = \frac{1}{2} [P^{K_w} + P^{K_a} + \log C]$
NH ₄ Cl [strong acid + weak base]	$x = \sqrt{\frac{K_w}{C K_b}}$	$K_h = \frac{K_w}{K_b}$	$P^H = \frac{1}{2} [P^{K_w} - P^{K_b} - \log C]$
CH ₃ COONH ₄ [weak acid +weak base]	$x = \sqrt{\frac{K_w}{K_a \times K_b}}$	$K_h = \frac{K_w}{K_a \times K_b}$	$P^H = \frac{1}{2} [P^{K_w} + P^{K_a} - P^{K_b}]$

Buffer solutions

Certain solutions, such as that of ammonium acetate, have a tendency to resist any change in its hydronium ion concentration or pH, whenever a small amount of a strong acid or a strong base is added to it. This property of a solution is known as buffer action.

Buffer solution:

A solution which resists any change of pH when a small amount of a strong acid or a strong base is added to it, is called a buffer solution or simply as a buffer, alternatively, a buffer solution may be defined as a solution whose pH value does not change appreciably upon the addition of small amounts of a strong acid, base and/or water from outside.

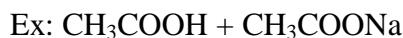
Thus, buffers have reserve acidity and reserve alkalinity.

Buffer solutions usually consist of a mixture of a weak acid and its salt with a strong base e.g., CH₃COOH and CH₃COONa, or that of a weak base and its salt with a strong acid e.g., NH₄OH and NH₄Cl. The solution of any salt of a weak acid and a weak base e.g., ammonium acetate, also shows buffering property.

Types of Buffers:

1) Acid buffer; 2) Basic buffer.

1) **Acid buffer:** A buffer solution containing large amounts of a weak acid and its salt with a strong base is termed as an acid buffer. Such buffer solutions have pH on the acidic nature i.e. pH is less than 7 at 298 K. The pH of an acid buffer is given by the equation.



The pH of the acidic buffer is given by

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Where K_a is the acid dissociation constant of the weak acid.

2) **Basic buffer:** A buffer solution containing relatively large amounts of a weak base and its salt with a strong acid is termed as a basic buffer. Such buffers have pH on the alkaline side i.e., pH is higher than 7 at 298 K.



The pH of the basic buffer is given by

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]} ; pH = 14 - pK_b + \log \frac{[\text{base}]}{[\text{salt}]}$$

Where K_b is the base dissociation constant of the weak base.

These equations are called **Henderson's equation** or **Henderson –Hasselbalen equations**.

Buffer – capacity and Buffer –range:

Buffer capacity:

The property of a buffer solution to resist alteration in its pH value is known as buffer capacity.

It has been found that if the ratio $\frac{[\text{Salt}]}{[\text{Base}]}$ or $\frac{[\text{Salt}]}{[\text{Acid}]}$ is unity, the pH of a particular buffer does not change at all. Buffer capacity is defined quantitatively as “number of moles of acid or base added in one litre of solution so as to change the pH by unity, i.e.”

$$(\phi) = \frac{\text{No.of moles of acid or base added to litre}}{\text{change in pH}}$$

$$\phi = \frac{\partial b}{\partial (\text{pH})}$$

Where ∂b = number of moles of acid or base added to 1 litre solution

$$\partial (\text{pH}) = \text{change in pH}$$

Buffer capacity is maximum

- a. When $[\text{Salt}] = [\text{Acid}]$, i.e. $\text{pH} = \text{pK}_a$ for acid buffer
- b. When $[\text{Salt}] = [\text{Base}]$, i.e. $\text{pOH} = \text{pK}_b$ for base buffer under above conditions, the buffer is called efficient

Buffer range in pH units

Acid buffer: $[\text{pK}_a - 1]$ to $[\text{pK}_a + 1]$

Basic buffer: $[(\text{pK}_w - \text{pK}_b) - 1]$ to $[(\text{pK}_w - \text{pK}_b) + 1]$

Consider acetic acid – sodium acetate buffer, an acid buffer. The acid dissociation constant (K_a) of acetic acid is 1.84×10^{-5} . Therefore, pK_a for acetic acid is 4.74. Then, the buffer range of an acetic acid – sodium acetate buffer is,

$$\text{pH} = (\text{pK}_a) - 1 \text{ to } (\text{pK}_a) + 1$$

$$= (4.74 - 1) \text{ to } (4.74 + 1)$$

$$= 3.74 \text{ to } 5.74$$

Thus, the acetic acid – sodium acetate buffer will act as an effective buffer over the pH range 3.74 to 5.74.

The pH of a buffer solution depends only on the ratio of the concentrations of the salt and the acid, or salt and the base. It does not depend on the individual concentration. Since, the ratio remains the same even when the solution is diluted. However, at higher dilutions, buffers do not remain effective as, they are not able to resist a change in the pH value due to the addition of a strong acid or strong base.

Mechanism of Buffer action:

The buffering action of buffer solutions can be explained in terms of the Bronsted-Lowry concept of acids and bases as follows

Mechanism:

- i. **Action of an acid buffer:** an acid buffer contains relatively large amounts of weak acid (HA) and its salt with a strong base (say NaA). The buffer solution thus contains large concentration of HA and A⁻ (due to the dissociation of the salt), apart from H₃O⁺ and OH⁻.

An addition of small amount of a strong acid causes the reaction,



To proceed in such a direction that an equivalent amount of A combines with to give the same amount of un-dissociated weak acid, HA. Thus, the added acid is picked up by the anions (from the salt) present in large concentrations in the buffer. As long as the added strong acid is in smaller amounts, the changes in the concentrations of salt and that of the weak acid, (HA) are small. Therefore the acid to salt ratio does not change appreciably by the addition of strong acid to the buffer solution. As a result nonnoticeable change is seen in the pH value of the buffer. Addition of a strong base to an acid buffer on the other hand causes the reaction



To proceed in the forward direction, resulting in the formation of an equivalent amount of the salt at the cost of the buffer acid. as long as the added base is in small amounts, the ratio of weak acid to salt remains virtually unchanged. As a result, no observable change in the pH value is seen.

- ii. **Action of basic buffer:** a basic buffer contains a weak base (BOH), and its salt with strong acid (BX). The buffer solution thus contains large amounts of the weak base BOH, and the cation B⁺ (coming from the dissociation of the salt BX), in addition to H₃O⁺ and OH⁻.

The addition of an acid or a base to the basic buffer causes the following reactions:



Proceeds in the forward direction, it is clear that the addition of an acid or base to any buffer solution does cause a change in the concentrations of the buffer acid (or base) and the salt. But, because of the relatively much larger concentrations of these in the buffer solution, for all practical purposes, the ratio, [Salt]/[Acid] or [Salt]/[Base] remains constant. Hence, the pH does not change.

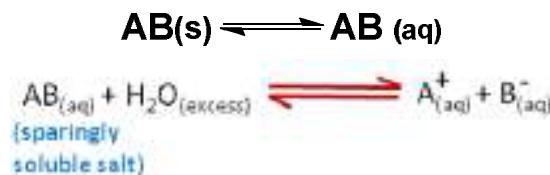
Applications of Buffers:

- a. Buffer solutions are used for comparing calorimetrically the hydrogen ion concentration of unknown solutions.
- b. Acetic acid-sodium acetate is used in the removal of phosphate radical during the qualitative analysis of the mixture.
- c. NaCl/NH₄OH buffer is used for the precipitation of hydroxides of third group basic radicals of qualitative analysis.
- d. In industries, buffer solutions are used in the alcoholic fermentation (pH 5 to 6.5), tanning of leather, electroplating, manufacture of sugar, paper manufacturing etc.
- e. In bacteriological research culture media are generally buffered to maintain the pH required for the growth of the bacterial being studied.

- f. In biological systems buffer system of carbonic acid and sodium bicarbonate is found in our blood. It maintains the pH of blood to a constant value (about 7.4) inspite of various acid and base-producing reactions going on in our body.

Solubility product and common ion effect:

Compounds such as AgCl, AgBr, AgI, BaSO₄ etc., dissolve to a very limited extent to produce ions in the aqueous solution. These sparingly soluble ionic substances (salts) establish an equilibrium between the solid phase and the ions in the solution. For example, for an ionic substance AB. The equilibrium is,



From the above equilibria, an equilibrium characterized by an equilibrium constant K can be given by

$$K = \frac{[\text{A}_{(aq)}^+][\text{B}_{(aq)}^-]}{[\text{AB}_{(s)}]}$$

As the concentration of the solid substance AB remains constant, at a particular temperature, no matter how much solid is in contact with the solution the above equilibrium (between ions and solid substance) can be described by a new constant, i.e.

$$K[\text{AB}(\text{S})] = [\text{A}_{(aq)}^+][\text{B}_{(aq)}^-] = K_{sp}$$

$$K \times \text{constant} = K_{sp} = [\text{A}_{(aq)}^+][\text{B}_{(aq)}^-]$$

K_{sp} is called the solubility product constant or simply as solubility product of the sparingly salt concerned.

For a sparingly soluble ionic salt of the type AB₂ the dissolution leads to the equilibrium



Such an equilibrium may be represented by the solubility product constant (K_{sp}) given by,

$$K_{sp} = [\text{A}_{(aq)}^{2+}][\text{B}_{(aq)}^-]^2$$

Similarly for a salt of the type $A_mB_n(s)$, dissolution leads to the dissociation according to the reaction,



The solubility product constant for the A_mB_n is then expressed as

$$K_{sp} = [A_{(aq)}^{n+}]^m \cdot [B_{(aq)}^{m-}]^n$$

Then, the solubility product constant (K_{sp}) of a sparingly salt is defined as the product of the molar concentrations of the ions in a saturated solution of the sparingly soluble salt, each raised to the power equal to the stoichiometric coefficient of the species, in the balanced equation for ionization.

The K_{sp} values are generally very small, such numbers are expressed in terms of ten raised to certain negative powers. For convenience, the solubility product constants (K_{sp}) can be expressed as pK_{sp} described by, $pK_{sp} = -\log K_{sp}$

Relationship between solubility and solubility product:

1. For a salt of the type AB:

Let the solubility of sparingly soluble salt AB, at a certain temperature, be 'S' moles per litre. Then



Therefore,

$$[A_{(aq)}^+] = S \text{ mol L}^{-1} \text{ and } [B_{(aq)}^-] = S \text{ mol L}^{-1}$$

The solubility product constant is then expressed as,

$$K_{sp} = [A_{(aq)}^+][B_{(aq)}^-] = (S \text{ mol L}^{-1})(S \text{ mol L}^{-1}) = S^2 (\text{mol L}^{-1})^2$$

This gives,

$$S = \sqrt{K_{sp}}$$

Thus, for salts of the type AB (i.e. 1:1 type salt), the solubility of the salt at any temperature is given by

2. For a salt of the type AB_2 :

A salt of AB_2 type (i.e. 1:2 type) dissociates as follows:



If the solubility of AB_2 is $S \text{ mol L}^{-1}$, then

$$[A_{(aq)}^{2+}] = S \text{ mol L}^{-1} \text{ and } [2B_{(aq)}^-] = 2S \text{ mol L}^{-1}$$

$$\text{Then, } K_{sp} = (S) \times (2S)^2$$

$$\text{or } 4S^3 = K_{sp}$$

$$\text{or } S = (K_{sp}/4)^{1/3}$$

Thus, the solubility product of a substance can be calculated if its solubility is known and vice versa. Since the solubility of a substance changes with temperature, K_{sp} also changes with temperature.

Significance of the solubility product, K_{sp}

Applications of solubility product:

1. Solubility product is an important concept that is used in explaining phenomena like solubility and precipitation of compounds in analytical chemistry.
2. **Calculation of solubility:**

Knowing the solubility product of a sparingly soluble salt like AgCl , PbI_2 , BaSO_4 etc. the solubility of the salt can be calculated.

3. **In predication the precipitation in reactions:**

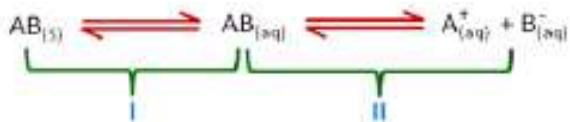
Knowing the solubility of a salt, it is possible to predict whether on mixing the solution of its ions, a precipitate will be formed or not. For precipitation to occur, its ionic product should exceed solubility product. Therefore, to predict the precipitation reaction, we calculate the ionic product of the ions and find out whether it is greater than K_{sp} or not. Thus, if

Ionic product is greater than K_{sp} \longrightarrow precipitation occurs

Ionic product is less than K_{sp} \longrightarrow no precipitation occurs

Common ion effect:

The solubility of an electrolyte (salt, acid, base) in water decreases on addition of a strong electrolyte (acid, base, salt) which has one ion (cation or anion) common with the electrolyte. For example the solubility of NaCl decreases on addition of HCl to solution of NaCl in water. This is because of the two equilibria existing in a saturated solution and because of these two equilibria are dynamic in nature.



If A^+ or B^- is added through another strong electrolyte AX or YB the equilibria I and II shift towards left and hence the extent of ionization and consequently the solubility decreases.

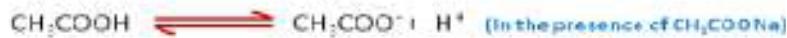
But this phenomenon is more perceptible in the dissociation of weak electrolytes in aqueous solution

For example

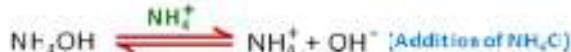
CH_3COOH ionizes in aqueous solution as



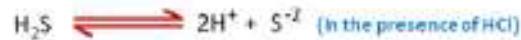
Addition of CH_3COO^- ions (common ion) in the form of sodium acetate diminishes the ionization of acetic acid. This is because of increase of CH_3COO^- ions concentration shifts the equilibrium to the left and more un-dissociated acid is formed



The dissociation of NH_4OH is diminished by the addition of NH_4Cl due to the common ion, NH_4^+ ion



Similarly,



The common ion effect principle is therefore advantageously used in these systematic qualitative analysis of cations. It is also used in the purification of common salt by passing dry HCl gas into impure salt solution.

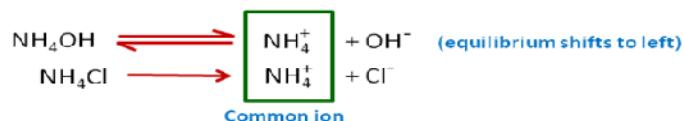
Applications of solubility product and common ion effect:

1. In inorganic qualitative analysis:

The concepts common ion effect play an important role in qualitative analysis for the separation of basic radicals (cations) into different groups.

If solid NH_4Cl is added to the solution, the concentration of NH_4^+ ions increases. According to Le Chatelier's principle, the equilibrium shifts to the left. As a result, the

concentration of OH^- is considerably decreased and the weak base NH_4OH becomes even weaker in the presence of its salt.



III group radical's are precipitated in the presence of low concentrations of OH^- ions as their hydroxides as $\text{Al}(\text{OH})_3$; $\text{Fe}(\text{OH})_3$.

2. Qualitative analysis:

The common ion effect is generally employed in qualitative analysis.

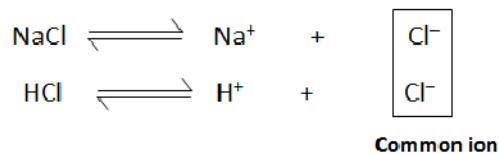
The cations of group II (Hg^{2+} , Pb^{2+} , Bi^{3+} , Cu^{2+} , As^{3+} , Sb^{3+} , Sn^{2+}) are precipitated as their sulphide (such as CuS , PbS) by passing H_2S gas in the presence hydrochloric acid (common H^+ ions).

The cations of group III are precipitated as their hydroxides by NH_4OH in the presence of NH_4Cl .

3. Purification of sodium chloride:

NaCl obtained from sea water or lakes is always impure. It can be purified on the basis of common ion effect described below:

The saturated solution of impure NaCl is prepared by dissolving in minimum quantity of water. HCl gas is then passed through this solution to saturation point. The following are set up:



Due to the presence of common ion (Cl^- ion), the ionic product of NaCl in the solution becomes greater than its K_{sp} . The ionic product of NaCl exceeds its solubility product and it is thrown down as a precipitate.

Organic Chemistry Introduction

Introduction:

- ## ➤ Organic compounds are vital for sustaining life

Ex: DNA, RNA, Cellulose

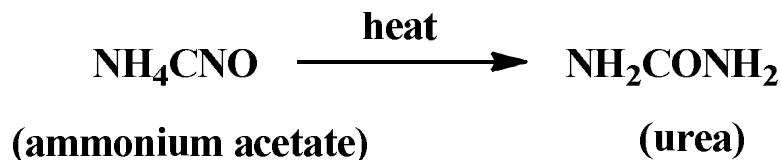
- # ➤ Organic compounds present in materials

Ex: Fuels, Polymers, dyes, medicines and Cloths.

- Organic compounds attained from animals and plants

- ## ➤ Inorganic compounds obtained from minerals

- ## ➤ In 1828, Wohler



Shape of Carbon Compounds

- Carbon valence is 4 and it forms covalent bonds
- Methane (CH_4), Ethene (C_2H_4), Ethyne (C_2H_2)
- sp^3 , sp^2 , sp
- Hybridisation effects the bond length and bond enthalpy
- sp – **50 % s and 50 % p**
- sp^2 – **33.3 % s and 66.6 % p**
- sp^3 - **25 % s and 75 % p**

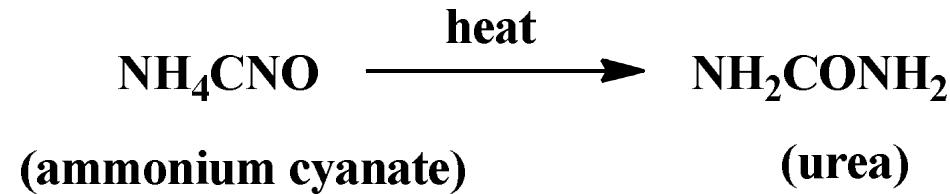
σ , π -bonds

- Overlap along inter nuclear axial overlap or along the z- axis
- Lateral overlapping of p-orbitals

Ex:

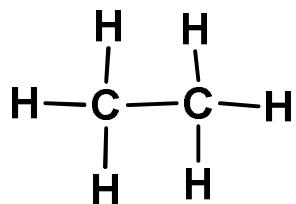
- 1) $\text{CH}_3 - \text{CH}_3$
- 2) $\text{CH}_2 = \text{CH}_2$
- 3) $\text{HC} \equiv \text{CH}$

- ## ➤ In 1828, Wohler

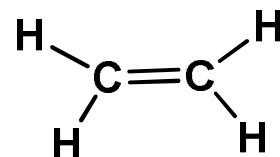


Structural representation of organic compounds

- Complete structural formulas, Condensed structural formulas, Bond-line structural formulas.
- **Complete structural formulas:**



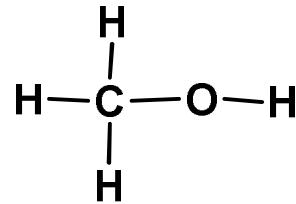
Ethane



Ethene



Etyne



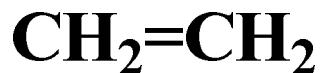
Methanol

Structural representation of organic compounds

➤ Condensed structural formulas:



Ethane



Ethene



Etyne



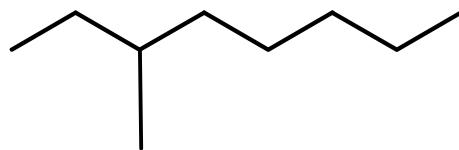
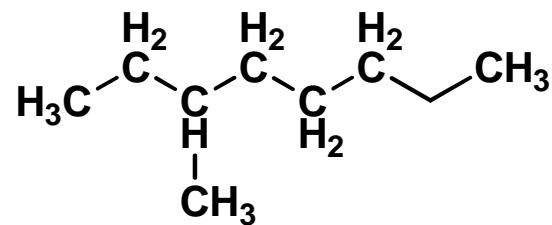
Methanol



Structural representation of organic compounds

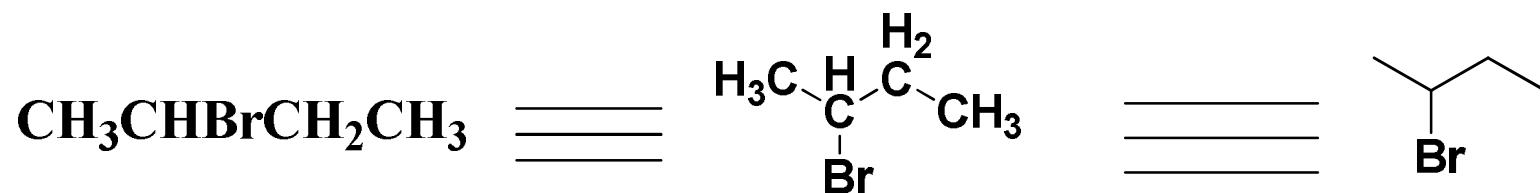
➤ Bond-line structural formulas:

3-methyloctane:

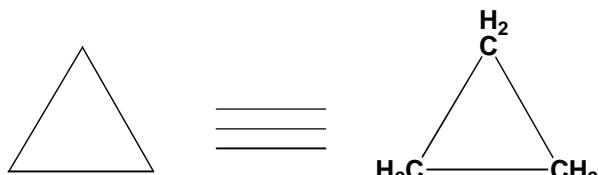


Structural representation of organic compounds

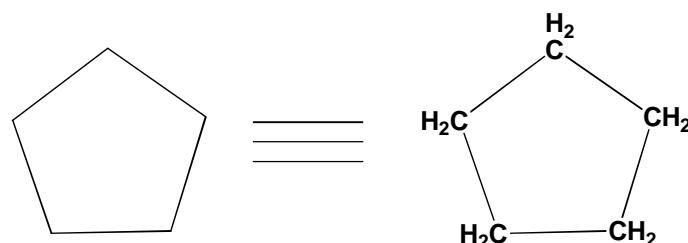
➤ 2-bromobutane



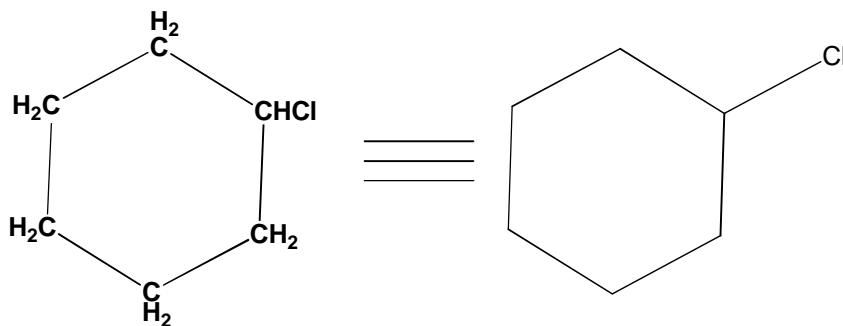
Structural representation of organic compounds



Cyclopropane

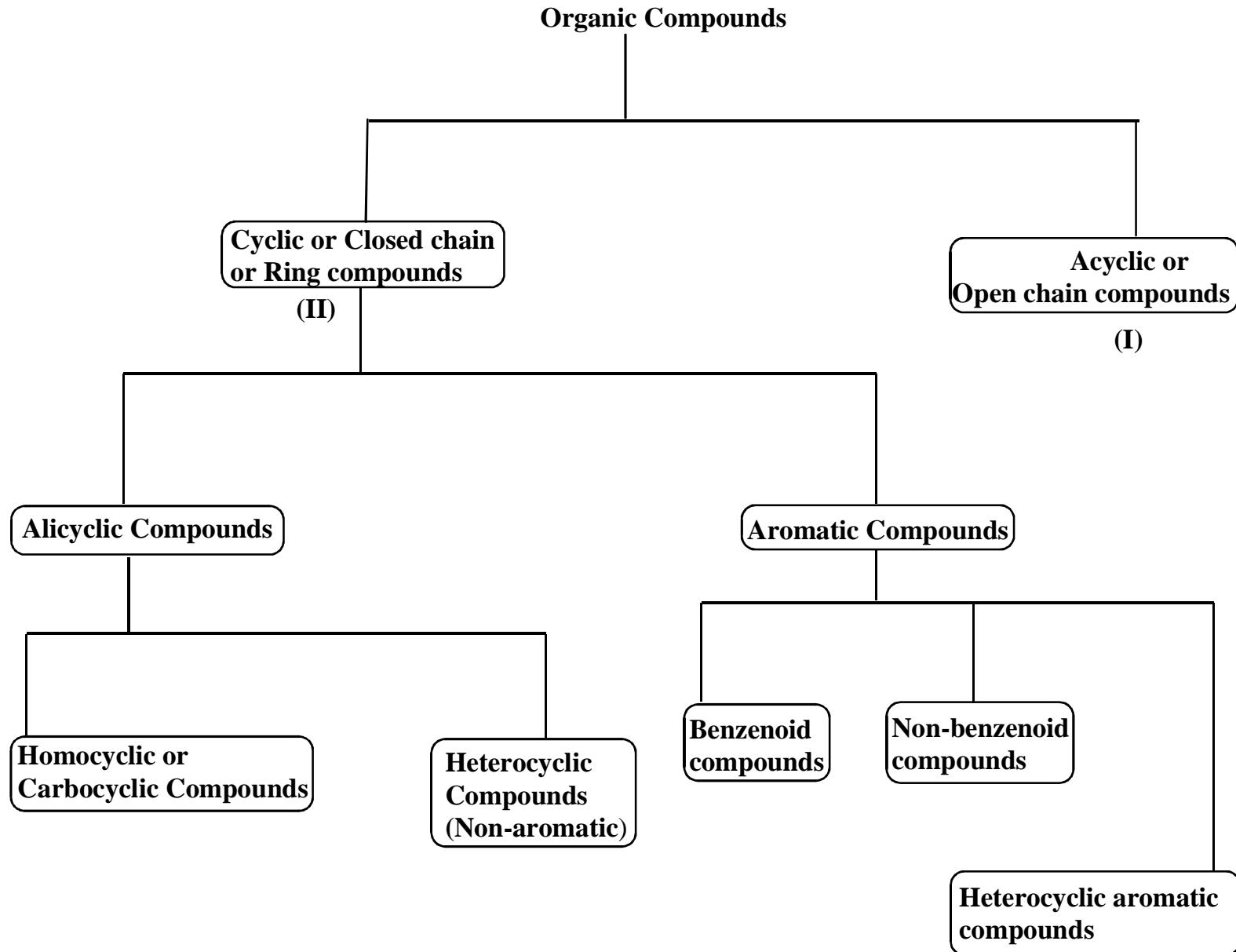


Cyclopentane



chlorocyclohexane

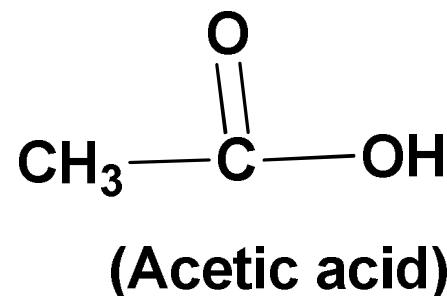
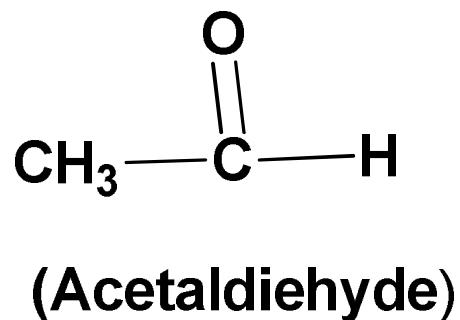
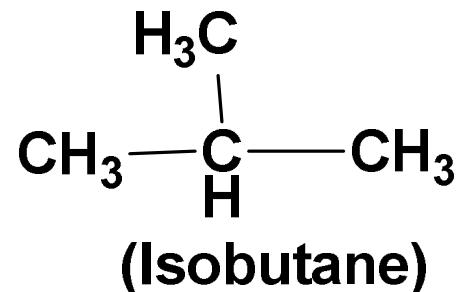
Classification of Organic Compounds



I. Acyclic or Open Chain Compounds

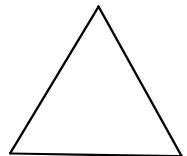
Aliphatic compounds.

Ex:

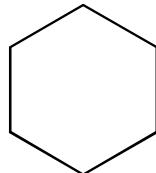


II. Cyclic or Closed chain or Ring Compounds

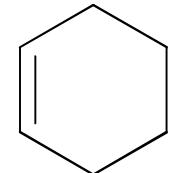
(a) Alicyclic compounds:



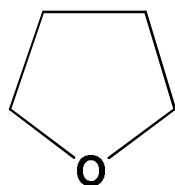
Cyclopropane



Cyclohexane



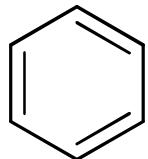
Cyclohexene



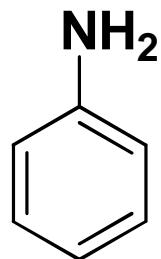
Tetrahydrofuran

II. Cyclic or Closed chain or Ring Compounds

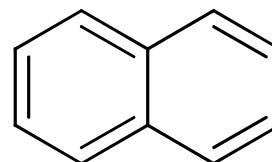
(b) Aromatic compounds:



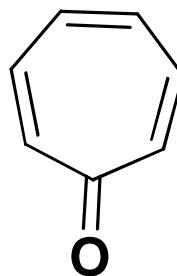
Benzene



Aniline



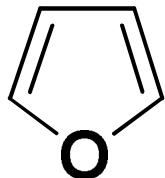
Naphthalene



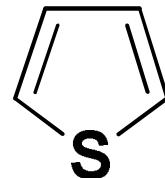
Tropone

II. Cyclic or Closed chain or Ring Compounds

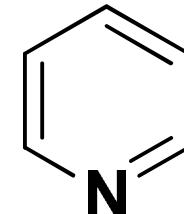
Heterocyclic aromatic compounds



Furan



Thiophene



Pyridine

II. Functional Group

Ex:

hydroxyl group-OH

aldehyde group-CHO

carboxylic acid group-COOH

Homologous Series:

Nomenclature of organic compounds

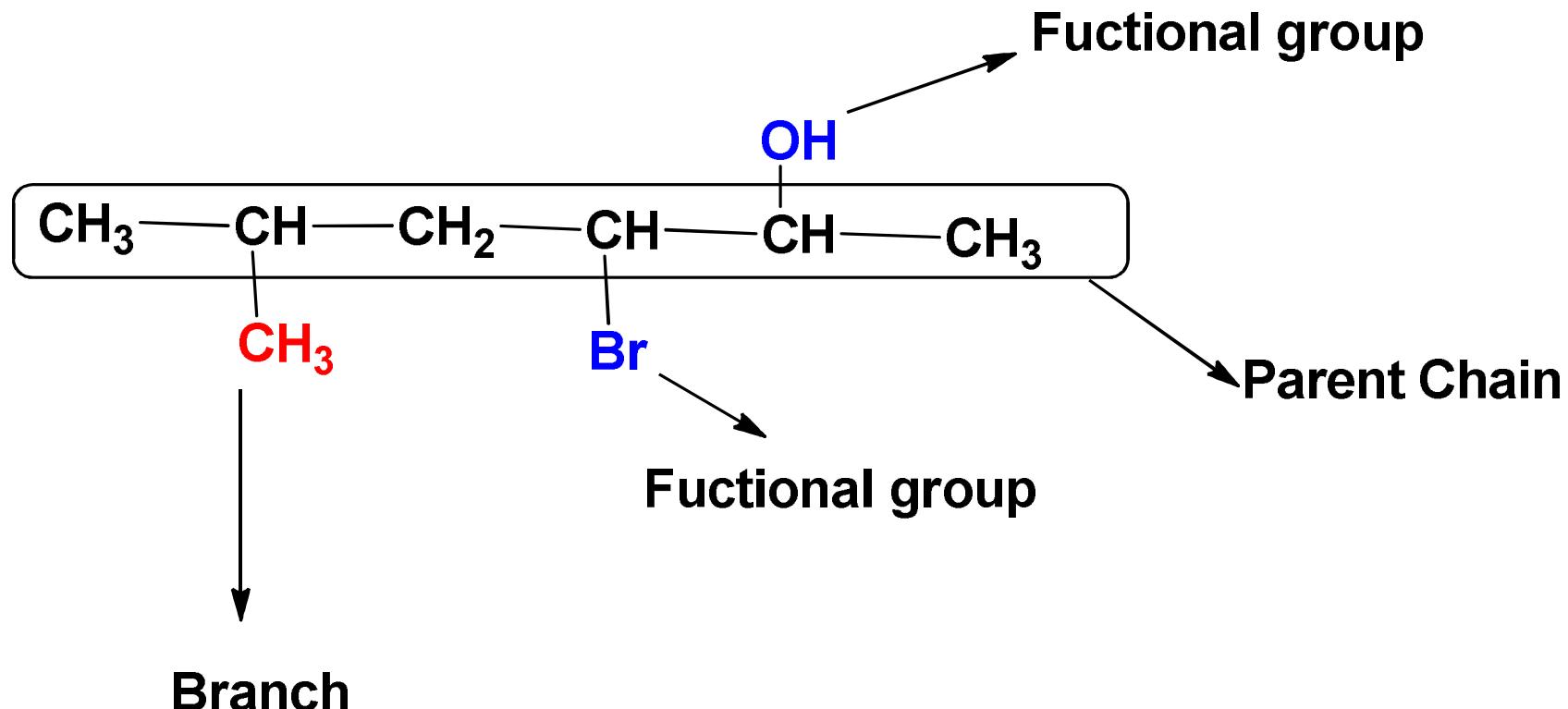
Common or Trivial Names of Some Organic Compounds

Compound	Common names
CH_4	Methane
$\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_3$	n-Butane
$(\text{H}_3\text{C})_2\text{CHCH}_3$	Isobutane
$(\text{CH}_3)_4\text{C}$	Neopentane
$\text{H}_3\text{CCH}_2\text{CH}_2\text{OH}$	n-Propyl alcohol
HCHO	Formaldehyde
$(\text{H}_3\text{C})_2\text{CO}$	Acetone
CHCl_3	Chloroform
CH_3COOH	Acetic acid
C_6H_6	Benzene
$\text{C}_6\text{H}_5\text{OCH}_3$	Anisole
$\text{C}_6\text{H}_5\text{NH}_2$	Aniline
$\text{C}_6\text{H}_5\text{COCH}_3$	Acetophenone
$\text{CH}_3\text{OCH}_2\text{CH}_3$	Ethyl methyl ether

The IUPAC System of Nomenclature

Compounds containing carbon and hydrogen only are called hydrocarbons.

IUPAC = International Union of Pure and Applied Chemistry



The IUPAC System of Nomenclature

No. of C-C bonds

prefix

-C-	meth-
-C-C-	eth-
-C-C-C-	prop-
-C-C-C-C-	but-
-C-C-C-C-C-	pent-
-C-C-C-C-C-C-	hex-
-C-C-C-C-C-C-C-	hept-
-C-C-C-C-C-C-C-C-	oct-
-C-C-C-C-C-C-C-C-C-	non-
-C-C-C-C-C-C-C-C-C-C-	dec-

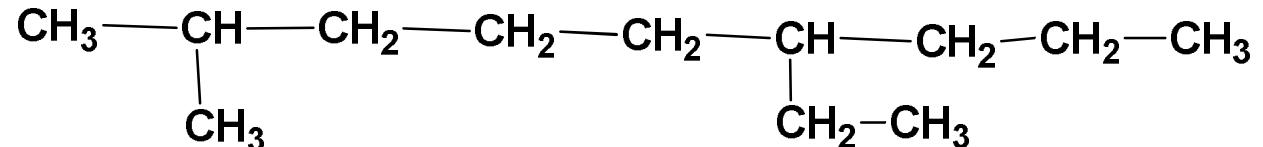
IUPAC Nomenclature of Alkanes

- IUPAC Names of Some Unbranched Saturated Hydrocarbons
- Prefix + suffix = name of the organic compound

Alkane	prefix	suffix	Name
CH_4	meth-	-ane	Methane
$\text{CH}_3\text{-CH}_3$	eth-	-ane	Ethane
$\text{CH}_3\text{-CH}_2\text{-CH}_3$	prop-	-ane	Propane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$	but-	-ane	Butane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	pent-	-ane	Pentane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	hex-	-ane	Hexane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	hept-	-ane	Heptanes
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	oct-	-ane	Octane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	non-	-ane	Nonane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	dec-	-ane	Decane

The IUPAC System of Nomenclature

- Alkyl groups



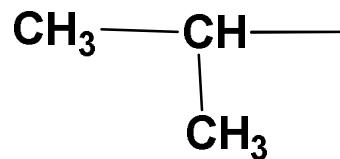
Molecular formula	Name of alkane	Structural formula	Name of alkyl group
CH_4	Methane	$-\text{CH}_3$	Methyl
C_2H_6	Ethane	$-\text{CH}_2\text{CH}_3$	Ethyl
C_3H_8	Propane	$-\text{CH}_2\text{CH}_2\text{CH}_3$	Propyl
C_4H_{10}	Butane	$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Butyl
$\text{C}_{10}\text{H}_{22}$	Decane	$-\text{CH}_2(\text{CH}_2)_8\text{CH}_3$	Decyl

The IUPAC System of Nomenclature

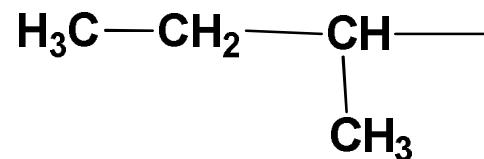
- Abbreviations:
- methyl = Me
- ethyl = Et
- propyl = Pr
- butyl = Bu

The IUPAC System of Nomenclature

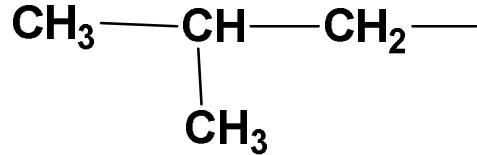
- Branched alkyl groups



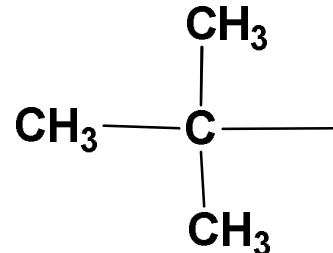
Isopropyl-



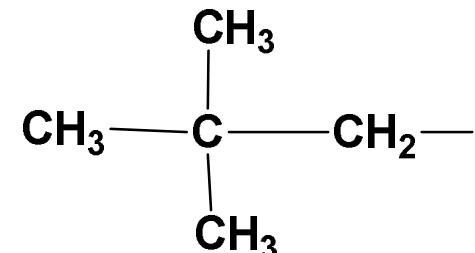
sec-Butyl-



Isobutyl-



tert-butyl-



Neopentyl-

IUPAC Nomenclature of Alkanes

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$ n-butane

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ n-pentane

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ n-hexane

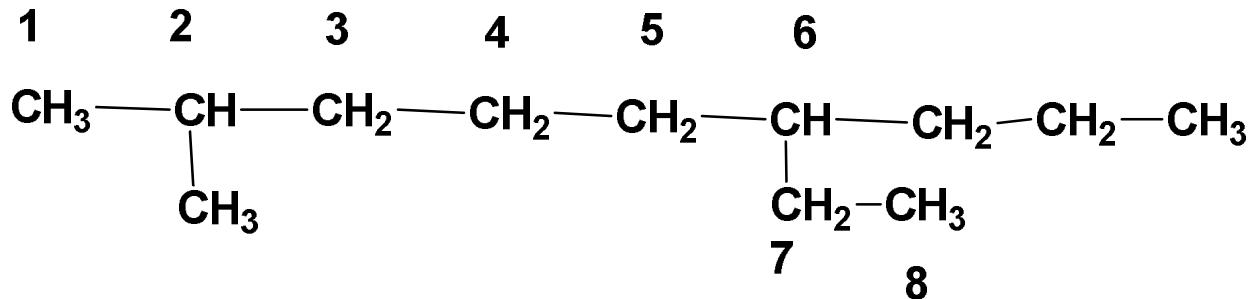
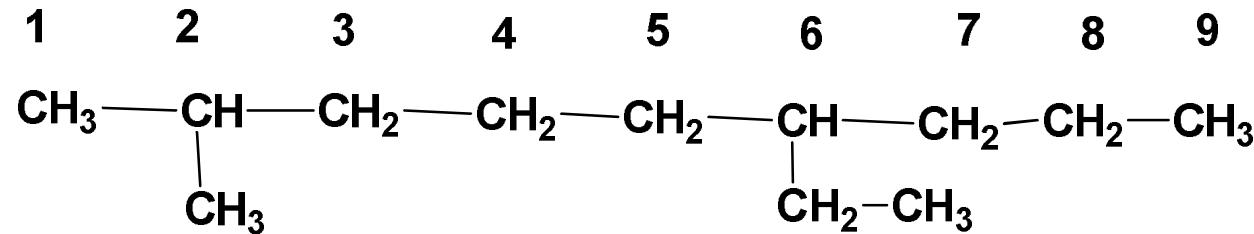
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ n-heptane

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ n-octane

Nomenclature of branched chain alkanes

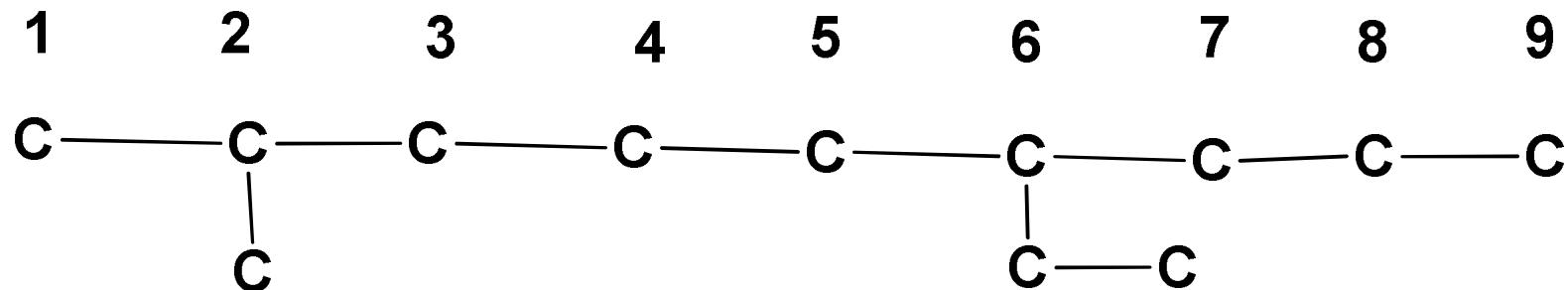
Rules:

1. First, longest carbon chain in the molecule is identified



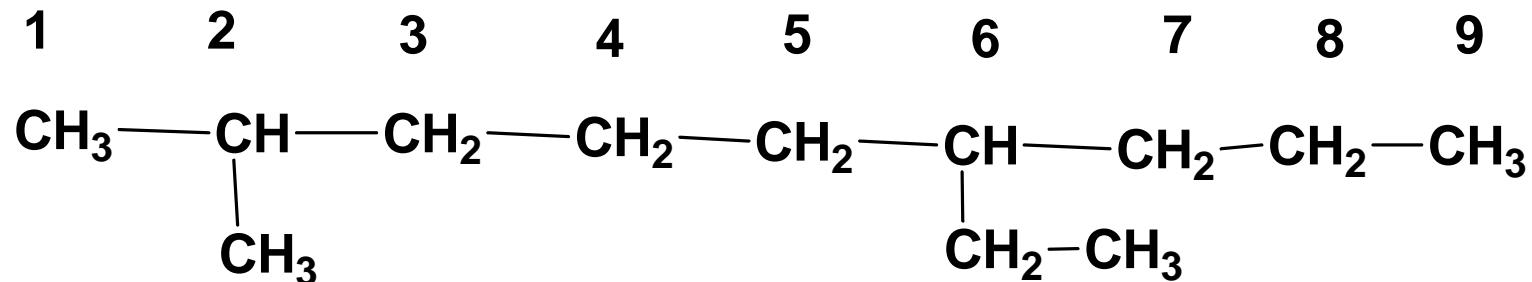
Nomenclature of branched chain alkanes

2. The numbering is done in such way that the branched carbon atoms get the lowest possible numbers.



Nomenclature of branched chain alkanes

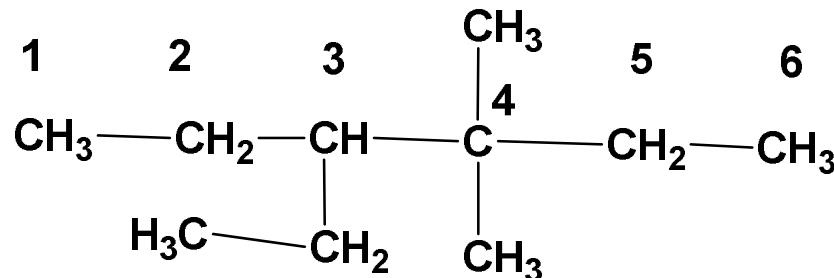
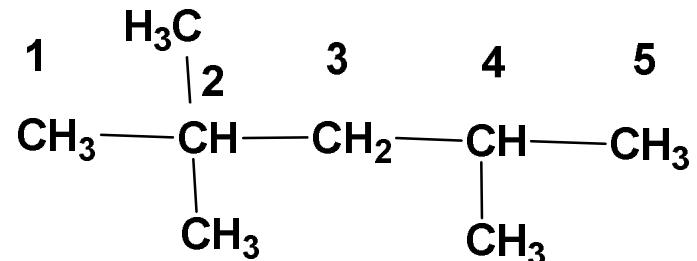
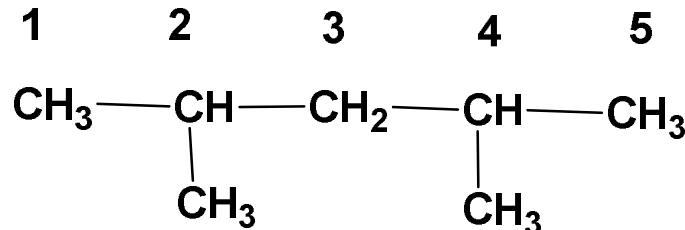
3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers.
- Ex: 6-ethyl-2-methylnonane



Nomenclature of branched chain alkanes

4. If 2 or more identical substituent groups are present then the numbers are separated by commas. di, tri, tetra, penta, hexa

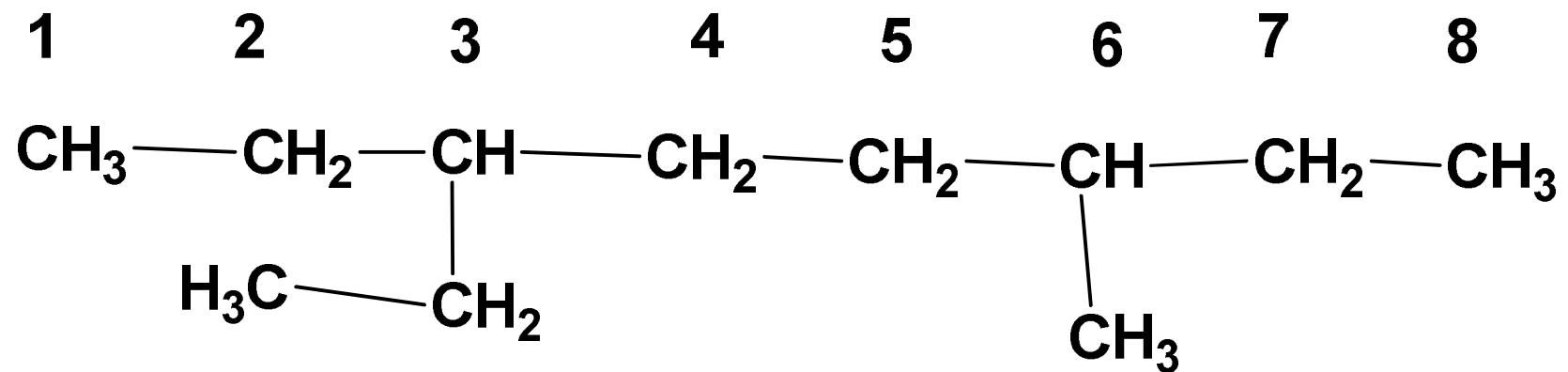
- Ex:



Nomenclature of branched chain alkanes

5. Lower numbering is given to the one coming first in the alphabetical listing.

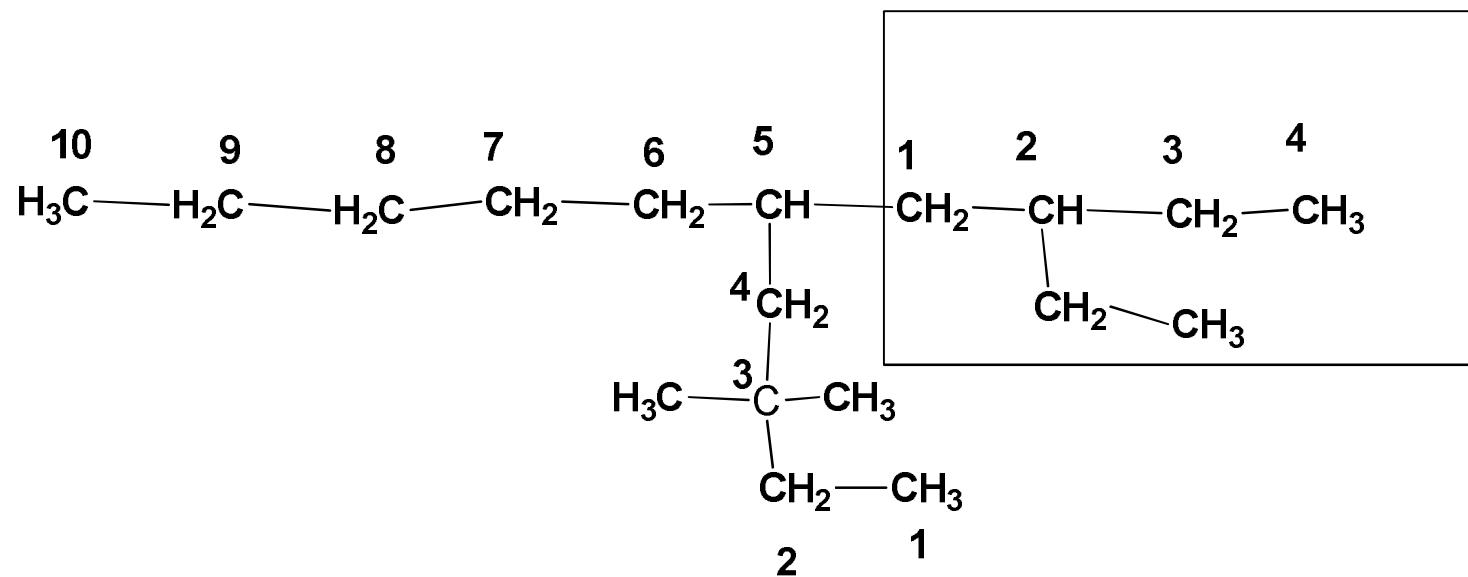
- Ex:



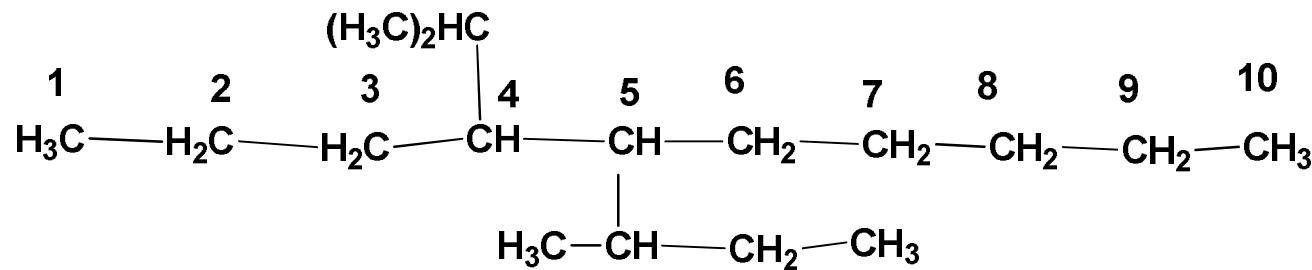
Nomenclature of branched chain alkanes

6. Carbon atom of the branch that attaches to the root alkane is numbered as.

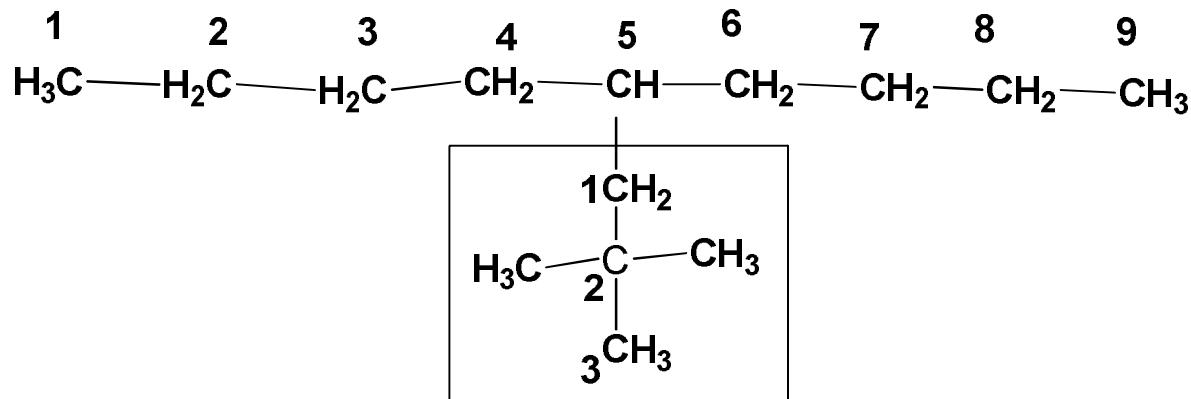
- In alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not considered.



Nomenclature of branched chain alkanes

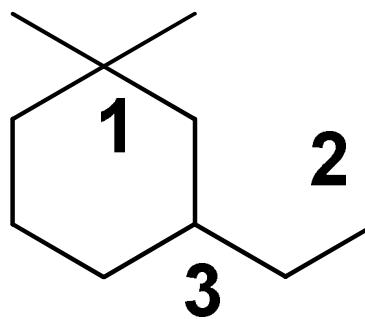
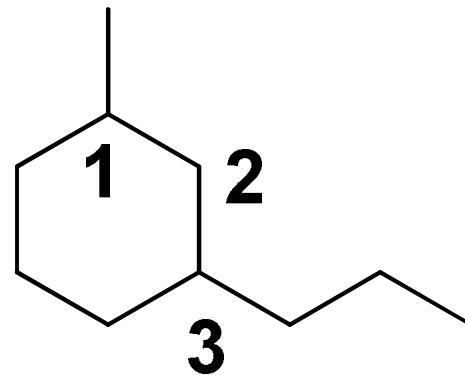
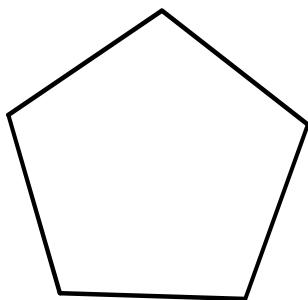


5-sec-Butyl-4-isopropyldecane



5-(2,2-Dimethylpropyl)nonane

Cyclic compounds



The IUPAC System of Nomenclature

- IUPAC Names of Some Unbranched unsaturated Hydrocarbons
- Prefix + suffix = name of the organic compound

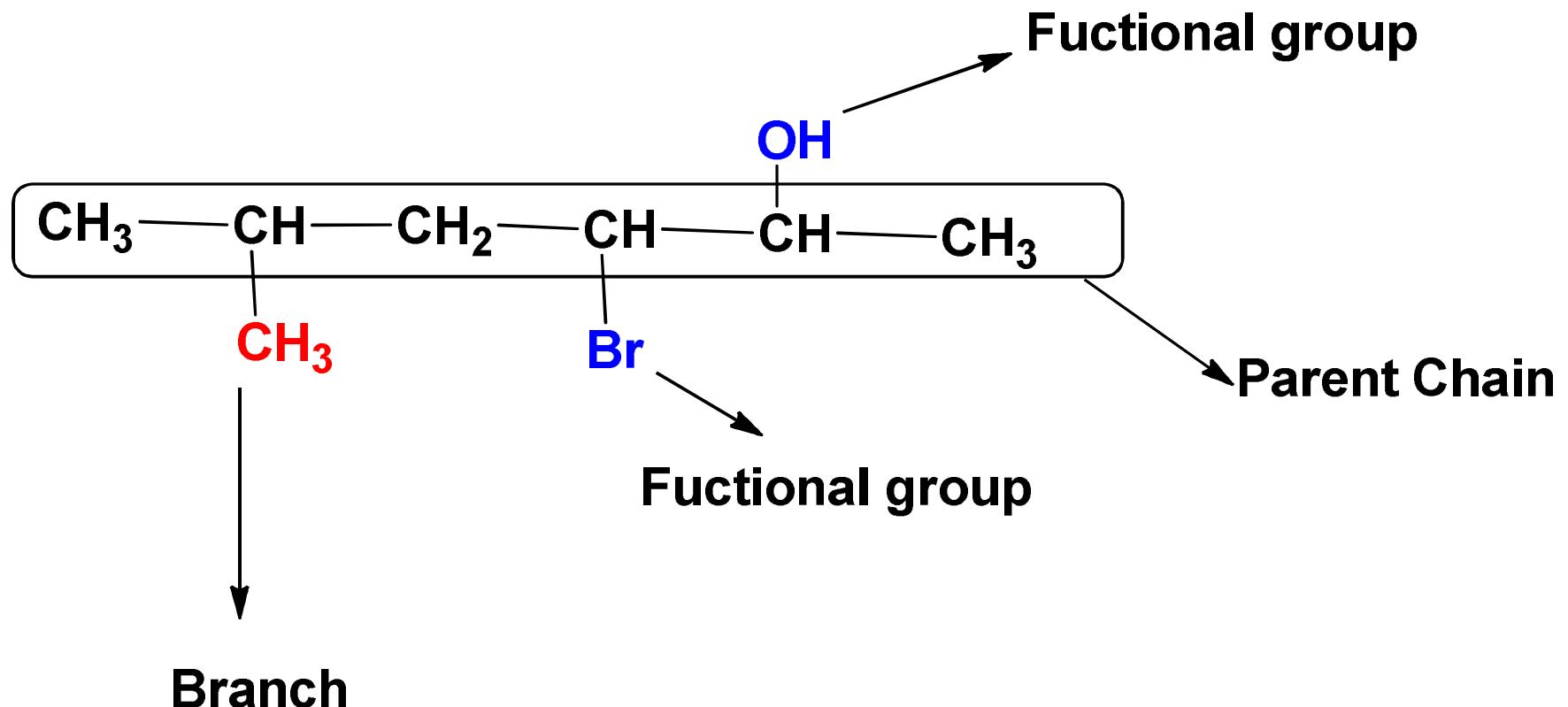
Alkene	prefix	suffix	Name
$\text{CH}_2=\text{CH}_2$	eth-	-ene	Ethene
$\text{CH}_2=\text{CH-CH}_3$	prop-	-ene	Propene
$\text{CH}_2=\text{CH-CH}_2\text{-CH}_3$	but-	-ene	1-Butene
$\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CH}_3$	pent-	-ene	1-Pentene
$\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	hex-	-ene	1-Hexene
$\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	hept-	-ene	1-Heptene
$\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	oct-	-ene	1-Octene
$\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	non-	-ene	1-Nonene
$\text{CH}_2=\text{CH-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$	dec-	-ene	1-Decene

The IUPAC System of Nomenclature

- IUPAC Names of Some Unbranched unsaturated Hydrocarbons
- Prefix + suffix = name of the organic compound

Alkyne	prefix	suffix	Name
$\text{HC}\equiv\text{CH}$	eth-	-yne	Ethyne
$\text{HC}\equiv\text{C}-\text{CH}_3$	prop-	-yne	Propyne
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_3$	but-	-yne	1-Butyne
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	pent-	-yne	1-Pentyne
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	hex-	-yne	1-Hexyne
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	hept-	-yne	1-Heptyne
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	oct-	-yne	1-Octyne
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	non-	-yne	1-Nonyne
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	dec-	-yne	1-Decyne

Nomenclature of organic compounds having functional groups



Nomenclature of organic compounds having functional groups

- The longest chain of carbon atoms having functional group is numbered as lowest possible number in the chain.
- Polyfunctional compounds:
principal functional group and substituents.

The order of decreasing priority for some functional groups is: -COOH, -SO₃H, -COOR (R=alkyl group), COCl, -CONH₂, -CN, -HC=O, ->C=O, - OH, -NH₂, >C=C<, -C=C-

Nomenclature of organic compounds having functional groups

Ex:

- 1) HOCH₂(CH₂)₃CH₂COCH₃ 7-hydroxyheptan-2-one and not as 2-oxoheptan-7-ol.
- 2) BrCH₂CH=CH₂ is named as 3-bromoprop-1-ene and not 1-bromoprop-2-ene.

[The alkyl (R), -C₆H₅ (Ph), halogens (F, Cl, Br, I), -NO₂, alkoxy (OR) etc. are always prefix substituents]

- 3) CH₂(OH)CH₂(OH) is named as ethane-1,2-diol.
- 4) CH₂=CH-CH=CH₂ is named as 1,3-butadiene or buta-1,3-diene.

Some functional groups and Classes of organic compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Alkanes	-	-	-ane	Butane $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$
Alkenes	$>\text{C}=\text{C}<$	-	-ene	But-1-ene $\text{CH}_2=\text{CHCH}_2\text{CH}_3$
Alkynes	$-\text{C}\equiv\text{C}-$	-	-yne	But-1-yne $\text{CH}\equiv\text{CCH}_2\text{CH}_3$
Arenes	-	-	-	Benzene 
Halides	$-\text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)	halo	-	1-Bromobutane $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Br}$

Some functional groups and Classes of organic compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Alcohols	-OH	hydroxy	-ol	Butan-2-ol, $\text{CH}_3\text{CH}_2\text{CHOHCH}_3$
Aldehydes	-CHO	formyl or oxo	-al	Butanal, $\text{CH}_3(\text{CH}_2)_2\text{CHO}$
Ketones	>C=O	oxo-	-one	Butan-2-one, $\text{CH}_3\text{CH}_2\text{COCH}_3$
Nitriles	-C≡N	cyano	nitrile	Pentanenitrile, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}$
Ethers	-R-O-R-	alkoxy-	-	Ethoxyethane $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

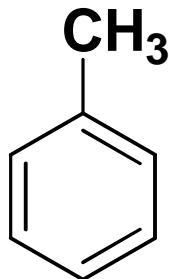
Some functional groups and Classes of organic compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Carboxylic acids	-COOH	carboxy	-oic acid	Butanoic acid $\text{CH}_3(\text{CH}_2)_2\text{COOH}$
Carboxylate ion	-COO ⁻	-	-oate	Sodium butanoate, $\text{CH}_3(\text{CH}_2)_2\text{COO}^-\text{Na}$
Esters	>COOR	alkoxycarbon yl	-oate	Methyl propanoate, $\text{CH}_3\text{CH}_2\text{COOCH}_3$
Acyl halides	-COX (X = F, Cl, Br, I)	halocarbonyl	-oyl halide	Butanoyl chloride, $\text{CH}_3(\text{CH}_2)_2\text{COCl}$
Amines	-NH ₂ , >NH, >N-	amino-	-amine	Butan-2-amine, $\text{CH}_3\text{CHNH}_2\text{CH}_2\text{CH}_3$

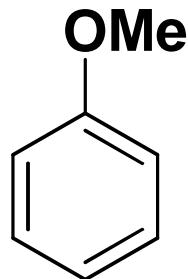
Some functional groups and Classes of organic compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Amides	-CONH ₂ , -CONHR, -CONR ₂	-carbamoyl	-amide	Butanamide, $\text{CH}_3(\text{CH}_2)_2\text{CONH}_2$
Nitro compounds	-NO ₂	nitro	-	1-nitrobutane, $\text{CH}_3(\text{CH}_2)_3\text{NO}_2$
Sulphonic acids	-SO ₃ H	sulpho	-sulphonic acid	Methylsulphonic acid, $\text{CH}_3\text{SO}_3\text{H}$

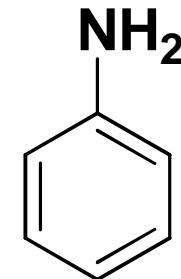
Nomenclature of substituted Benzene Compounds



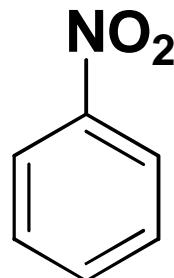
**Methylbenzene
(Toluene)**



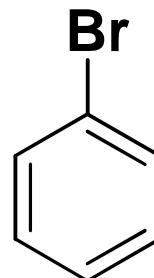
**Methoxybenzene
(Anisole)**



**Aminobenzene
(Aniline)**

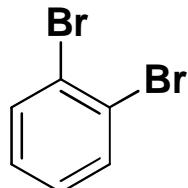


Nitrobenzene

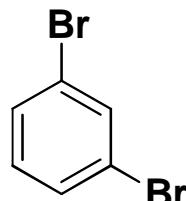


Bromobenzene

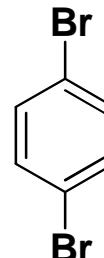
Nomenclature of substituted Benzene Compounds



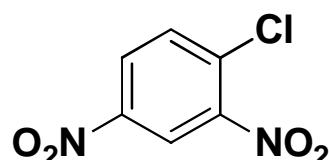
1,2-dibromobenzene



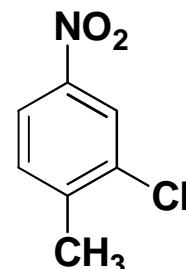
1,3-dibromobenzene



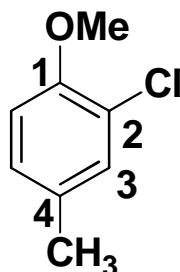
1,4-dibromobenzene



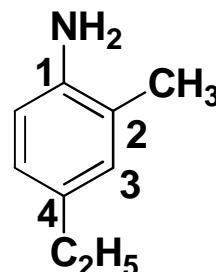
1-Chloro-2,4-dinitrobenzene
(not 4-chloro,1,3,-dinitrobenzene)



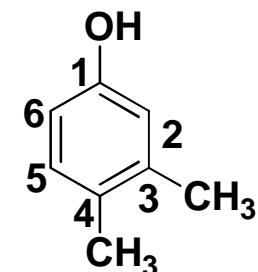
2-Chloro-1-methyl-4-nitrobenzene
(not 4-methyl-5-chloro-nitrobenzene)



2-Chloro-4-methylanisole

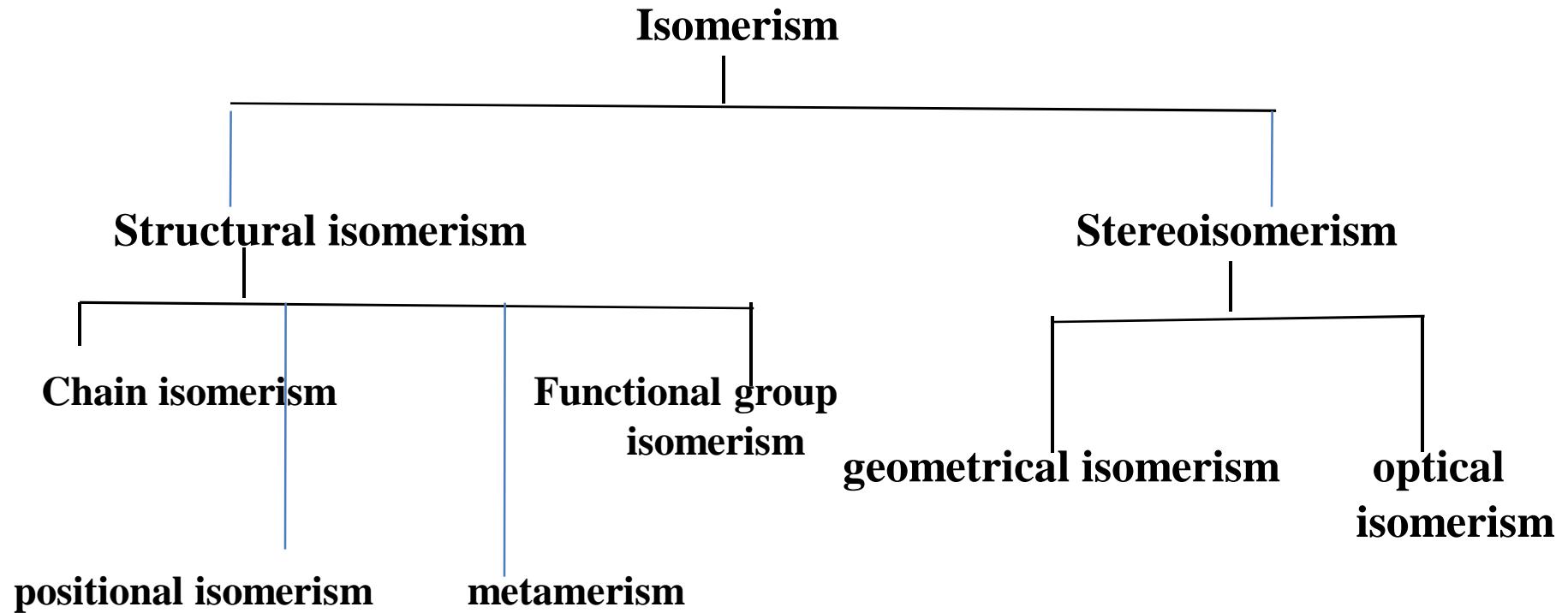


4-Ethyl-2-methylaniline



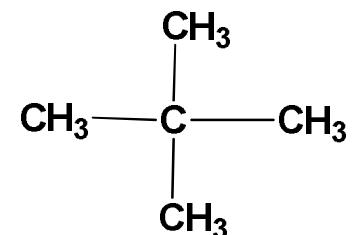
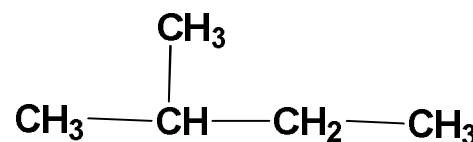
3,4-dimethylphenol

Isomerism

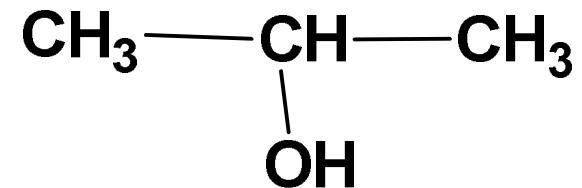
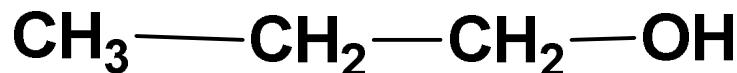


Structural Isomerism

1) Chain isomerism:

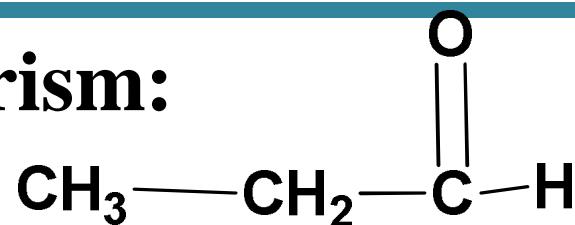
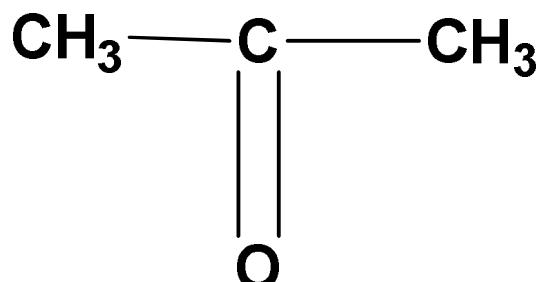


2) Positional isomerism:

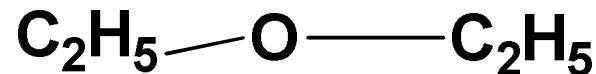


Structural Isomerism

3) Functional group isomerism:



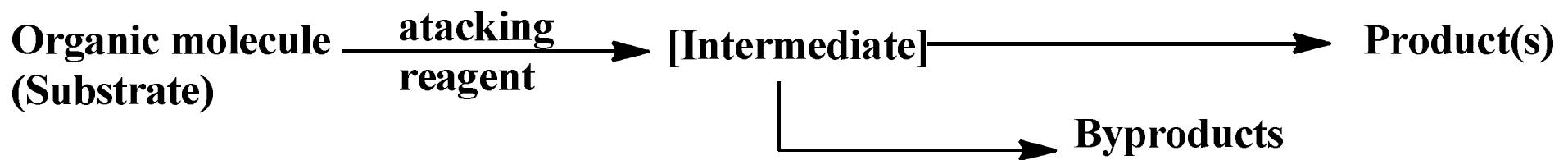
4) Metamerism: $\text{CH}_3 - \text{O} - \text{C}_3\text{H}_7$



- Stereoisomerism:
- cis-2-butene and trans-2-butene

Fundamental concepts in organic reaction mechanism

Organic reaction:



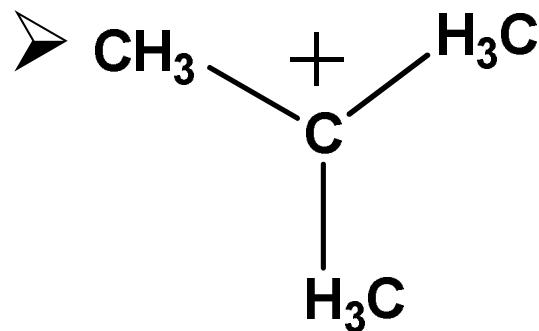
A covalent bond can be cleaved in two ways

- i) Heterolytic cleavage,
- ii) Homolytic cleavage.

Heterolytic Cleavage



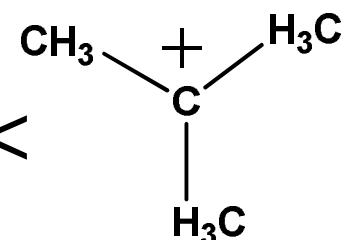
- H_3C^+ : methyl carbocation
- $\text{H}_3\text{C}-\text{H}_2\text{C}^+$: ethyl carbocation (1°)
- $\text{H}_3\text{C}-\text{HC}^+-\text{CH}_3$: Isopropyl carbocation (2°)



: tertiary carbocation (3°)

Heterolytic Cleavage

- Carbocation stability order is
- $\text{H}_3\text{C}^+ < \text{H}_3\text{C}-\text{H}_2\text{C}^+ < \text{H}_3\text{C}-\text{HC}^+-\text{CH}_3 <$
- H_3C^+ : sp^2 hybridisation: trigonal planar



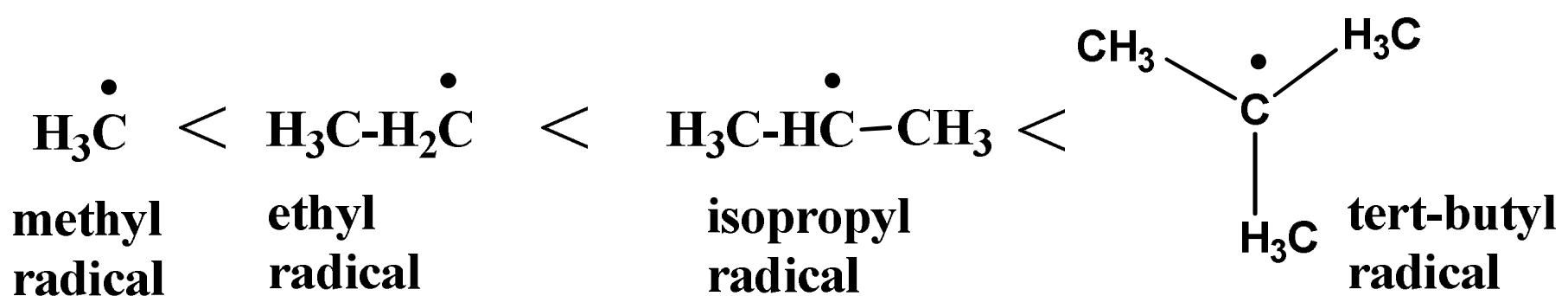
- H_3C^- : methyl carbanion: sp^3 hybridisation: distorted tetrahedron
- $\text{H}_3\text{C}-\text{H}_2\text{C}^-$: ethyl carbanion (1°)

Homolytic Cleavage

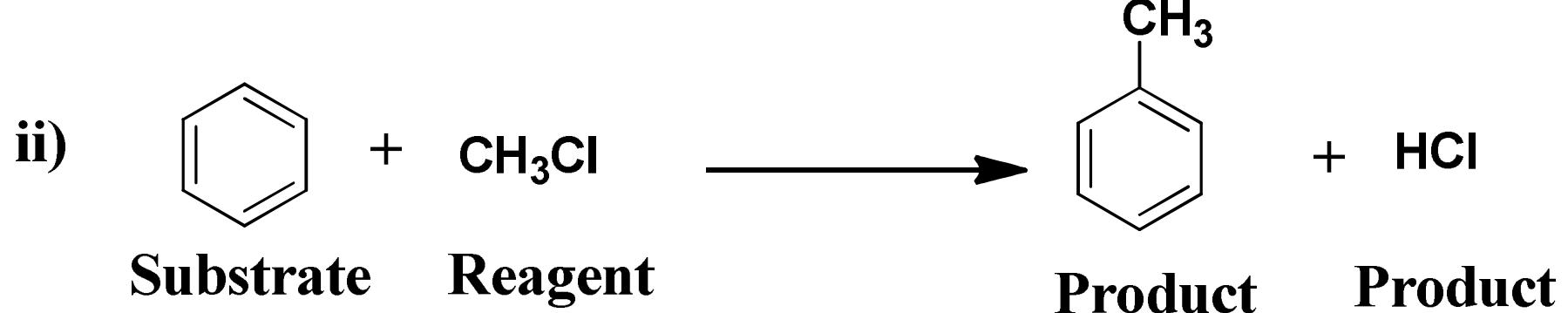
- Homolytic cleavage:



- Radical stability order is:



Substrate and Reagent



Nucleophiles and Electrophiles

➤ Nucleophile (Nu⁻):

Which attracts nucleons (+ve charge).

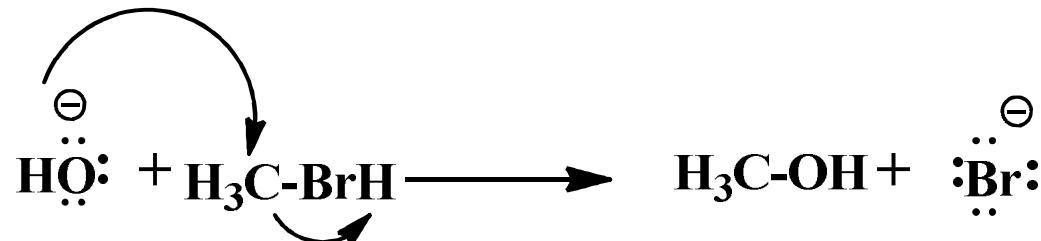
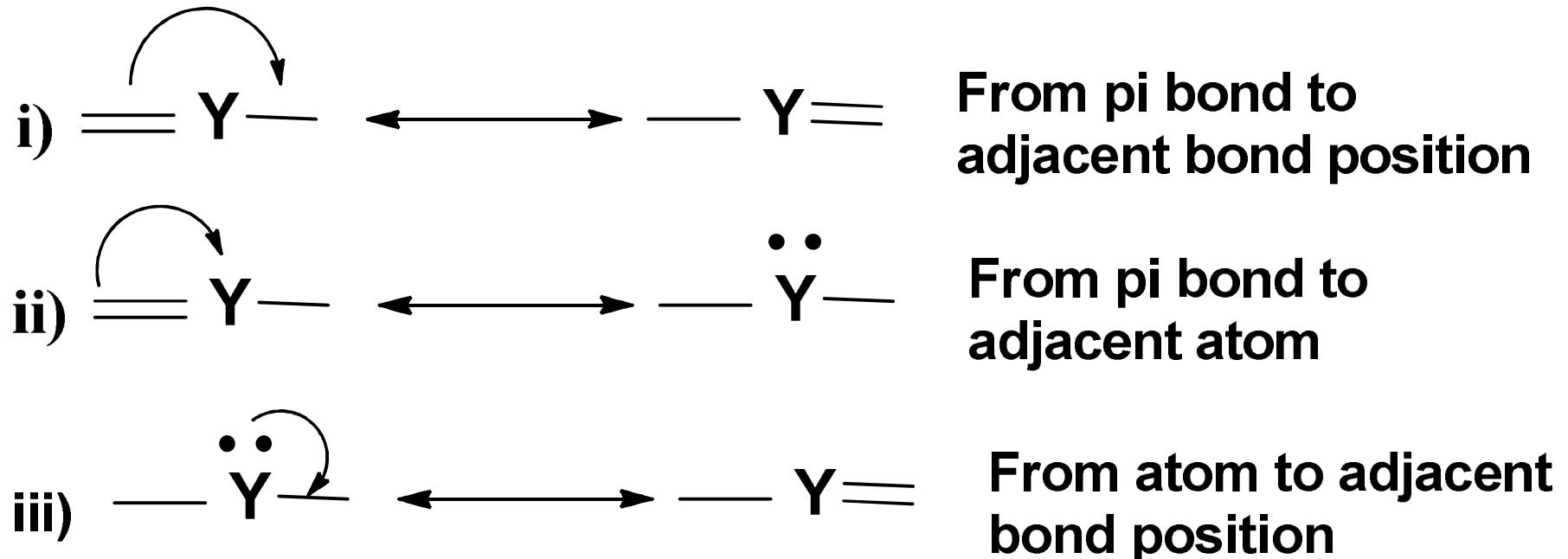
Ex: HO⁻, NC⁻, H₂O, R₃N etc.,

➤ Electrophile (E⁺):

Which attracts electrons (-ve charge).

Ex: ⁺CH₃, >C=O, R₃C-X.

Electron Movement in organic reactions



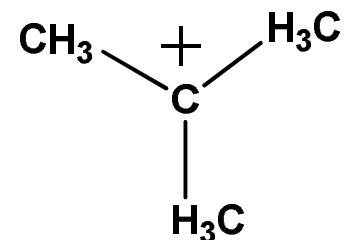
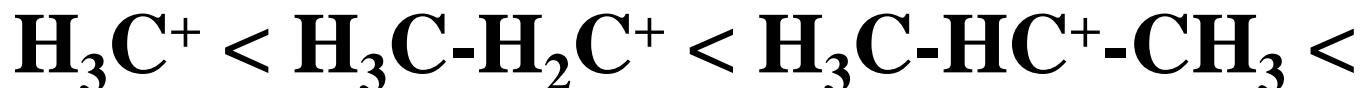
Electron Displacement Effects in Covalent Bonds

- **Inductive effect:**
- **Resonance effect:**
- **Electromeric effect:**
- **Hyperconjugation:**

Inductive Effect



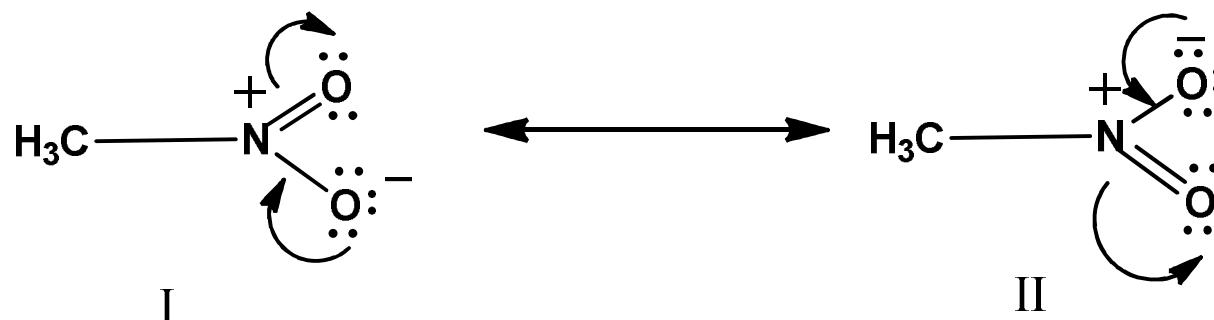
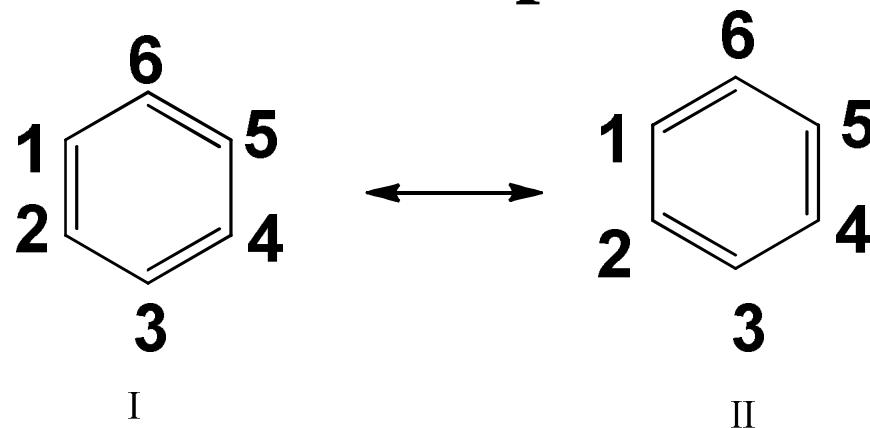
- Electron donating groups: (+ I groups)
-CH₃, -CH₂-CH₃, -O-CH₃
- Electron withdrawing groups: (- I groups)
-NO₂, -CN, -COOH, COOR, -OC₆H₅



Resonance

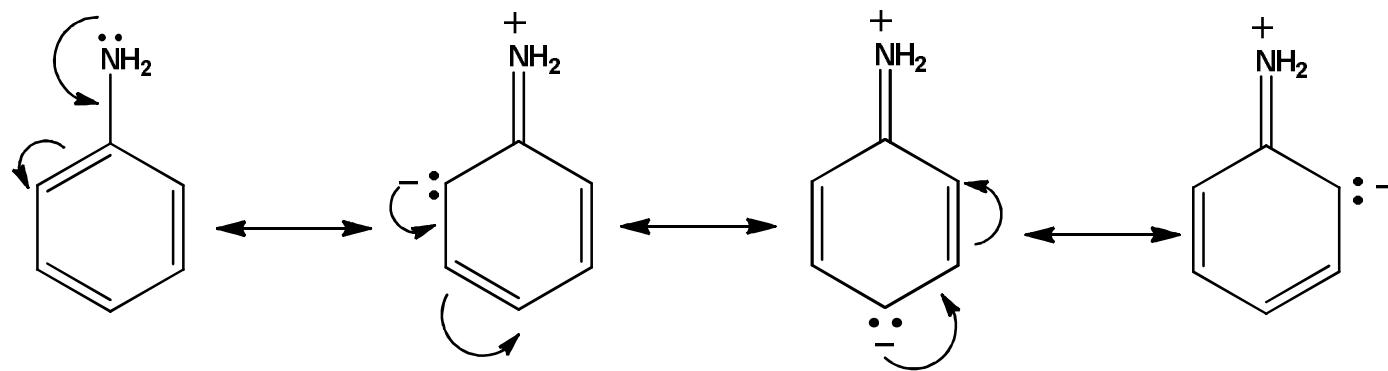
➤ Resonance structure:

- i) The same positions of nuclei,
- ii) The same number of unpaired electrons.



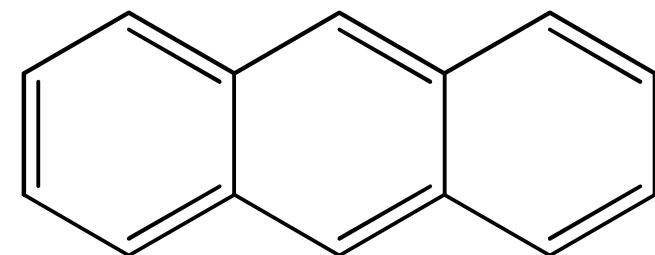
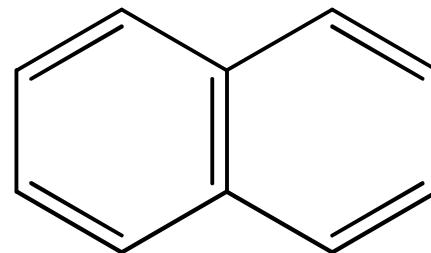
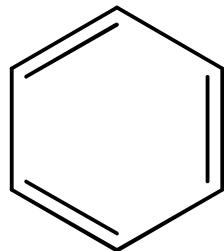
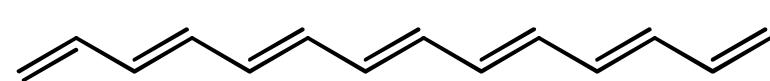
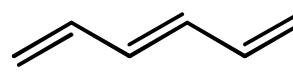
Resonance effect

i) + R effect (+ M effect):



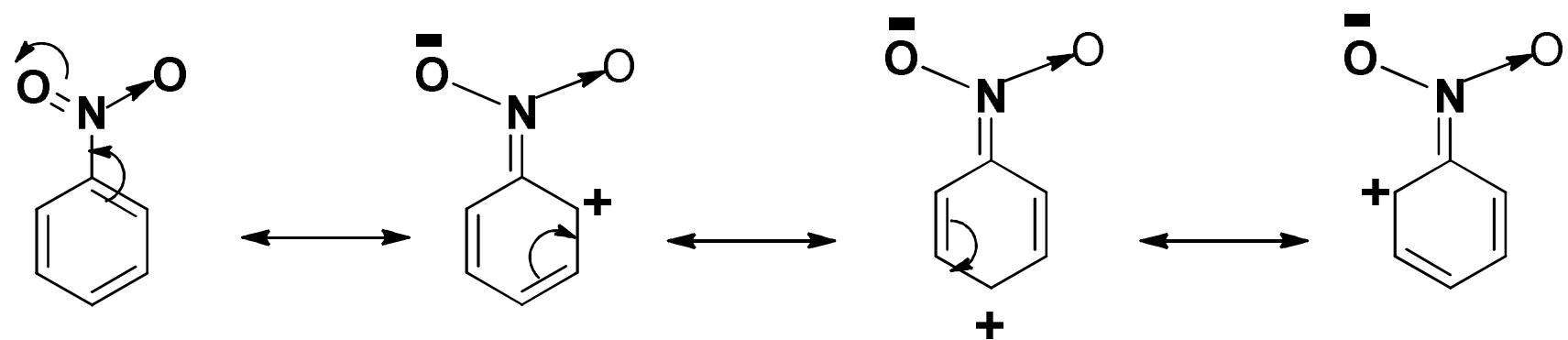
Ex: -halogen, -OH, -OR, -OCOR, -NH₂, -NHR, -NR₂, -NHCOR

Conjugation



Resonance effect

ii) - R effect (- M effect):

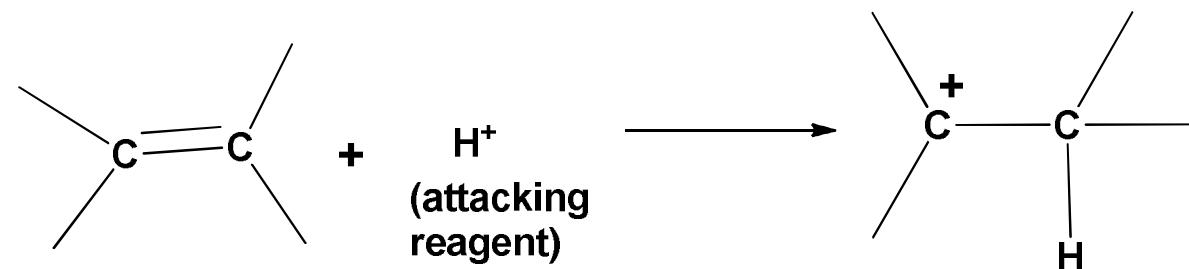


Ex: $-\text{COOH}$, $-\text{CHO}$, $>\text{C=O}$, $-\text{CN}$, $-\text{NO}_2$

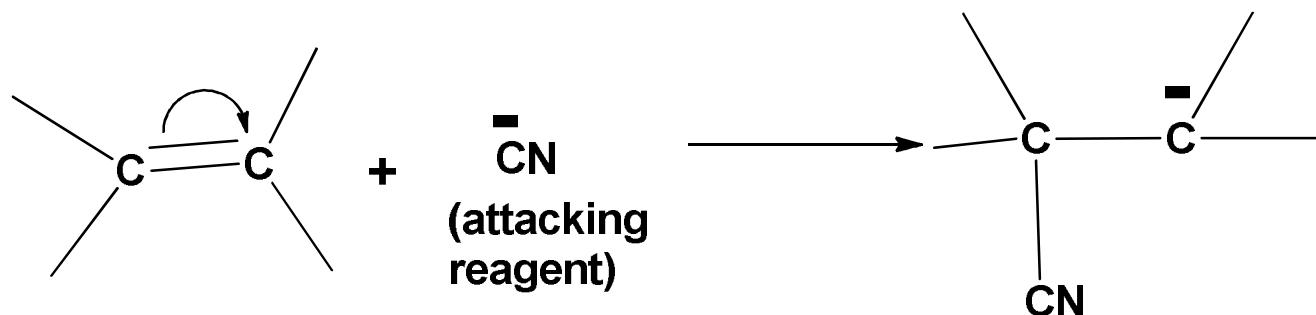
Electromeric effect

Multiple bond containing organic compounds depicts this effect in the presence of attacking reagent.

i) Positive electromeric effect (+ E effect):



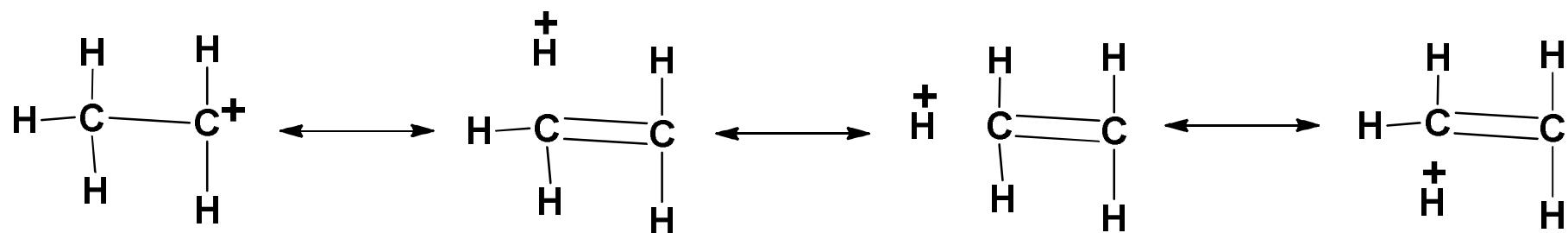
ii) Negative electromeric effect (- E effect):



Hyperconjugation

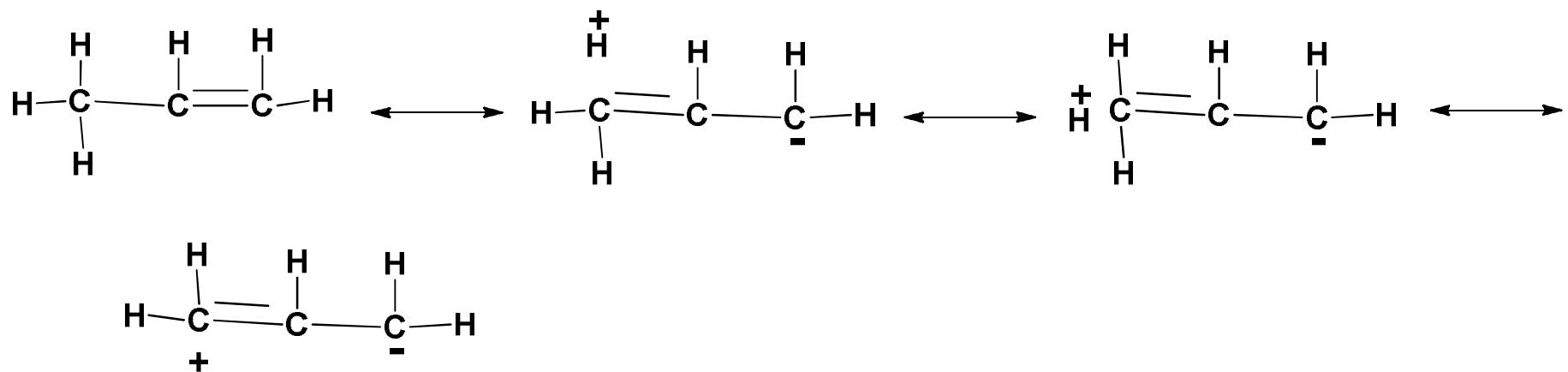
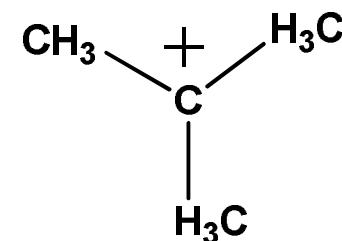
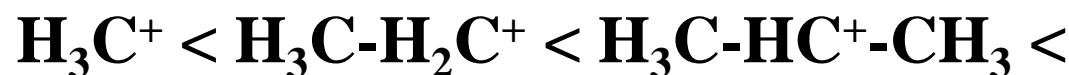
- It is permanent effect.
- Delocalization of σ electrons of C-H bond of alkyl group directly attached to an atom of unsaturated system or an atom with unshared p-orbital.

Ex: $\text{C}_2\text{H}_5\text{CH}_2^+$



Hyperconjugation

- Stability of carbocation:



Types of organic reactions and mechanisms

- Substitution reactions
- Addition reactions
- Elimination reactions
- Rearrangement reactions



Thank You

Organic chemistry

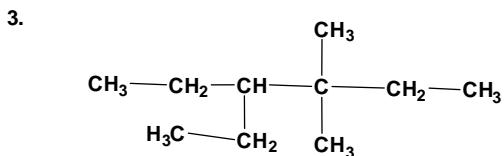
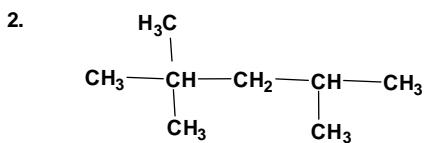
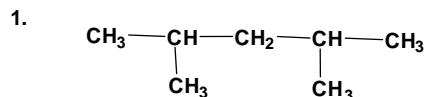
Alkanes

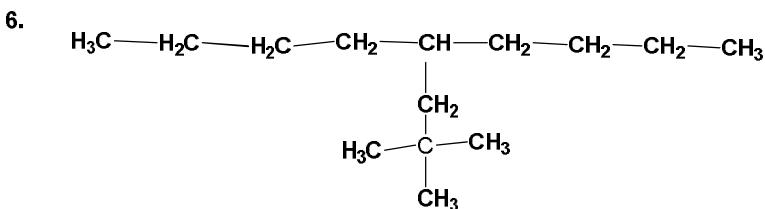
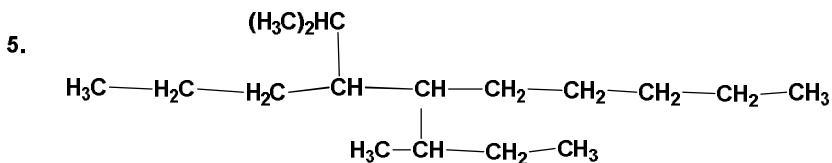
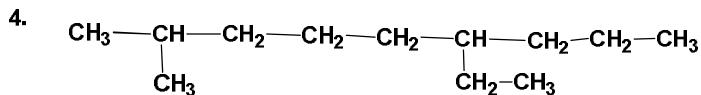
Nomenclature:

- IUPAC Names of Some Unbranched Saturated Hydrocarbons
- Prefix + suffix = name of the organic compound

Alkane	prefix	suffix	Name
CH ₄	meth-	-ane	Methane
CH ₃ -CH ₃	eth-	-ane	Ethane
CH ₃ -CH ₂ -CH ₃	prop-	-ane	Propane
CH ₃ -CH ₂ -CH ₂ -CH ₃	but-	-ane	Butane
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₃	pent-	-ane	Pentane
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	hex-	-ane	Hexane
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	hept-	-ane	Heptanes
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	oct-	-ane	Octane
CH ₃ -CH ₂ -CH ₃	non-	-ane	Nonane
CH ₃ -CH ₂ -CH ₃	dec-	-ane	Decane

Ex:



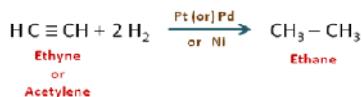
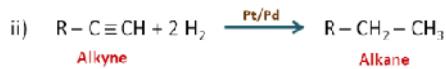
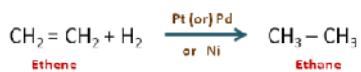
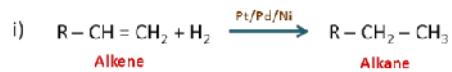


Preparation methods of alkanes

1. Preparation from alkenes:

Alkenes, when treated with H₂ gas in presence of a catalyst Pt, Pd or Ni, get hydrogenated and give alkanes.

The hydrogenation of unsaturated hydrocarbons in presence of Raney Nickel is known as Sabatier-Sandern's reactions.



2. Wurtz reaction:

A solution of alkyl halide in ether on heating with sodium metal gives alkane. This reaction is known as Wurtz reaction. This reaction leads to the formation of symmetrical alkane having an even number of carbon atoms.



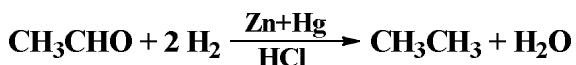
Alkanes formed from Wurtz reaction usually have double the number of carbon atoms in the products than in the reactant (R-X).

Two different alkyl halides, on Wurtz reaction give all possible alkanes.



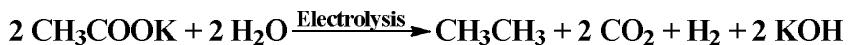
3. Clemmensen Reduction:

The reduction of carbonyl compounds by amalgamated zinc and conc. HCl gave alkanes. This reaction is known as Clemmensen Reduction.



4. Kolbe's electrolysis:

Potassium salt of a carboxylic acid in aqueous solution when subjected to electrolysis gives an alkane. The product has double the number of carbon atoms than in the alkyl part of the potassium salt.

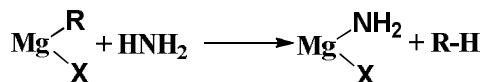


5. Grignard reagent:

Alkyl or aryl magnesium halides (R-Mg-X) are known as Grignard reagents.

Grignard reagent on decomposition with water or with other compounds having active H (the hydrogen attached on O, N, F or triple bonded carbon atom are known as active hydrogen) give alkane.

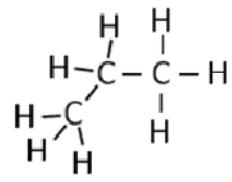
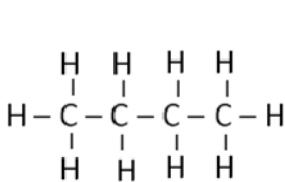
Eg:



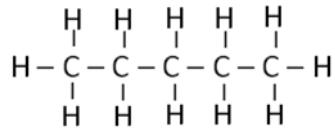
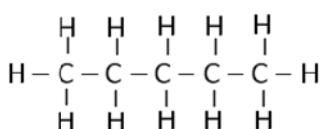
Physical properties of alkanes:

1. Alkanes are non-polar molecules. In alkanes all bonds are covalent bonds (C-C) and (C-H). Between the molecules van der Waals forces of attraction operate. The first four members of alkanes are gases. i.e. from (C₁ to C₄ compounds). From C₅ to C₁₁ compounds are liquids and from C₁₁a onwards they exist as solids.
2. Alkanes are insoluble in water. As alkanes are nonpolar molecules they dissolve in nonpolar solvents only. Alkanes are soluble on non-polar solvents like CCl₄ and benzene. They obey general principle "like dissolves like".
3. The Boiling points of alkanes increase with increase in the molecular weights in the series. Consider isomers of alkanes; straight chain compounds have higher boiling points than branched compounds. For branched

compounds surface area decreases such that intermolecular forces of attraction (weak van der Waal forces) decrease and so boiling points also decrease. That means greater the branching lesser the boiling point.

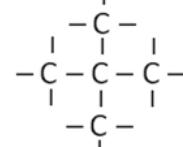
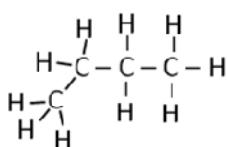


n-butane : Boiling point 0°C Iso butane Boiling point (-12°C)



n-pentane Boiling point 36°C

n-pentane Boiling point 36°C



Iso pentane Boiling point (28°C)

neo-pentane Boiling point 9.5°C

4. Melting points of alkanes increase with increase in the molecular weights. But there is no regular trend observed as for boiling points of isomers (iso; neo...etc or branched chains alkanes) of alkanes.

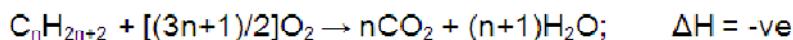
5. Specific gravity of alkanes increases with increase in the molecular weight.

Chemical Properties of alkanes:

1. Oxidation:

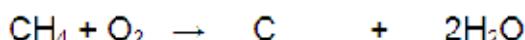
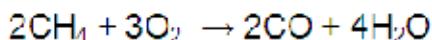
Complete oxidation or combustion:

Alkanes burn readily with non luminous flame in presence of air or oxygen to give CO_2 & water along with evolution of heat. Therefore alkanes are used as fuels.



a. Incomplete oxidation:

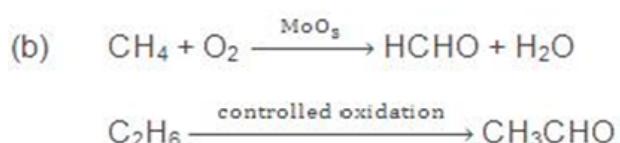
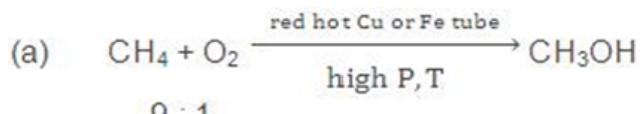
Incomplete oxidation of alkanes in limited supply of air gives carbon black and CO .



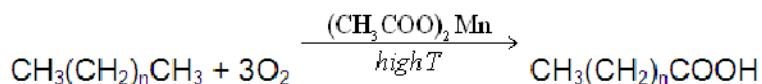
Carbon black

b. Catalytic oxidation:

Lower alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation.



Higher alkanes on oxidation in presence of manganese acetate give fatty acids.

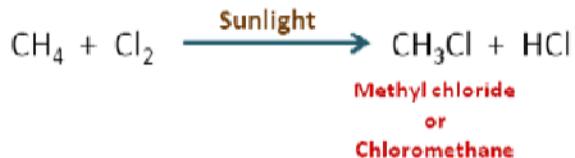


2. Substitution reactions:

Halogenation:

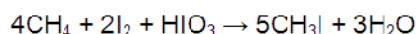
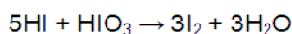
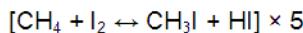
In the presence of sunlight or UV light or on heating alkanes react with halogens like Cl_2 or Br_2 . The reaction with Cl_2 is known as chlorination reaction. A reaction also may be used for the halogenation reaction. In this reaction all the hydrogen atoms of an alkanes are substituted by Cl atoms one after the other.

The extent of halogenations depends upon the amount of halogen used.

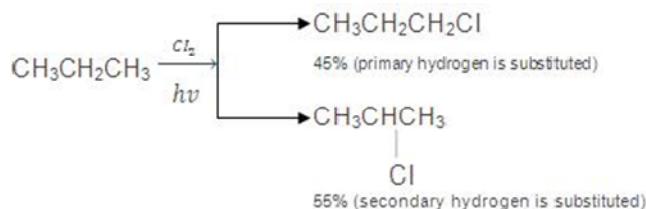


Similarly the halogenations reactions take place with other hydrocarbons. The reactivity order for halogens shows the order: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

F_2 reacts violently even in dark and reaction may be controlled by diluting fluorine with N_2 , whereas iodination is very slow and reversible. Therefore iodination is made in presence of HgO or HIO_3 (oxidants which decompose HI).



The reactivity order for H atom in alkane shows the order $3^\circ \text{H} > 2^\circ \text{H} > 1^\circ \text{H} > \text{CH}_4$.



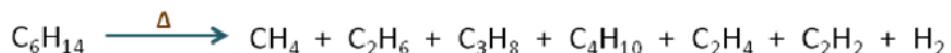
3. Pyrolysis:

Thermal decomposition of organic compounds in absence of air is known as pyrolysis. Pyrolysis, when particularly applied to alkanes, is known as cracking. Pyrolysis of alkanes is carried out between 500-1000 °C.

The product formed during cracking depends upon

- (a) Nature of alkane
- (b) Temperature and pressure
- (c) Presence or absence of catalyst

The ease of cracking in alkanes increases with increase in molecular weight and branching in alkane.



The pyrolysis of the alkanes may change them into their corresponding isomers. In these isomers the normal carbon chain may get converted into branched chain structures.

Cracking has an important role in petroleum industry. Higher alkanes are converted into lower one (petrol C_6 to C_{11}) by cracking.

Alkenes

Nomenclature:

- IUPAC Names of Some Unbranched unsaturated Hydrocarbons
- Prefix + suffix = name of the organic compound

Alkene	prefix	suffix	Name
$\text{CH}_2=\text{CH}_2$	eth-	-ene	Ethene
$\text{CH}_2=\text{CH}-\text{CH}_3$	prop-	-ene	Propene
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$	but-	-ene	1-Butene
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3$	pent-	-ene	1-Pentene
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	hex-	-ene	1-Hexene
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	hept-	-ene	1-Heptene
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	oct-	-ene	1-Octene
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	non-	-ene	1-Nonene
$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	dec-	-ene	1-Decene

Isomerism in alkenes:

Alkenes show structural and geometrical isomerism.

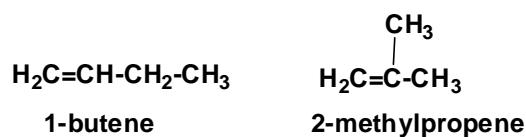
1) Structural isomerism:

The isomers having same molecular formula but differ in their structures are called as structural isomers. This phenomenon is known as structural isomerism. The structural isomerisms of alkenes are a) Chain isomerism b) Positional isomerism.

a) Chain isomerism:

The isomers having same molecular formula but differ in the carbon chain are called as chain isomers and the phenomenon is known as chain isomerism.

Ex:



b) Positional isomerism:

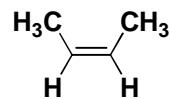
The isomers having same molecular formula but differ in the position of double bond in the carbon chain are called as positional isomers and the phenomenon is known as positional isomerism.

Ex:

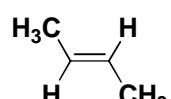


Geometrical isomerism:

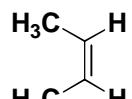
a) cis-trans isomerism:



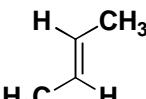
cis-2-butene



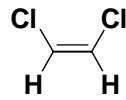
trans-2-butene



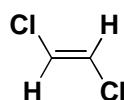
cis-2-butene



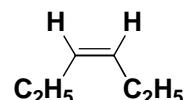
trans-2-butene



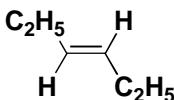
cis-1,2-dichloroethene



trans-1,2-dichloroethene



cis-3-hexene

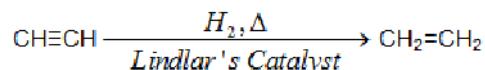


trans-3-hexene

Preparation methods of alkenes:

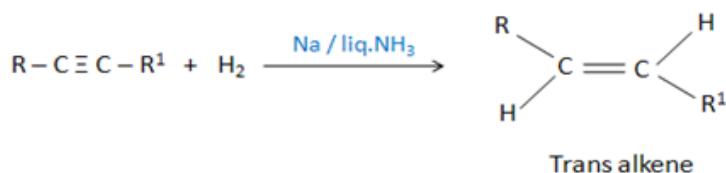
1. From alkynes (hydrogenation):

Hydrogenation of alkynes in presence of Lindlar catalyst gives cis alkenes.

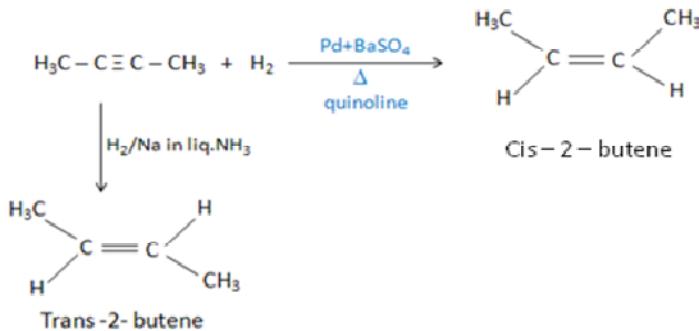


Lindlar catalyst is Pd on CaCO_3 deactivated by lead acetate which prevents further hydrogenation.

Alkynes on reduction with hydrogen in presence of Na and liq. NH_3 give trans alkene.

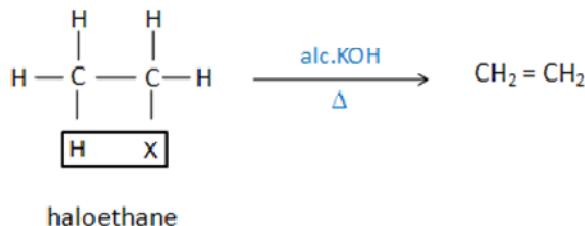


Ex:



2. From alkyl halides (dehydrohalogenation):

Alkyl halides, on dehydro-halogenation with alcoholic KOH or NaNH_2 by heating, give alkenes. This is called as dehydrohalogenation since HX is removed from alkyl halide and it is also called as β -elimination.



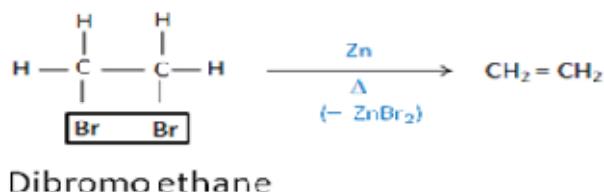
Rate of the reaction for dehydrohalogenation for different halogen follows the order is $\text{I}_2 > \text{Br}_2 > \text{Cl}_2$.

The order of the rate of the reaction for alkyl halides is,

Tertiary alkyl halides $>$ Secondary alkyl halides $>$ Primary alkyl halides

3. From vicinal dihalides (dehalogenation):

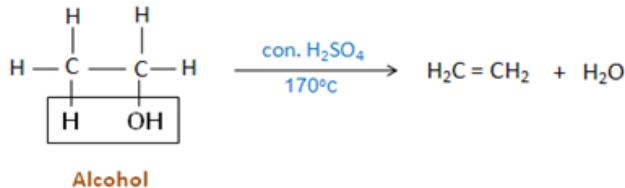
Vicinal dihalides on treatment with Zn dust/ CH_3OH or (Zn-Cu) couple in alcoholic solution give alkenes.



4. From alcohols (By dehydration):

When alcohols are heated to 170°C , in presence of conc. H_2SO_4 , lose a water molecule to give alkenes. This reaction is also known as β -elimination.

Removal H_2O from a substrate molecule by a suitable dehydrating agent like conc. H_2SO_4 , Al_2O_3 , H_3PO_4 , P_2O_5 is known as dehydration.



The case of dehydration shows the order: tertiary > secondary > primary alcohols.

Physical properties of alkenes:

- 1) First three members of alkenes are gases, next 14 members are liquids and higher ones are solids.
- 2) Alkenes are colorless, insoluble in water, soluble in non-polar solvents like benzene.
- 3) They show a regular increase in boiling points with increase in molecular weight.
- 4) Straight chain alkenes have higher boiling points than the branched chain alkenes have higher boiling points than the branched chain alkenes (similar to alkanes).

Chemical properties of alkenes:

Addition reactions:

1. Addition of hydrogen (hydrogenation):

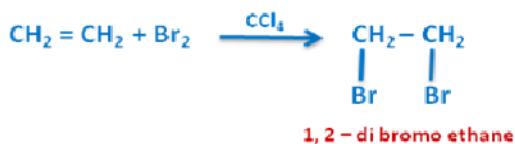
Alkenes undergo addition reactions with H_2 in presence of catalyst like Pt, Pd or Ni and on heating give saturated hydrocarbons (alkanes). The reaction is known as **Sabatier-Senderen's reaction**. The process is used to obtain vegetable ghee from hydrogenation of oil.

Ex:



2. Addition of halogen (halogenation):

Halogen like Br_2 or Cl_2 can be added to alkenes in CCl_4 at room temperature to give dihalides. Addition of Cl_2 on alkene is free radical addition, whereas addition of Br_2 shows electrophilic addition.



The addition of Br_2 on alkenes provides a useful test for unsaturation in molecule that is the reddish brown color of bromine being rapidly discharged from the solution. Thus decolorization of 5% Br_2 in CCl_4 by a compound suggests unsaturation in it.

3. Addition of hydrogen halide (hydro halogenation):

It is an electrophilic addition reaction. The reactivity order for hydrogen halides is:
 $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

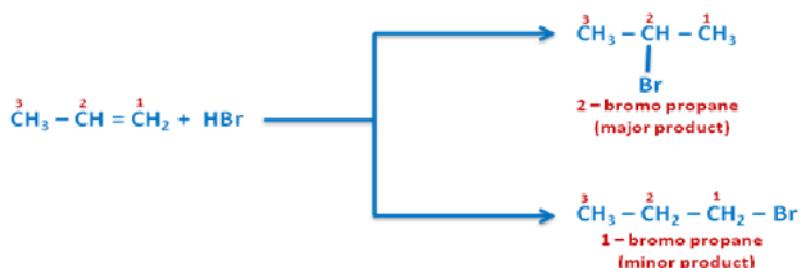
Addition reaction of HBr to symmetrical alkenes:

Addition reactions of HBr to symmetrical alkenes take place by electrophilic addition mechanism.



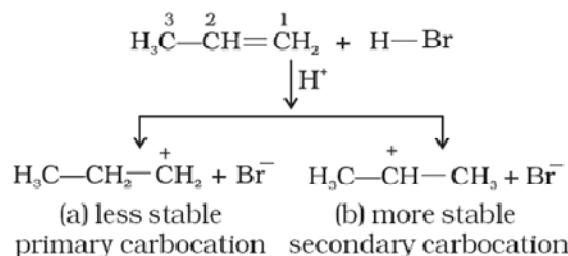
Addition reaction of HBr to unsymmetrical alkenes (Markovnikov's rule):

The addition of HBr to unsymmetrical alkenes can give rise to two types of products.

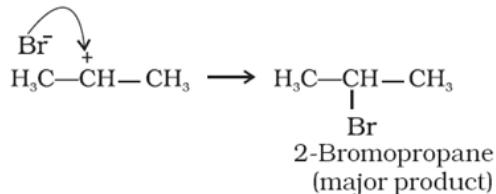


In this example, 2–bromo propane predominately formed than the 1–bromo propane. This is due to **Markovnikov's rule**.

Markovnikov's rule: it states that negative part of the adding molecule is attached to the carbon which is having less number of hydrogen atoms.

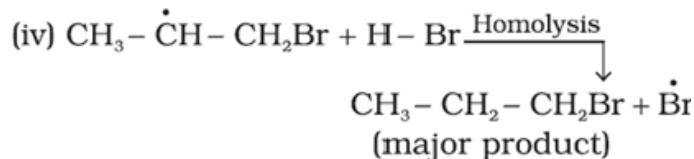
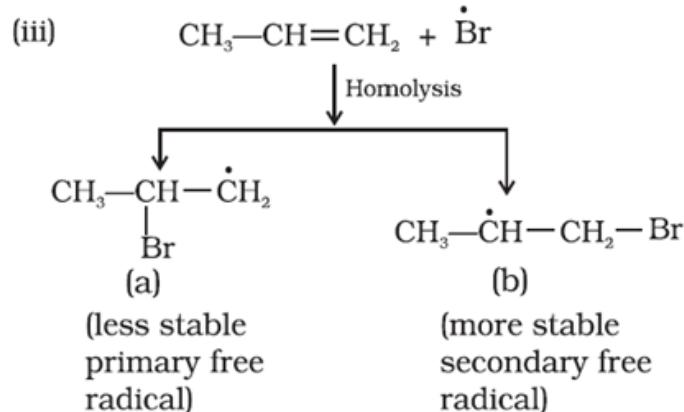
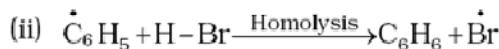
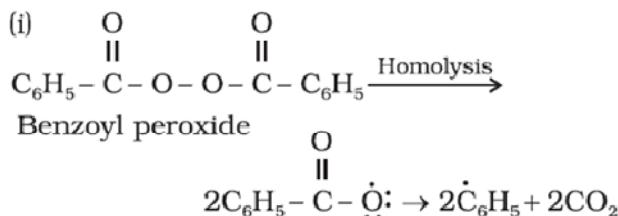
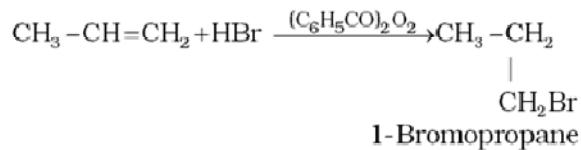


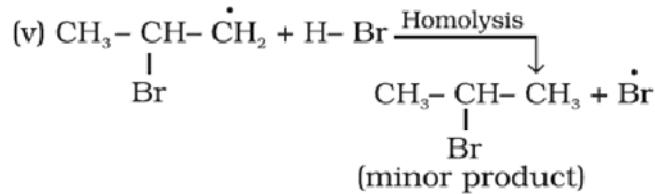
- i) The secondary carbocation (b) is more stable than the primary carbocation (a).
- ii) The carbocation (b) is attacked by Br^- ion to form the product as follows.



Anti Markovnikov's rule or Peroxide effect or Kharash effect:

In the presence of peroxide, addition of HBr to unsymmetrical alkenes (Ex: propene) takes place opposite to the Markovnikov's rule. This is possible only with HBr but not with HCl and HI. This addition reaction was identified by Kharash. **This reaction is known as peroxide effect or Kharash effect or anti Markovnikov's rule.**

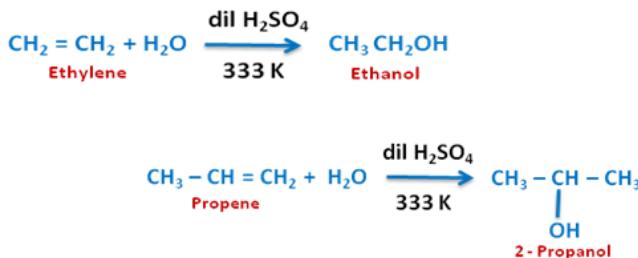




The secondary free radical obtained in the above mechanism (step iii) is more stable than the primary. This explains the formation of 1-bromopropane as the major product. It may be noted that the peroxide effect is not observed in addition of HCl and HI. This may be due to the fact that the H-Cl bond being stronger than the H-Br bond, is not cleaved by the free radical, whereas the H-I bond is weaker and iodine free radicals combine to form iodine molecules instead of adding to the double bond.

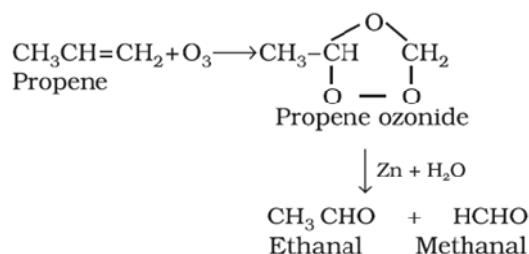
Addition of water:

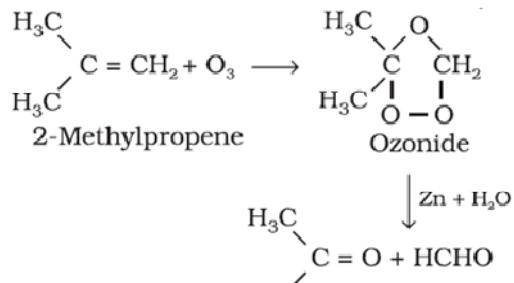
Alkenes undergo hydration in the presence of HgSO_4 and dil. H_2SO_4 at 333 K to give alcohols and carbonyl compounds respectively. This is according to Markovnikov's rule.



Ozonolysis:

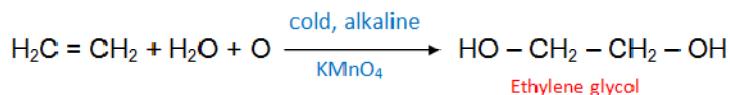
Ozonolysis is a test for unsaturation in molecule. Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by $\text{Zn-H}_2\text{O}$ to smaller molecules (carbonyl compounds). This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.



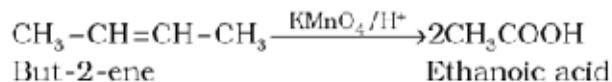
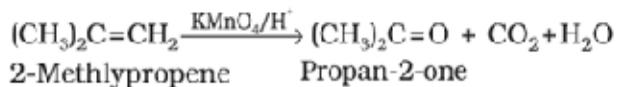


Oxidation reactions:

Alkenes undergo oxidation very easily and the oxidation takes place at the site of the π - bond.



Acidic KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ oxidizes alkenes to ketones or acids, depending on the nature of alkene.



Alkynes

Nomenclature of Alkynes:

The common names are given for alkynes as derivatives of acetylene. In IUPAC system, they are named by replacing 'ane' of alkane by 'yne'

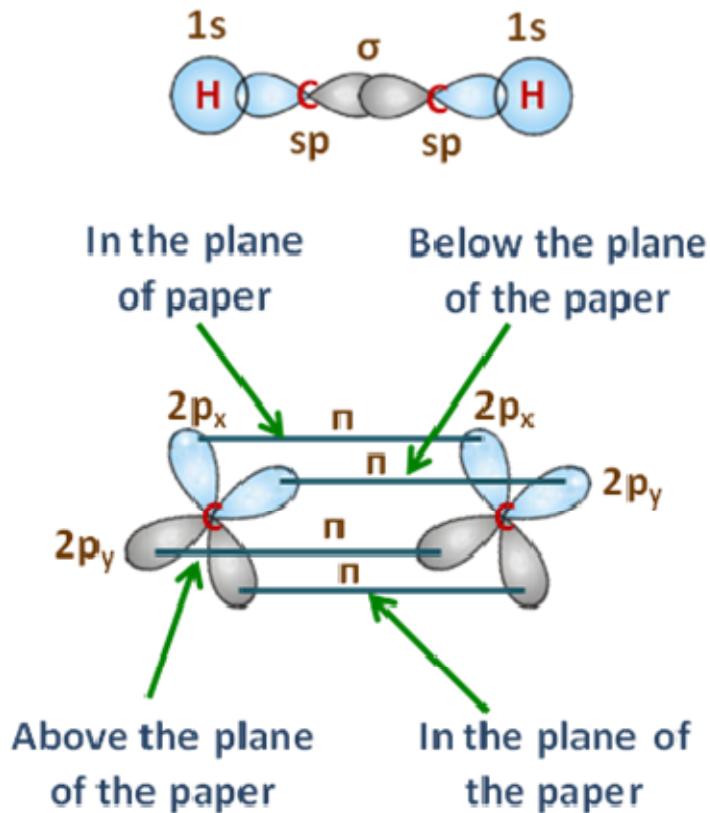
Structure	IUPAC name	Common name
$\text{CH} \equiv \text{CH}$	Ethyne	Acetylene
$\text{CH}_3 - \text{C} \equiv \text{CH}$	Propyne	Methyl acetylene
$\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$	2-Butyne	Dimethyl acetylene
$\text{CH}_3\text{CH}_2 - \text{C} \equiv \text{CH}$	1-Butyne	Ethyl acetylene
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H} - \text{C} \equiv \text{C} - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	3, 3-di methyl 1-butyne	Tertiary butyl acetylene

Nomenclature of Alkynes:

The general formula of alkynes is C_nH_{2n-2} . The first member is called as acetylene.

Structure of triple bond in alkynes:

Ethyne is the simplest molecule of alkyne series. Structure of ethyne is shown in figure.



Each carbon atom of ethyne has two sp hybridized orbitals. Carbon-carbon sigma (σ) bond is obtained by the head-on overlapping of the two sp hybridized orbitals of the two carbon atoms. The remaining sp hybridized orbitals of each carbon atom undergoes overlapping along the inter nuclear axis with the 1s orbital of each of the two hydrogen atoms forming two C —H sigma bonds. H-C-C bond angle is of 180° . Each carbon has two unhybridized p orbitals which are perpendicular to each other as well as to the plane of the C—C sigma bond. The 2p orbitals of one carbon atom are parallel to the 2p orbitals of the other carbon atom, which undergo lateral or sideways overlapping to form two pi (π) bonds between two carbon atoms. Thus ethyne molecule consists of one

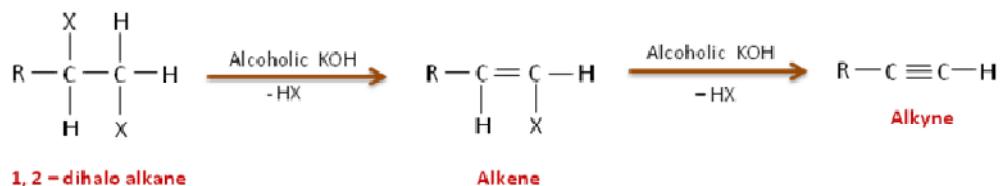
C-C σ bond, two C-H α bonds and two C-C π bonds. The strength of C=C bond (bond enthalpy 823 kJmol $^{-1}$) is more than those of C=C bond (bond enthalpy 681 kJmol $^{-1}$) and C-C bond (bond enthalpy 348 kJmol $^{-1}$). The C =C bond length is shorter (120pm) than those of C=C (133pm) and C-C (154pm).

Electron cloud between two carbon atoms is cylindrically symmetrical about the inter nuclear axis thus, ethyne is linear molecule.

Preparation methods of alkynes:

1. Dehydro halogenation of 1,2-dihalo alkanes:

When 1,2-dihalo alkenes are treated with alcoholic KOH at 100 °C, hydrogen atom and a halogen atom from adjacent carbon atoms are eliminated as hydrogen halide, finally forming alkyne.

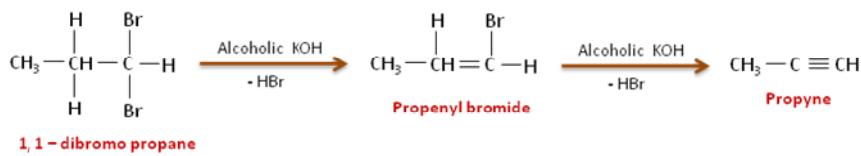
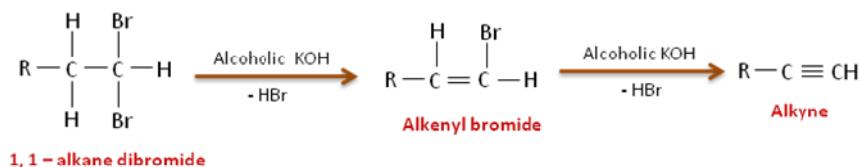


However when sodamide (NaNH_2) is used for dehydro halogenations the difficulty is overcome and this reagent causes the migration of the triple bond towards the end of the carbon chain to give pure 1-alkyne.



2. Dehydro halogenations of 1,1-dihalides:

When 1,1-dihalides are treated with either alcoholic KOH, (or) sodamide double dehydrohalogenation takes place giving 1-alkynes.



Physical Properties:

First three members of alkynes are gases, next eight members are liquids, and higher alkynes are solids. They are colourless, weakly polar, lighter than water not soluble in water but soluble in organic solvents like ethers, CCl_4 , C_6H_6 . Their melting points boiling points and density increase with increase in molecular weight.

General properties of alkynes:

The comparative chart of bond energy and bond length of alkane, alkene and alkyne is given below:

Their melting points boiling points and density increase with increase in molecular weight.

General properties of alkynes:

The comparative chart of bond energy and bond length of alkane, alkene and alkyne is given below:

	Bond	Hybridized bond orbitals	Bond length	Bond energy
Alkane	C—C	$\text{sp}^3\text{—sp}^3$	1.54 Å	82.76 kcal mol ⁻¹
	C—H	$\text{sp}^3\text{—1s}$	1.112 Å	98.67 kcal mol ⁻¹
Alkene	C=C	$\text{sp}^2\text{—sp}^2$	1.34 Å	143.1 kcal mol ⁻¹
	C—H	$\text{sp}^2\text{—1s}$	1.108 Å	98.69 kcal mol ⁻¹
Alkyne	C≡C	$\text{sp}\text{—sp}$	1.20 Å	192.00 kcal mol ⁻¹
	C—H	$\text{sp}\text{—1s}$	1.08 Å	102.38 kcal mol ⁻¹

Bond length	:	$\text{C}-\text{C} > \text{C}=\text{C} > \text{C}\equiv\text{C}$
Bond energy	:	$\text{C}-\text{C} < \text{C}=\text{C} < \text{C}\equiv\text{C}$
Stability of bond	:	$\text{C}-\text{C} < \text{C}=\text{C} < \text{C}\equiv\text{C}$
Reactivity of bond	:	$\text{C}-\text{C} < \text{C}=\text{C} < \text{C}\equiv\text{C}$
Rigidity in bond	:	$\text{C}-\text{C} < \text{C}=\text{C} < \text{C}\equiv\text{C}$

The more reactivity of $\text{C}\equiv\text{C}$ inspite of higher bond energy is due to the presence of π bonds.

Acetylene and all terminal alkynes are acidic in nature i.e., H atom attached on triple bonded C atom behaves as acidic. The acidic character is due to the fact that in acetylene or triply bonded C atom, an increase in s Character (sp hybridization) give rise to higher electronegativity to C atom and thus H atom in C-H (i.e. sp-1s) bond acquires more polarity to show acidic nature.

The acidic nature order however shows,



Chemical properties of alkynes:

Acidity of alkynes:

This can be shown by the following reactions

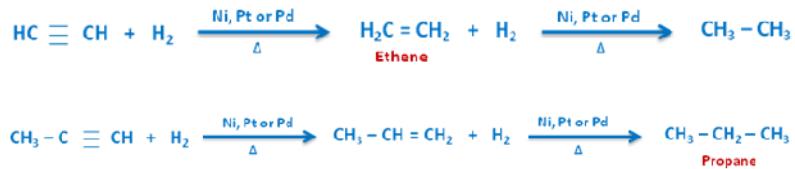


Addition reactions:

Alkenes are the rich source of loosely held electrons, due to which they show addition reactions in which the electrophiles add on to the carbon –carbon double bond to form the addition products (electrophilic addition).

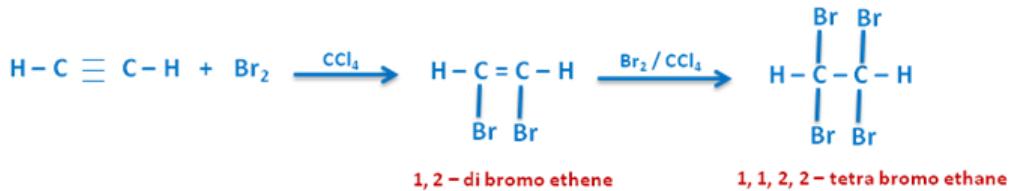
Addition of dihydrogen:

Alkynes undergo addition reactions with H_2 in presence of catalyst like Pt, Pd or Ni and on heating, give saturated hydrocarbons (alkanes). The reaction is known as Sabatier-Senderen's reaction.



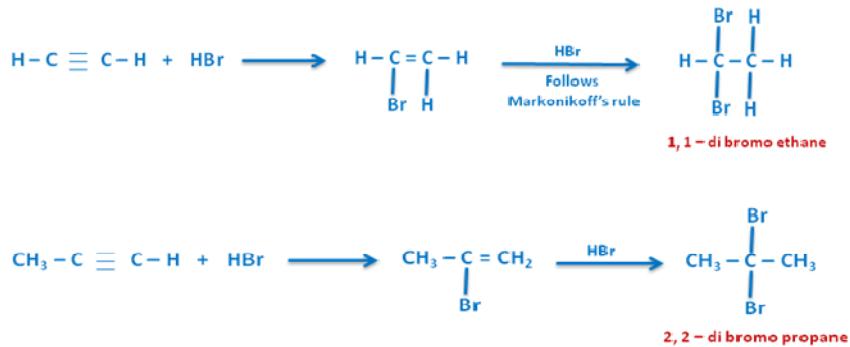
Addition of halogen (halogenation):

Halogen like Br_2 or Cl_2 can be added to alkynes in CCl_4 , at room temperature, to give tetrahalides.



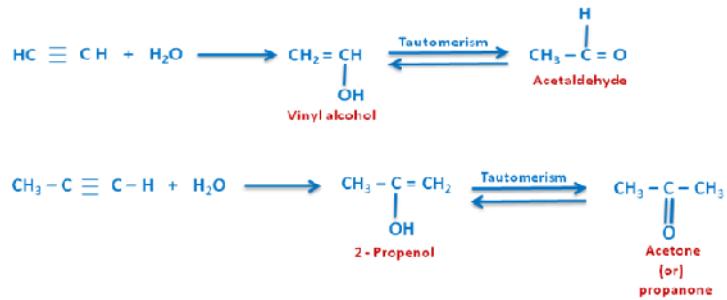
Addition of hydrogen halide (hydro halogenation):

Addition of hydrogen halide to alkynes gives gem dihalides.



Addition of water:

Alkynes undergo hydration in the presence of HgSO_4 and dil. H_2SO_4 at 333 K to give carbonyl compounds respectively.

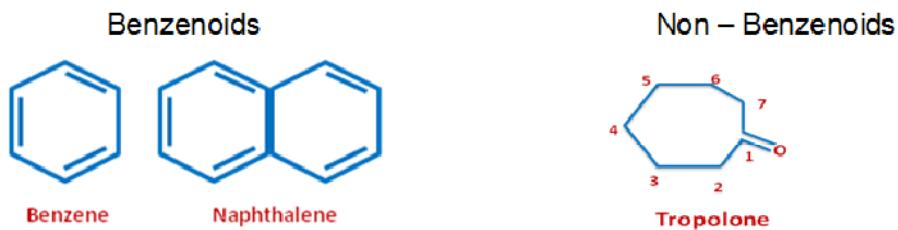


Unit-VI

Aromatic Hydrocarbons

Organic compounds are classified as aliphatic and aromatic compounds. The original meaning of aliphatic is "fat like" and aromatic means fragrant. Kekule was the first person to introduce the word "aromatic".

The meaning of aromatic hydrocarbons relates to stable ring compounds with unsaturation. In most of the aromatic compounds benzene ring is present. In these actions of aromatic compounds, the unsaturation of benzene ring is retained. Some of the aromatic compounds do not contain rings with benzene ring but contain highly unsaturated structure. These compounds are called as non-benzenoid compounds. Aromatic hydrocarbons with benzene ring are called as benzenoid compounds.

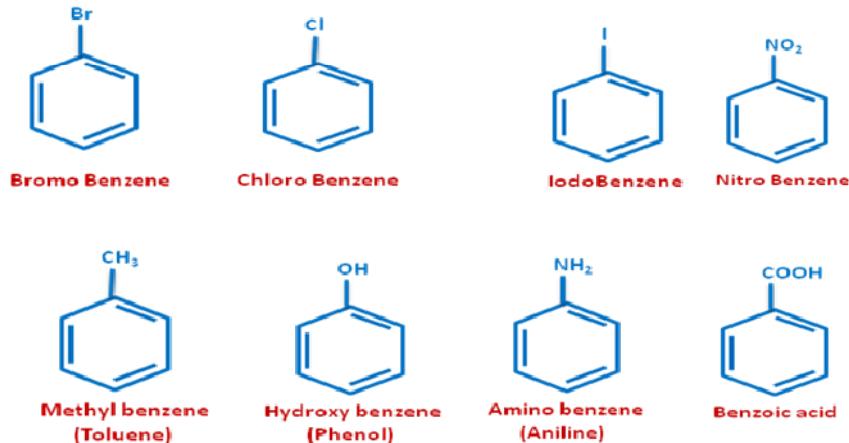


Nomenclature & Isomerism:

For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word *benzene* as shown in the following examples. However, common names (written in bracket below) of many substituted benzene compounds are also universally used.

A. Nomenclature of mono substituted benzene derivatives:

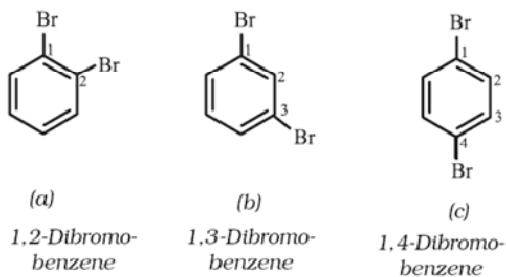
Mono substituted benzenes have anyone (H) atom substituted by an atom or a group. As all the six carbon atoms and six hydrogen atoms in the benzene ring are equivalent, benzene has only one mono substituted product. For writing the name of the compound; substituent name is given as a prefix followed by the word benzene.



Note: The names given in brackets are the common names
 C_6H_5- is called as Phenyl.
 $C_6H_5-CH_2-$ is called as Benzyl.

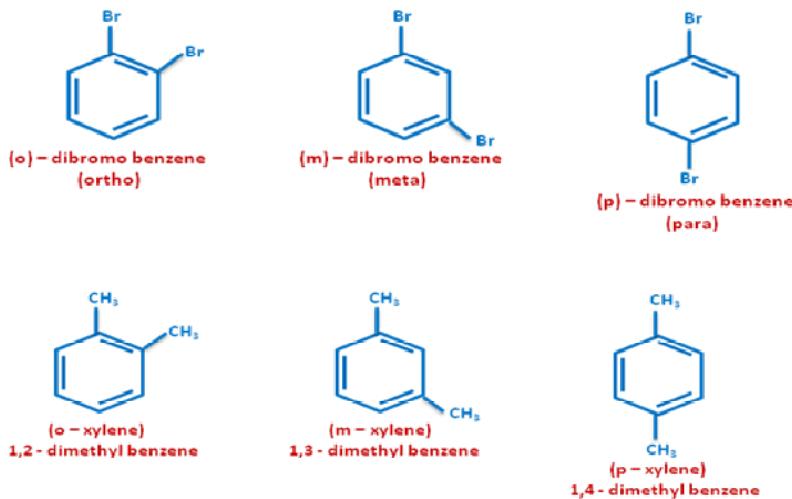
B. Disubstituted benzenes Nomenclature:

If benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible. For example, the compound (b) below is named as 1,3-dibromo benzene and not as 1,5-dibromobenzene.



Based on the position of the second substituent, three positional isomers are possible for disubstituted benzene. If the two substituent's are present on 1st and 2nd carbon atoms (i.e. adjacent if positions of the benzene ring, the isomer is called as "orthon (o-) compound.) substituents are present on 1st and 3rd carbon atoms of the benzene ring the isomer is called as "metan (m-) compound. If the two substituents are present on 1st and 4th carbon atoms the isomer is called as para (p-). This terminobgy of ortho, meta and para compounds is used with the trivial names of the parent compounds.

Exmaple:



C. Trisubstituted benzenes:

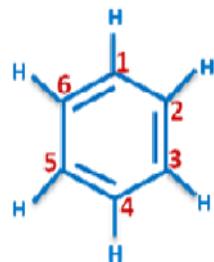
Based on the position of second and third substituents, different positional isomers are possible.



Structure of Benzene:

- 1) Eilhard Mitscherlich determined the molecular formula of Benzene as C₆H₆. As it has very less no.of (H) atoms, benzene must be a highly unsaturated compound. (Compared to n-hexane; molecular formula - CsH₆,).
- 2) Benzene, with the molecular formula C₆H₆, is highly unsaturated, if it is to be a straight chain compound. It should give the properties of unsaturation and must be highly reactive. Ex-addition reactions. But,
 - i) Benzene does not decolourise Br₂ – water
 - ii) Benzene does not react with alkaline KMnO₄
 - iii) Benzene does not undergo hydration in dil. Acid (all are specific reactions of unsaturated compounds).

Kekulé in 1858 proposed ring structure for benzene



- Benzene reacts with Br_2 (in presence of FeBr_3 catalyst) gives only one mono substituted product, Bromo benzene.

∴ In Benzene all six 'C' atoms and six hydrogen atoms are equivalent.

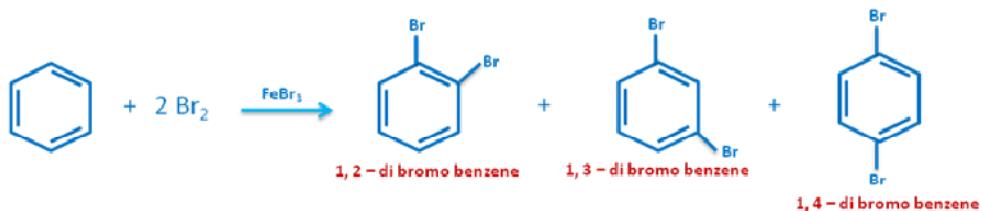


- Benzene reacts with 3 moles of H_2 with Ni catalyst and produces cyclohexane.



Therefore it is inferred that Benzene exists in ring structure.

- Benzene reacts with 2 moles of Br_2 in FeBr_3 catalyst and gives three isomeric disubstituted compounds.



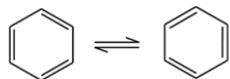
In ortho disubstituted Benzene two isomers are possible.

Ex:



The Kekulé structure indicates the possibility of two isomeric 1,2-dibromo benzenes. In

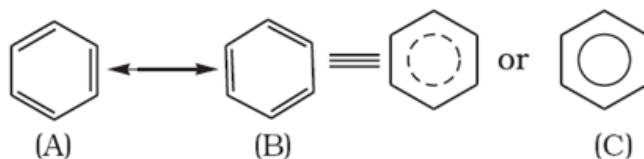
one of the isomers, the bromine atoms are attached to the doubly bonded carbon atoms where as in the other, they are attached to the singly bonded carbons. However, benzene was found to form only one ortho disubstituted product. This problem was over come by Kekule by suggesting the concept of oscillating nature of double bonds in benzene as given below.



Even with this modify cabon, Kekulé structure of benzene fails to explain unusual stability and preference to substitution reactions than addition reactions, which could later on be explained by resonance.

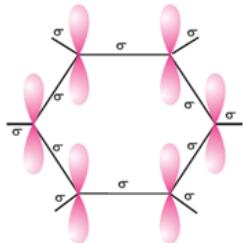
Resonance and stability of benzene:

According to Valence Bond Theory, the concept of oscillating double bonds in benzene is now explained by resonance. Benzene is a hybrid of various resonating structures. The two structures, A and B given by Kekulé are the main contributing structures. The hybrid structure is represented by inserting a circle or adotted circle in the hexagon as shown in the figure. The circle represents the six electrons which are delocalized between the six carbon atoms of the benzene ring.

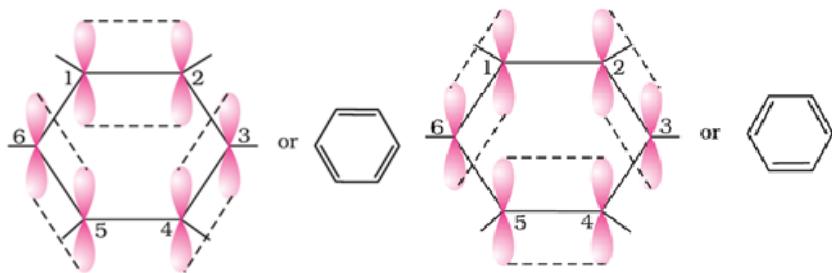


The difference in energy between the calculated energy of actual structure and the experimental energy of resonance hybrid is called Resonance energy or resonance stabilization energy. Resonance energy of benzene is 36 cal mol⁻¹.

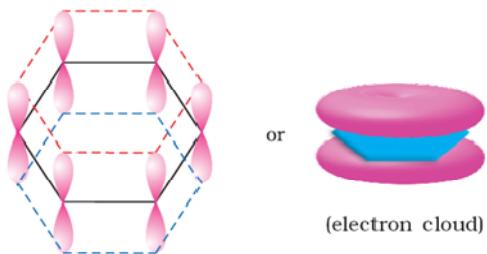
The orbital overlapping gives us better picture about the structure of benzene. All the six carbon atoms in benzene are sp^2 hybridized. Two sp^2 hybrid orbitals of each carbon atom overlap with sp^2 hybrid orbitals of adjacent carbon atoms to form six C-C sigma bonds which are in the hexagonal plane. The remaining sp^2 hybrid orbital of each carbon atom overlaps with s orbital of a hydrogen atom to form six C-H sigma bonds. Each carbon atom is now left with one un-hybridised p orbital perpendicular to the plane of the ring as shown below:



The unhybridised p -orbital of carbon atoms are close enough to form a π bond by lateral overlap. There are two equal possibilities of forming three π bonds by overlap of p -orbitals.



The inter nuclear distance between all the carbon atoms in the ring has been determined by the X-ray diffraction to be the same; there is equal probability for the p -orbital of each carbon atom to overlap with the p -orbitals of adjacent carbon atoms. This can be represented in the form of two rings of electron clouds, one above and one below the plane of the hexagonal ring as shown below:



The six π electrons are thus delocalized and can move freely about the six carbon nuclei, instead of any two. The delocalized π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localized between two carbon atoms. Therefore, presence of delocalized n electrons in benzene makes it more stable than the Hypothetical cyclohexatriene. X-Ray diffraction data reveals that benzene is a planar molecule. Two types of C-C bond lengths were expected. However, X-ray data indicates that all the six C-C bond lengths are of the same order (139 pm) which is intermediate

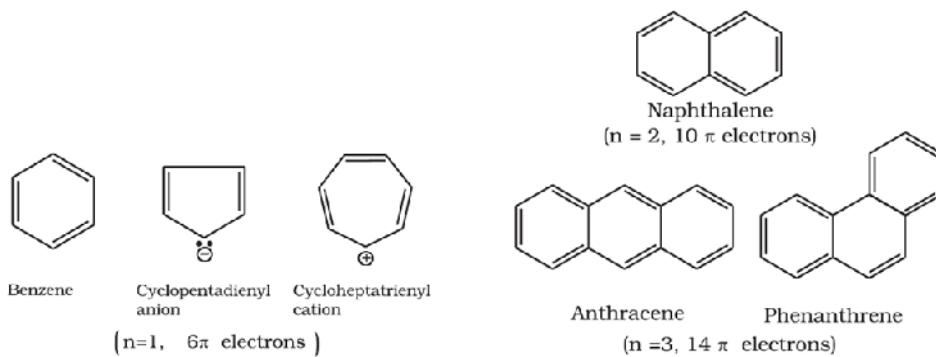
between C-C single bond (154pm) and C-C double bond (133 pm). Thus the absence of pure double bond in benzene accounts for the reluctance of benzene to show addition reactions under normal conditions, thus explaining the unusual Behavior of benzene.

Aromatic character (Aromaticity):

Benzene was considered to be the parent aromatic compound. But now the name aromatic character is better described for the aromatic compounds which possess the following characteristics. (These compounds may or may not contain benzene ring)

- a. Flat ring structure.
- b. Delocalization of πe^- cloud and possess Resonance energy. They are highly stable and undergo mostly substitution reactions.
- c. Each atom in an aromatic ring has a p orbital. These p-orbitals must be parallel.
- d. The molecules obeys Huckel's rule.

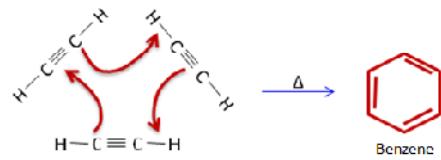
Huckel rule states that in a ring the delocalized π -orbitals must contain a total no.of $(4n+2)$ π -electrons. (Where 'n' stands for an integer).



Preparation methods of benzene:

(i) Cyclic polymerisation:

Alkynes undergo cyclic polymerization. For example, when acetylene is passed through a red hot iron tube at 873 K undergoes cyclic polymerization to give benzene.

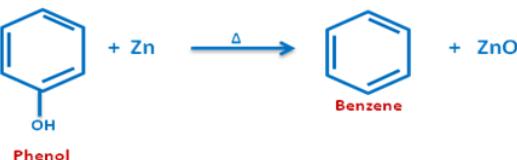


(ii) Decarboxylation of sodium salt of benzoic acid:

Heat sodium salt of Benzoic acid (sodium benzoate) with soda lime gives benzene.



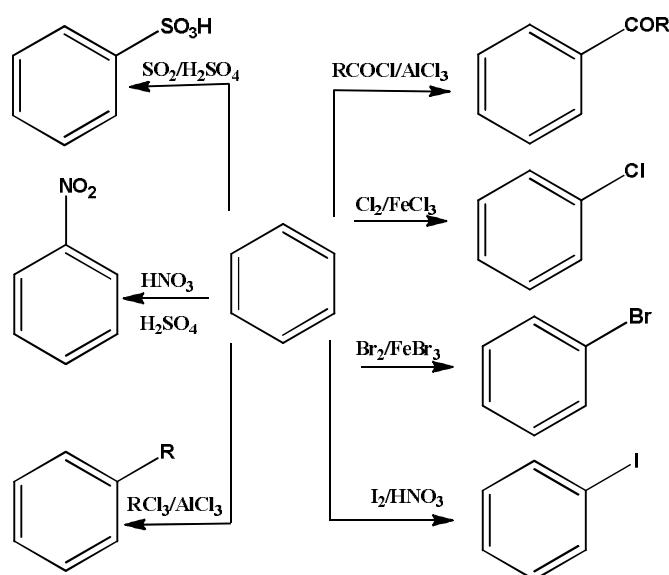
(iii) Reduction of phenol: Heat phenol with Zn dust gives benzene.



Chemical properties of Aromatic hydrocarbons (Arenes):

The characteristic reactions of arenes are electrophilic aromatic substitution reactions. The most important electrophilic aromatic substitution reactions are halogenations, nitration, sulphonation, Friedel-Crafts alkylation and Friedel-Crafts acylation.

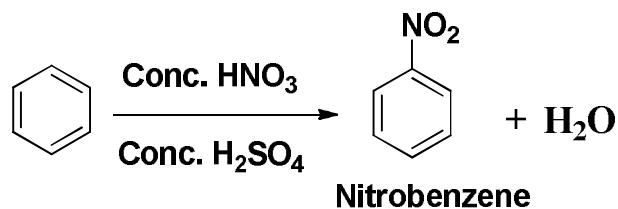
1. Electrophilic aromatic substitution reactions of benzene:



a. Nitration:

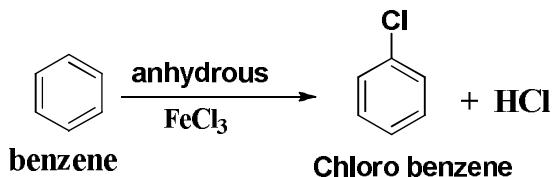
A nitro group is introduced into benzene ring when benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid.

Nitration mixture: Conc. HNO_3 + Conc. H_2SO_4



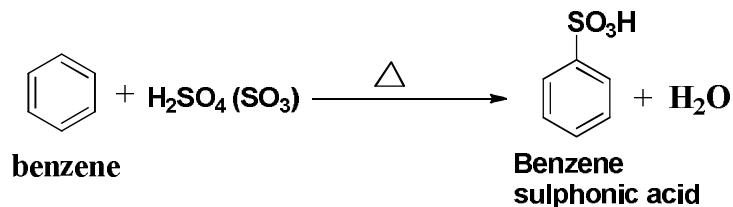
b. Halogenation:

Benzene reacts with halogens in the presence of a Lewis acid (catalyst) like anhydrous AlCl_3 , FeCl_3 and FeBr_3 produces halobenzene.



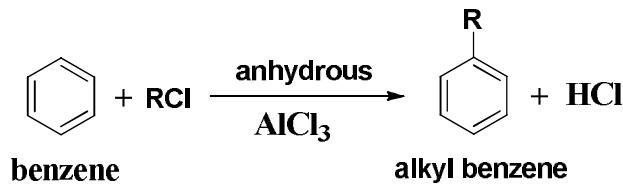
c. Sulphonation:

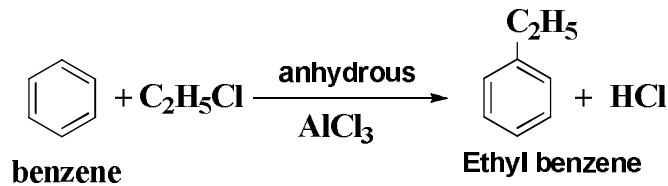
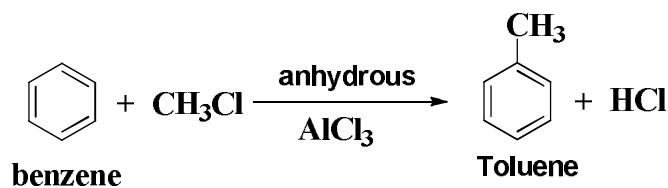
The replacement of a hydrogen atom by a sulphonic acid group in a ring is called sulphonation. It is carried out by heating benzene with fuming sulphuric acid (oleum).



d. Friedel-Craft's alkylation

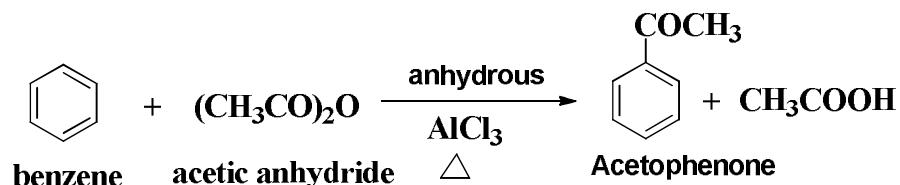
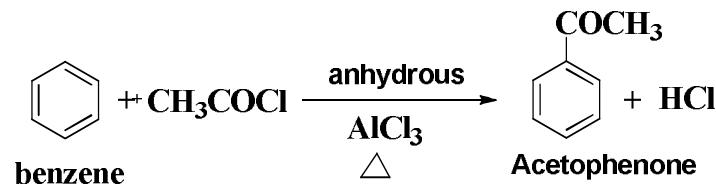
Benzene reacts with alkyl halides in presence of Lewis acids i.e (anhydrous AlCl_3 , or FeCl_3 or FeBr_3) and produces alkyl benzene.





e. Friedel-Craft's acylation:

Benzene reacts with acyl halides in presence of Lewis acid (anhydrous AlCl_3 or FeCl_3 or FeBr_3) and produces acyl benzene.



Mechanism of electrophilic aromatic substitution reactions:

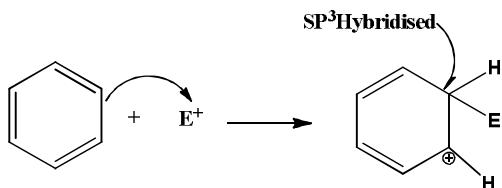
Electrophilic aromatic substitution reactions are supposed to proceed via the following three steps:

- Generation of the eletrophile (Formation of electrophile)
- Formation of carbocation intermediate (attack of eletrophile)
- Removal of proton from the carbocation intermediate (Removal of internal electrophile)

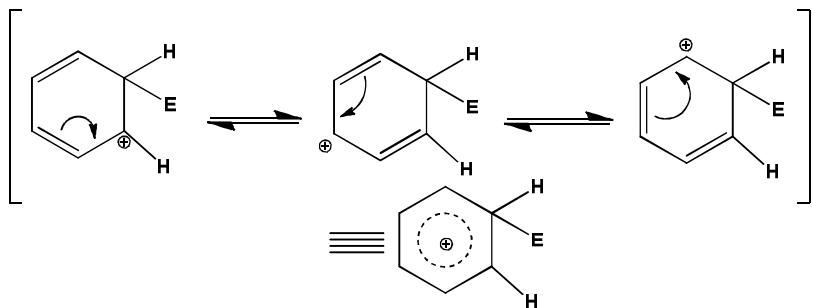
(a) Generation of electrophile: During chlorination, alkylation and acylation of benzene, anhydrous AlCl_3 , being a Lewis acid helps in generation of the elctrophile Cl^+ , R^+ , RC^+O (acylium ion) respectively by combining with the attacking reagent.

(b) Formation of Carbocation (arenium ion):

Attack of electrophile results in the formation of sigma -complex or arenium ion in which one of the carbon is sp^3 hybridised.



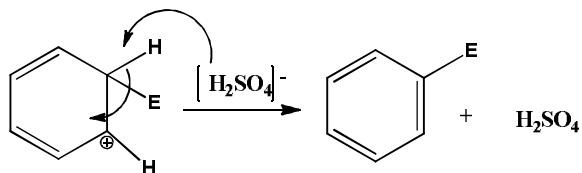
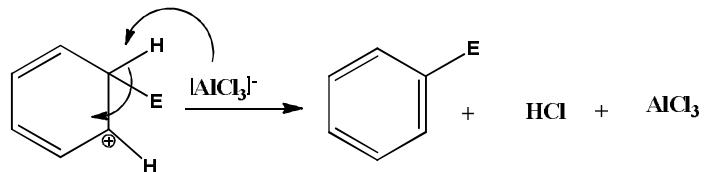
sigma complex (arenium ion) The arenium ion gets stabilised by resonance:



Sigma complex or arenium ion loses its aromatic character because delocalisation of electrons stops at sp^3 hybridised carbon.

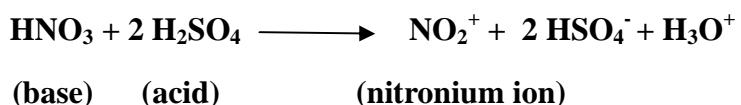
(c) Removal of proton:

To restore the aromatic character, a -complex releases proton from sp^3 hybridised carbon on attack by $[AlCl_3]$ (in case of halogenation, alkylation and acylation) and $[H_2SO_4]$ (in case of nitration).

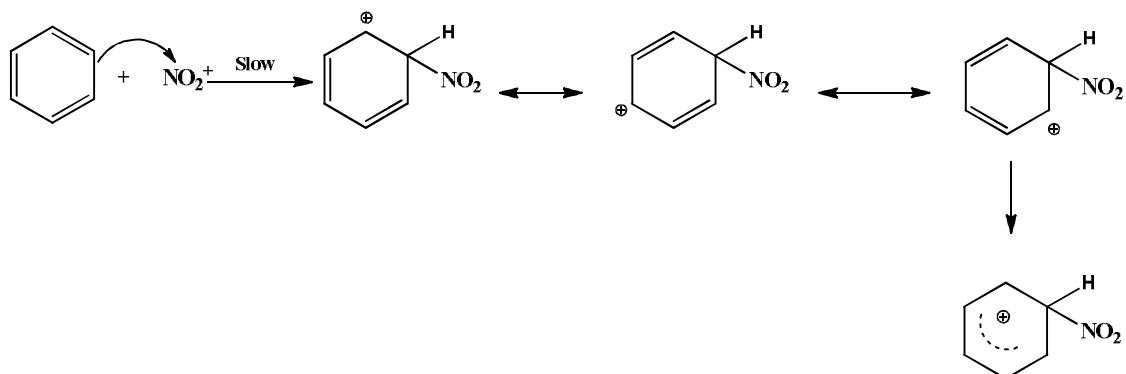


Nitration:

Step I: Formation of electrophile:



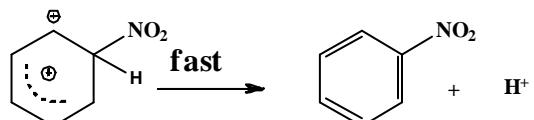
Step II: Electrophilic attack leads to form carbocation (areneum ion):



In the intermediate stage, attacked carbon atom changes its state of hybridization from trigonal planar to tetrahedral.

$$\text{Rate} = K[\text{substrate}] [\text{NO}_2]$$

Step III: Loss of proton:

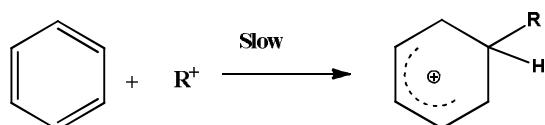


Friedel- craft alkylation:

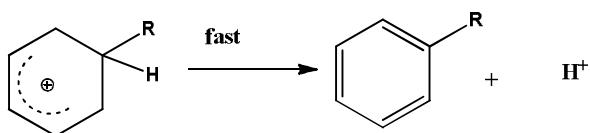
Step-1: Formation of electrophile (carbonium ion) stability order of carbonium ion is



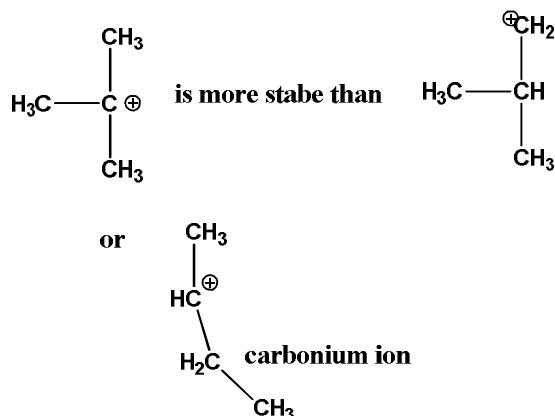
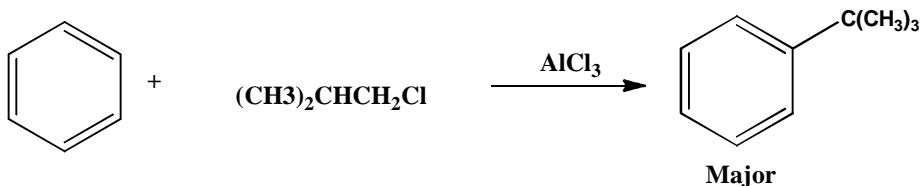
Step-2:



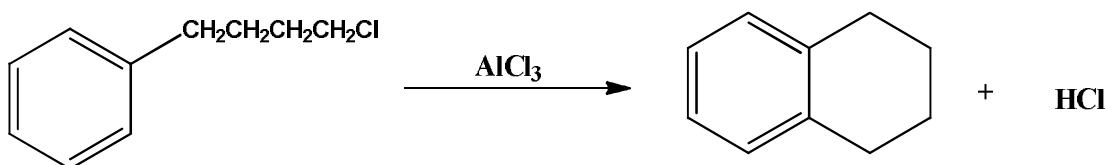
Step-3



Examples:



This is an example of intermolecular Fridal Craft alkylation. But if the side chain contain four or five carbons with halogen at the end then it may undergo intramolecular Fridal- Craft reaction.



Aromatic Hydrocarbons

Substitution in monosubstitutedbenzenes:

All hydrogen atoms of benzene ring are equivalent. Therefore, only one mono substituted product is possible a substituent already on the benzene ring exercises two types of influence on further substitution.

1) Direction or Orientation Effect:

The first substituent may direct the next incoming substituent to ortho, meta or para position, depending on the nature of the first substituent. This is called the directive or the orientation effect.

2) Activity Effect:

The substituent already present may activate or deactivate the benzene ring toward further substitution. These effects are called the activity effects.

Substituted rings are divided into two groups based on the type of the substituent that the ring carries:

1. Activated rings: the substituents on the ring are groups that donate electrons.
2. Deactivated rings: the substituents on the ring are groups that withdraw electrons.

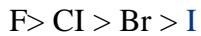
Examples of activating groups in the relative order from the most activating group to the least activating:

-NH₂, -NR₂, -OH, -OR > -NHCOR > -CHP and other alkyl groups (Here R= alkyl group)

Examples of deactivating groups in the relative order from the most deactivating to the least deactivating:

-NO₂, -CF₃ > -COR, -CN, -CO₂R, -SO₃H > Halogens

The order of reactivity among halogens from the more reactive (least deactivating substituent) to the least reactive (most deactivating substituent) halogen is:

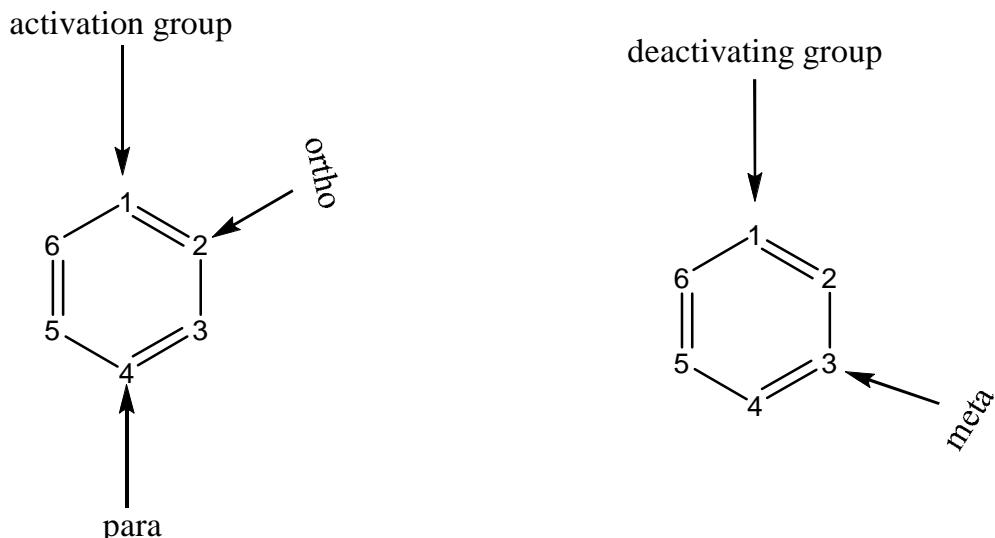


The order of reactivity of the benzene rings toward the electrophilic substitution when it is substituted with a halogen group, follows the order of electronegativity. The ring that is substituted with the most electronegative halogen is the most reactive ring (less deactivating substituent) and the ring that is substituted with the least electronegative halogen is the least reactive ring (more deactivating substituent), when we compare rings with halogen substituents.

Also the size of the halogen affects the reactivity of the benzene ring that the halogen is attached to. As the size of the halogen increases, the reactivity of the ring decreases.

The direction of the reaction

The activating group directs the reaction to the ortho or para position, which means the electrophile substitute the hydrogen that is on carbon 2 or carbon 4. The deactivating group directs the reaction to the meta position, which means the electrophile substitute the hydrogen that is on carbon 3 with the exception of the halogens that is a deactivating group but directs the ortho or para substitution.



Substituents determine the reaction direction by resonance or inductive effect

Resonance effect is the conjugation between the ring and the substituent, which means the delocalizing of the pi electrons between the ring and the substituent.

Inductive effect is the withdraw of the sigma (the single bond) electrons away from the ring toward the substituent, due to the higher electro negativity of the substituent compared to the carbon of the ring.

Activating groups, ortho or para directors:

When the substituents like -OH have an unshared pair of electrons, the resonance effect is stronger than the inductive effect which make these substituents stronger activators, since this resonance effect direct the electron toward the ring. In cases where the substituents is esters or

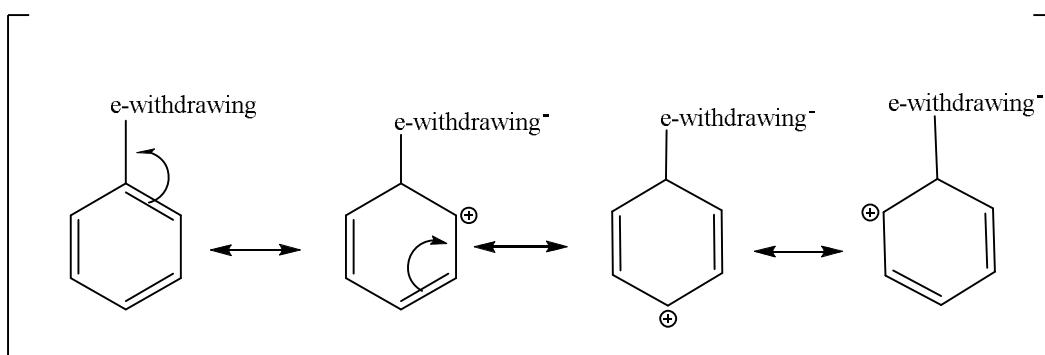
amides, they are less activating because they form resonance structure that pull the electron density away from the ring.

By looking at the mechanism above, we can see how groups donating electron direct the ortho, para electrophilic substitution. Since the electrons location transfer between the ortho and para carbons, then the electrophile prefer attacking the carbon that has the free electron.

Inductive effect of alkyl groups activates the direction of the ortho or para substitution, which is when s electrons gets pushed toward the ring.

Deactivating groups meta directors:

The deactivating groups deactivate the ring by the inductive effect in the presence of an electronegative atom that withdraws the electrons away from the ring.



We can see from the mechanism above that when there is an electron withdraws from the ring, that leaves the carbons at the ortho, para positions with a positive charge which is unfavourable for the electrophile, so the electrophile attacks the carbon at the meta positions.

Halogens are an exception of the deactivating group that directs the ortho or para substitution. The halogens deactivate the ring by inductive effect not by the resonance even though they have an unpaired pair of electrons. The unpaired pair of electrons gets donated to the ring, but the inductive effect pulls away the s electrons from the ring by the electronegativity of the halogens.

Substituents determine the reactivity of rings

The reaction of a substituted ring with an activating group is faster than benzene. On the other hand, a substituted ring with a deactivated group is slower than benzene.

Activating groups speed up the reaction because of the resonance effect. The presence of the unpaired electrons that can be donated to the ring, stabilize the carbocation in the transition state. Thus; stabilizing the intermediate step, speeds up the reaction; and this is due to the decrease of the activating energy. On the other hand, the deactivating groups, withdraw the electrons away from the carbocation formed in the intermediate step, thus; the activator energy is increased which slows down the reaction.

Orientation and reactivity effects of some of the functional groups are given in the followings.

1. Ortho, para directors or ring activating groups: (Strongly activating groups) - OH, - NH₂ -NHR, -NR₂ -NHCOCH₃, -OCH₃

(Weakly activating groups): -C₂H₅, -R, —CH₃

2. Ortho, para directors but deactivating groups: (Strongly activating groups) -F, -Cl, - Br, - I

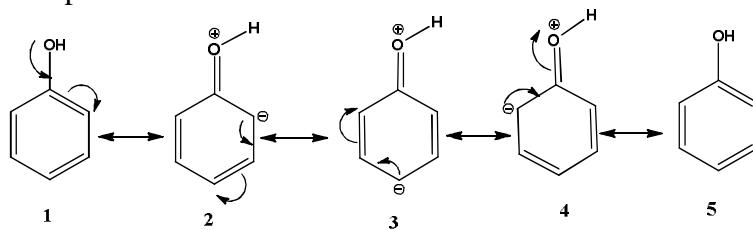
3. Meta directors and strongly deactivating groups: (Strongly activating groups) -CN, - SO₃H, COOH, - COOR, -CHO, -COR, -NO₂, -NR₃, -CF₃, -CCl₃

The reactivity of compounds with activating groups is more than that of Benzene. The reactivity of compounds with deactivating groups is less than that of Benzene

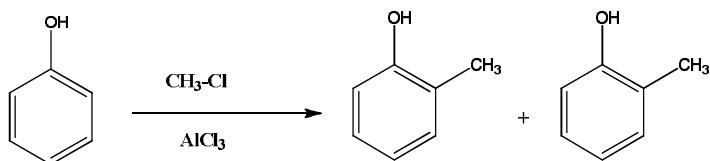
Directional effects with examples:

a. ortho — para directors:

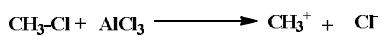
Example: Consider phenol



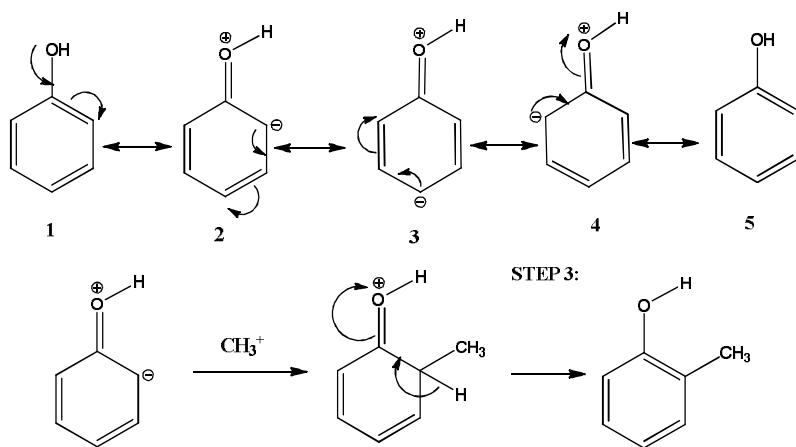
In phenol oxygen has lone pair of electrons. This lone pair of electrons are utilized in resonance in the benzene ring. It results in the high electron density at ortho and para positions. Electrophilic substitution taken place at ortho or para position (major product). In phenols due to high electronegativity of oxygen atom — I effect (inductive effect) operates: as a result of the inductive effect electron density at ortho - para position is reduced. However resonance effect overweight (stronger) inductive effect. Hence electron density centers are created at ortho and para positions only. Therefore ortho or para disubstituted product is the major product. The other ortho and para directing groups also operate in a similar way are — NH₂ —NHR, — NHCOCH₃, -NR₂, — OCH₃, -CH₃, -C₂H₅ etc.



STEP 1:



STEP 2:



In the case of aryl halides, halogens are moderately deactivating. Because of their strong — I effect, overall electron density on benzene ring decreases. It makes further substitution difficult. However, due to resonance the electron density on o—and p—positions are greater than that at the m-position. Hence, they are also o—and p—directing groups.

b. Meta — directors:

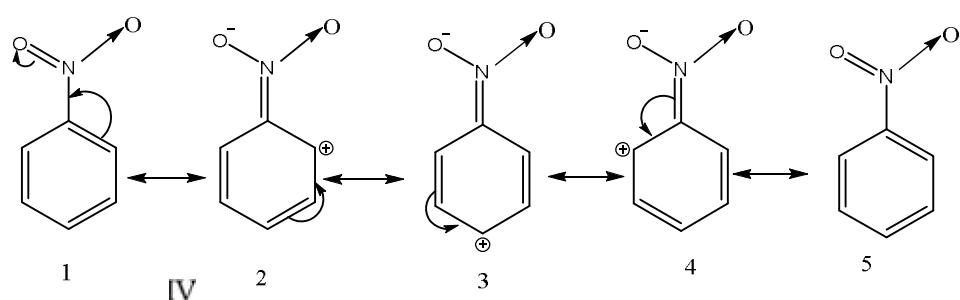
The functional groups or substituents, which generate carbocation at the ortho or para positions in the resonating structures, are meta directors. Some examples of *meta* directing groups are —NO₂, CN, —CHO, —COR, —COOH, —COOR, —SO₃H, etc.

They form meta disubstituted benzene as the major product. In the resonating structures

positive charge is at ortho, para position but not on meta position. Electrophilic substitution occurs on meta position. Therefore there is less scope for electrophilic attack at ortho or para positions. This decreases the reactivity of m-directing mono substituted benzene compared to simple benzene. These groups are called as ring deactivating groups.

Ex: nitro benzene nitro group is ring deactivating and meta directing.

Resonating structures are given below



In this case, the overall electron density on benzene ring decreases making further substitution difficult, therefore these groups are also called ‘deactivating groups’. The electron density on o—and p—position is comparatively less than that at meta position. Hence, the electrophile attacks on comparatively electron rich *meta* position resulting in *meta* substitution.