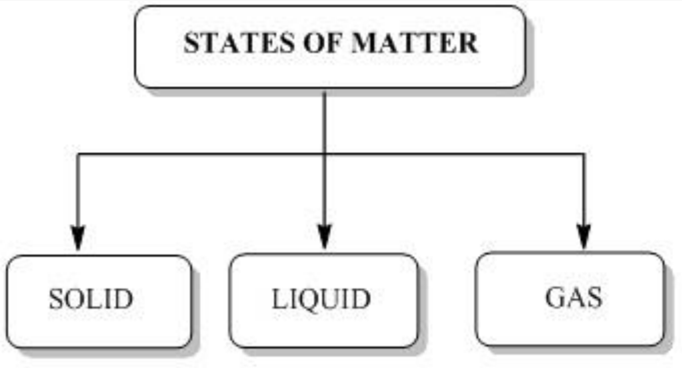
Introduction

Everything in our surroundings is known as matter that can be categorized into three states.



In our day to day life solids plays a crucial role to pursue different purposes. Different types of solids with different properties are required for different purposes. The constituent particles and the type of bonds between the particles determine the nature of a specific solid. For eg. Bucket or a container used to carry water, utensils used for cooking food, computer, vehicles, electronic gadgets, notebooks, pencils, papers etc. are all solid substances used in our day to day life.

Liquids and gases on the other hand are another state of matter and are also known as *fluids* due to their ability to flow. They attain the ability to flow due to the free movement of molecules.

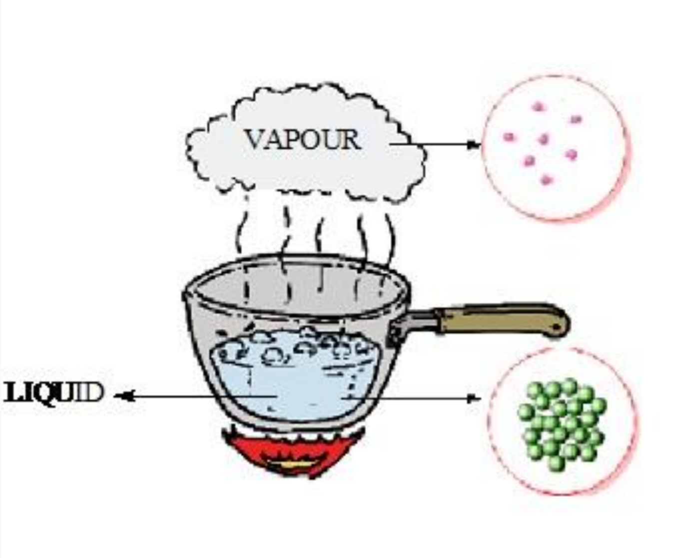


Fig. Particles of liquid (water) are loosely packed than solid and have space between them whereas particles of gas are loosely packed and have excess space between the particles

Characteristics of solid state

- They have definite shape due to strong Intermolecular forces of attraction.
- They have distinct boundaries.
- They have a fixed volume.
- They cannot flow.
- They have negligible compressibility due to negligible distance between the neighbouring molecules.
- They possess a tendency to uphold their shape when exposed to external force.
- They break under force but it is difficult to change their shape so they are rigid.
- They have high density and do not diffuse at all.

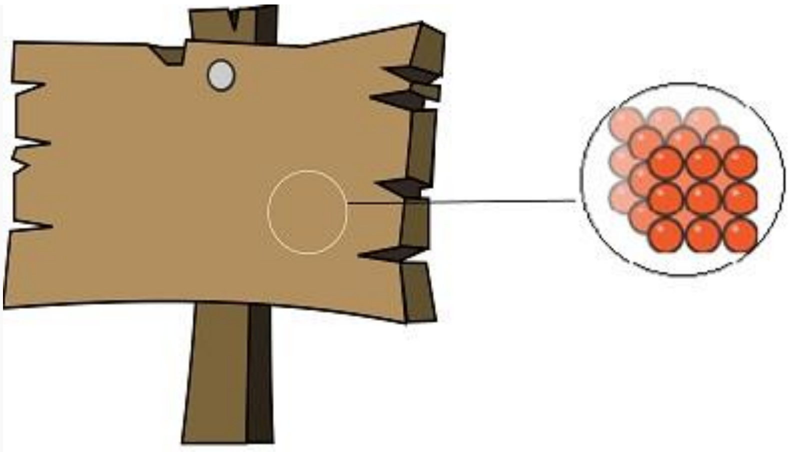


Fig. Particles of solid (Wooden plank) are compact together and have less space between them

Amorphous Solids

- The term amorphous solid is derived form a Greek word ***amorphous*** meaning ***no form***.
- The constituent particles are arranged in a *short range order* with a regular and periodically repeating pattern over short distances.
- These solids get softened at a certain temperature and hence can be moulded and drawn into various desired shapes. Solids may also acquire crystalline form at some temperature when heated.
- These solids have the ability to flow very slowly due to which they are also termed as pseudo solids or super cooled liquids.
- These solids are isotropic in nature due to the absence of long range order and irregular arrangement of the constituent particles in all direction. This leads to same value of physical property along all the direction.

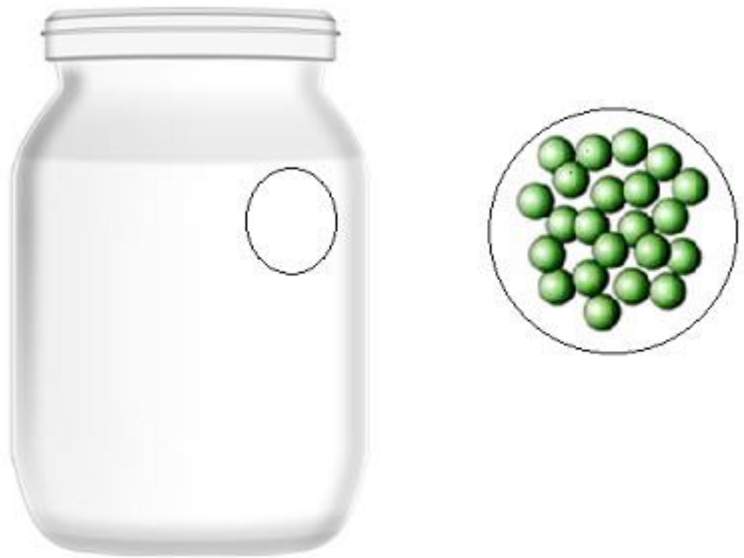


Fig. Irregular arrangement of particles in an amorphous solid

- Glass, rubber, amorphous silicon and plastics are typical examples of amorphous solids.
- Amorphous silicon is a photovoltaic material widely used for conversion of sunlight into electricity.

Fig. The glass used in making glassware, rubber used in making hot water bags and cotton candy are amorphous solids

Crystalline Solids

- This range of solids consists of a broad range of small crystals having a definite characteristic geometrical shape.

Fig. Crystals are crystalline solids

- The constituent particles are arranged in a long range order (symmetry and regularity of arrangement of constituent particles that repeat at any distance from a given atom due to the interaction between the particles) with a regular and periodically repeating pattern over the entire crystal.

- Crystalline solids possess a sharp melting point.
- Crystalline solids are *anisotropic* in nature due to different arrangement of particles in different directions. This leads to different value of physical property along different directions in the same crystals.
- Metallic elements including iron, copper and silver are typical examples of crystalline solids.
- On the other hand non – metallic elements like sulphur, phosphorus and iodine and compounds like sodium chloride, zinc sulphide and naphthalene and quartz are typical examples of crystalline solids.

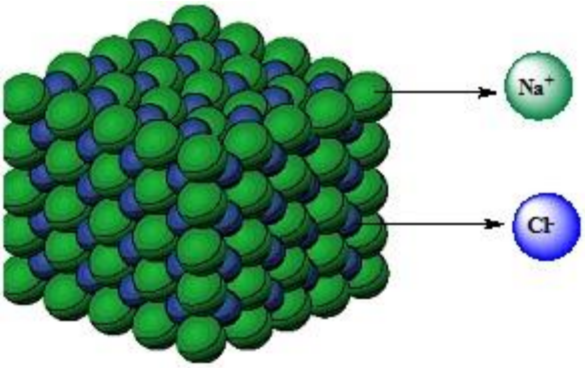
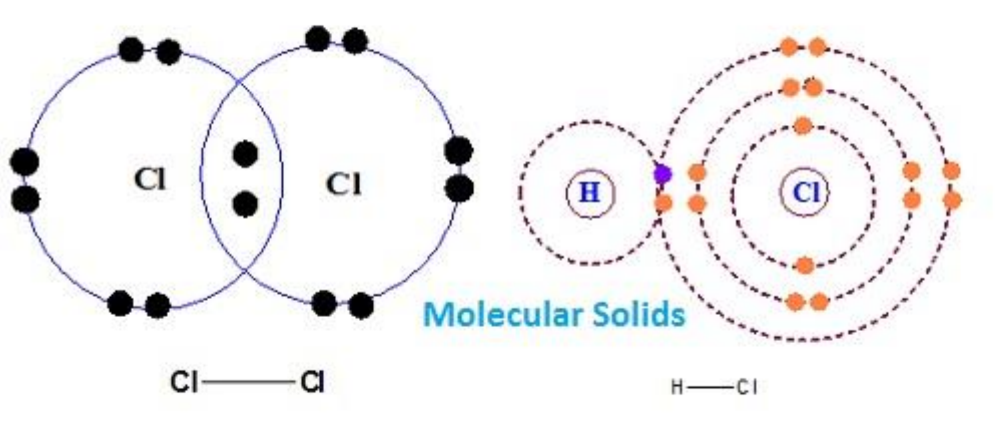


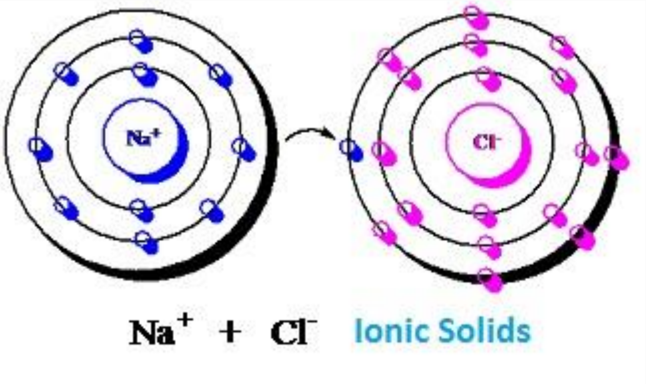
Fig. Crystalline form of Sodium Chloride

- These solids can be further be into four categories the basis of the nature of intermolecular forces acting over them

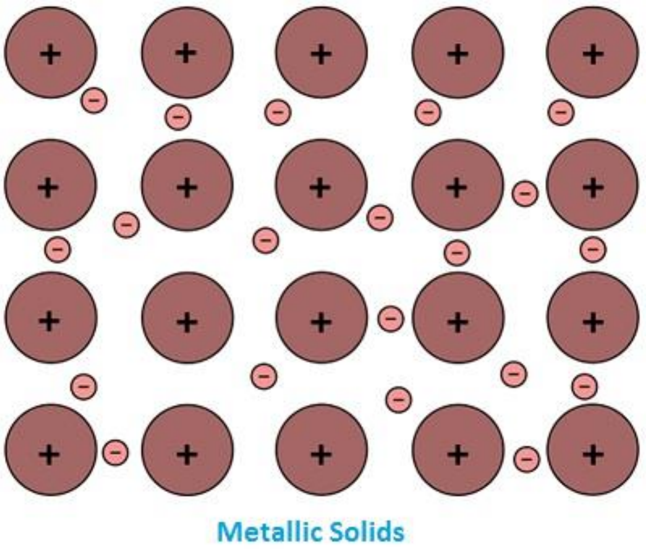
Molecular solids



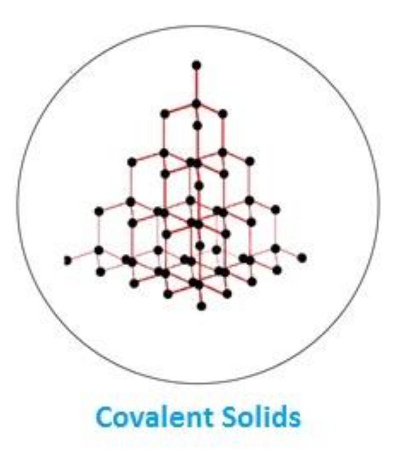
Ionic solids



Metallic solids



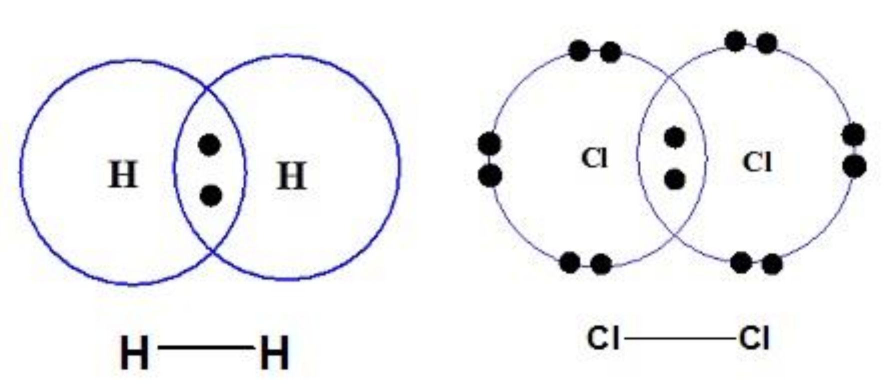
Covalent solids



Molecular Solids

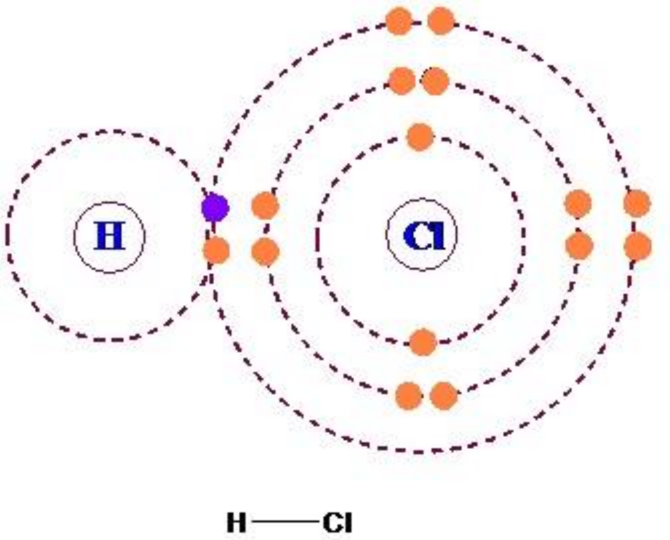
Solid composed of molecules as constituent particles. These solids can further be categorized into following types:

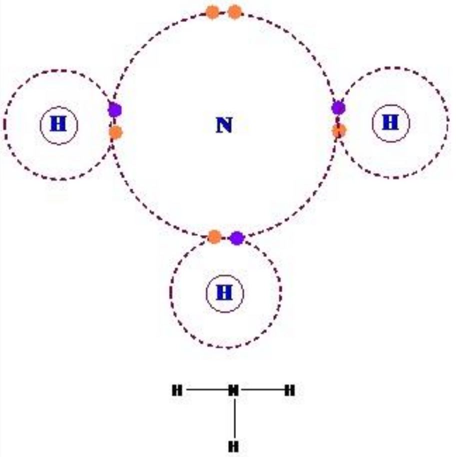
- **Non polar Molecular Solids**:
- They are composed of either atom.
- H2, Cl2 and I2.are some of the typical example.
- In non-polar Molecular solids the comprised atoms or molecules are held together by weak dispersion forces or London forces.
- They are soft and non-conductors of electricity.
- They have low melting points and usually exist in liquid or gaseous state at room temperature and pressure.



(ii) **Polar Molecular Solids:**

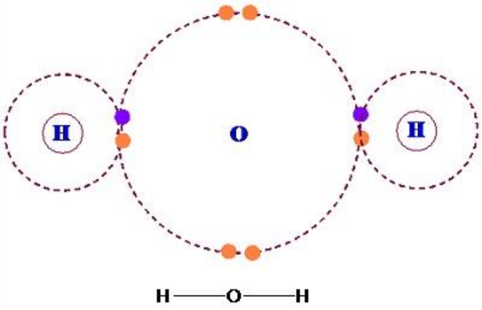
- The molecules like HCl, SO2, are formed by polar covalent bonds.
- In polar Molecular solids the comprised atoms or molecules are held together by stronger dipole-dipole interactions.
- They are soft and non-conductors of electricity.
- The melting points of these solids are higher than those of non-polar molecular solids and usually exist in liquid or gaseous state at room temperature and pressure.
- Molecules like SO2 and solid NH3 are some examples of such solids.





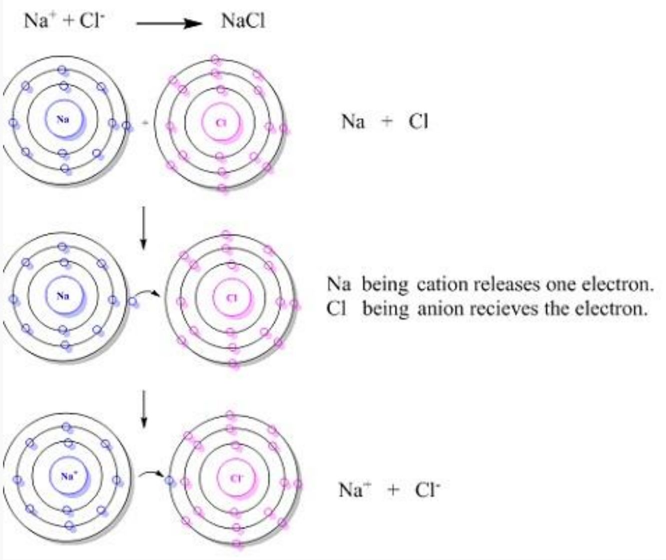
(iii) **Hydrogen Bonded Molecular Solids:**

- Hydrogen Bonded Molecular Solids contain polar covalent bonds between H and F, O or N atoms.
- Strong hydrogen bonding binds molecules of such solids like H_2O (ice).
- They are non-conductors of electricity and are volatile liquids or soft solids under room temperature and pressure.



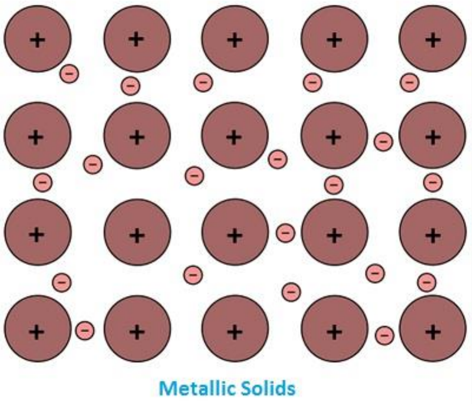
Ionic Solids

- The constituent particles of these solids are ions.
- The solid is composed of three dimensional arrangements of cations and anions that are bonded by strong coulombic (electrostatic) forces.
- These solids are hard and brittle in nature and have high melting and boiling points.
- They are electrical insulators in solid state due to the absence of movement of free electrons but are good conductors in molten state due to the movement of ions.



Metallic Solids

- In these solids positive ions is surrounded by mobile free electrons and are evenly spread all over the crystal.



- Each metal atom donates one or more electrons to the group of mobile electrons which increases the electrical and thermal conductivity of the metallic elements.
- Application of electric field makes these electrons flow through the linkage of positive ions.
- Whereas application of heat to one portion of a metal makes the thermal energy spread uniformly throughout by free electrons.
- Presence of free electrons in metals makes them lustrous, malleable and ductile. For example, Cr, Fe etc.

Covalent solids

- Crystalline solids of non-metals comprises of covalent bonds between adjacent atoms that are strong and directional in nature due to which atoms are held very strongly at their positions all over the crystal.

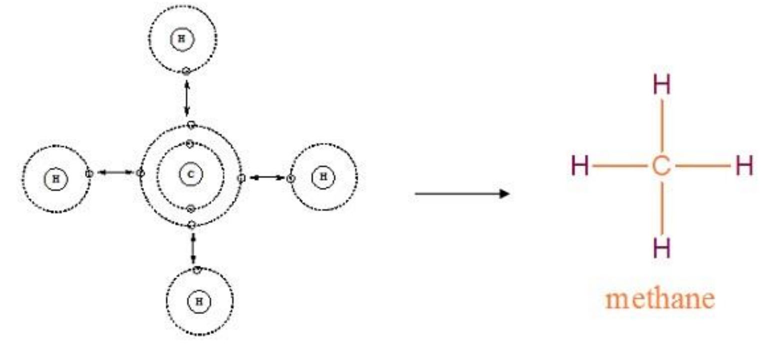
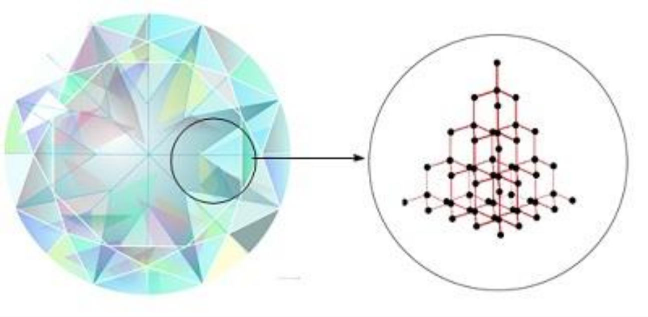


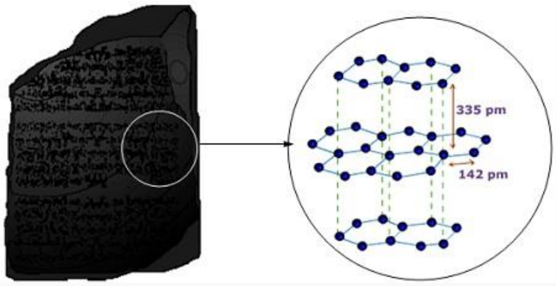
Fig. Covalent bonding between Carbon and hydrogen

- They are also called **giant molecules**.
- These solids are very hard and brittle.
- They have extremely high melting points and may decompose before melting.
- They are insulators and do not conduct electricity.
- Diamond and silicon carbide are typical examples of such solids but Graphite is an exception as it is soft and a good conductor of electricity.

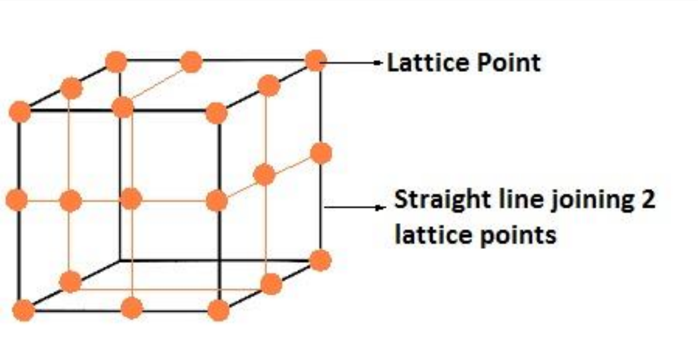


What makes graphite soft and a good conductor of electricity?

- Graphite is a covalent solid that act as a good conductor of electricity and is soft.
- The carbon atoms of graphite are prescribed in different layers and are covalently bonded to three of its surrounding atoms in the same layer.
- The fourth valence electron of each atom is present between different layers and is free to move which makes graphite a good conductor of electricity.
- The characteristic of sliding between different layers makes graphite a soft solid and a good solid lubricant.



Crystal Lattices

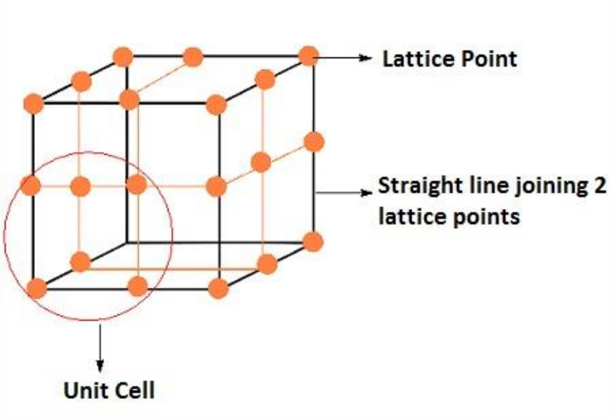


Crystalline solids have a regular and periodically repeating pattern of constituent particles.

- The diagrammatical representation of three dimensional arrangements of constituent particles of a crystal in space with each particle depicted as a point is called *crystal lattice*.
- There are only 14 possible three dimensional lattices and are known **Bravais Lattices.**
- Each point in a lattice is called lattice point or lattice site.
- Each point in a crystal lattice signifies one constituent particle which can be an atom, a molecule or an ion.
- Lattice points are joined together using straight lines to identify the geometry of the lattice.

Unit Cells

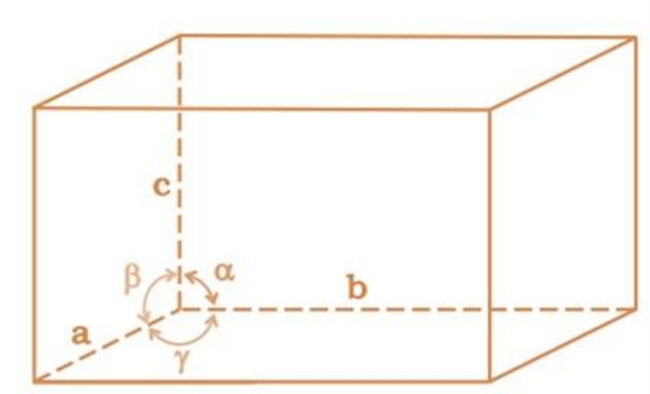
Unit cell can be described as the smallest portion of a crystal lattice.



A unit cell is characterized by:

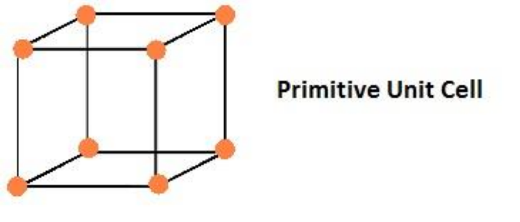
(i) Its dimensions along the three edges, *a*, *b* and *c* which may or may not be mutually perpendicular.

- Angles between the edges, α (between b and c) β (between and c) and γ (between a and b). Thus, a unit cell is characterized by six parameters a, b, c, α, β and γ.



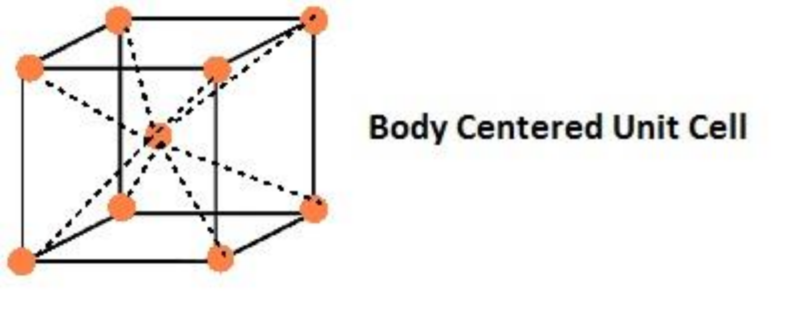
Primitive Unit Cells

If the constituent particles of a crystal lattice are present only on the corner positions of a unit cell, it is known as **primitive unit cell**.



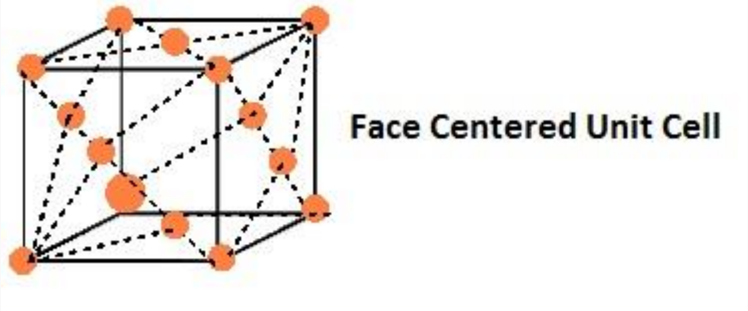
Centered Unit Cells

- If the constituent particles of a crystal lattice are present at positions other than corners in addition to those at corners, it is known as **centered unit cell**.
- Centered unit cells are of three types:
  - *Body-Centred Unit Cells:*



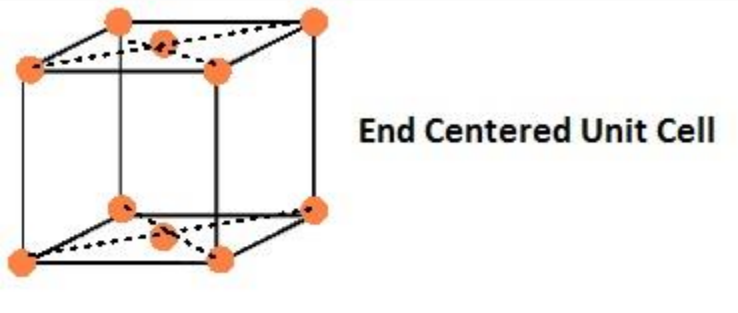
If the constituent particles of a unit cell are present at its body-centre besides the ones that are at its corners.

- *Face-Centred Unit Cells:*



If the constituent particles of a unit cell are present at the center of each face, besides the ones that are at its corners.

End-Centred Unit Cells:



If the constituent particles of a unit cell are present the center of any two opposite faces besides the ones present at its corners.

Number of atoms per unit cell : Primitive Cubic Unit Cell

Each cubic unit cell has 8 atoms on its corners.

Therefore total number of atoms in one unit cell = 8 * 1/8 = 1 atom

Number of atoms per unit cell : Body Centered Cubic Unit Cell

In a body-centered cubic (*bcc*) unit cell, the atoms are present in the body-center besides the ones that are at its corners that wholly belongs to the unit cell in which it is present. Thus in a body-centered cubic (bcc) unit cell:

8 corners X 1/8 per corner atom = 8 * 1/8 = 1 atom

1 body center atom = 1 X 1 = 1 atom

Total number of atoms per unit cell = 2 atoms

Question: Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm-3, calculate atomic radius of niobium using its atomic mass 93 u.

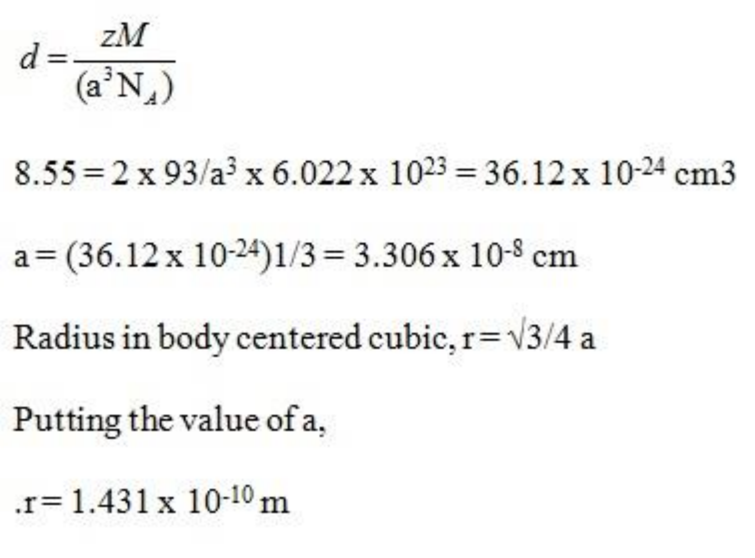
Answer: Density = 8.55 gcm^{-3}

Consider length of the edge = a cm

Number of atoms per unit cell, Z = 2

M = 93 u

Using the formula



$$d = \frac{zM}{(a^3 N_A)}$$

$8.55 = 2 \times 93/a^3 \times 6.022 \times 10^{23} = 36.12 \times 10^{-24}$ cm3

$a = (36.12 \times 10^{-24})1/3 = 3.306 \times 10^{-8}$ cm

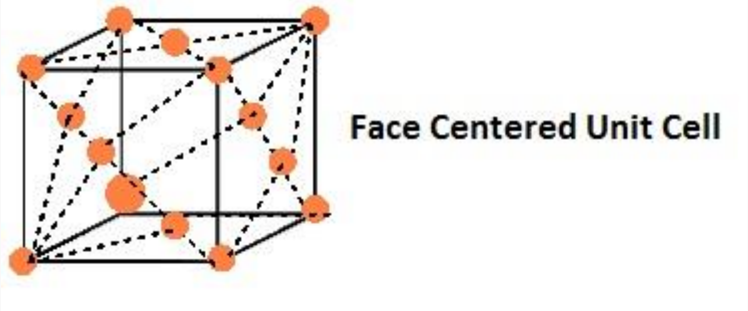
Radius in body centered cubic, $r = \sqrt{3}/4\ a$

Putting the value of a,

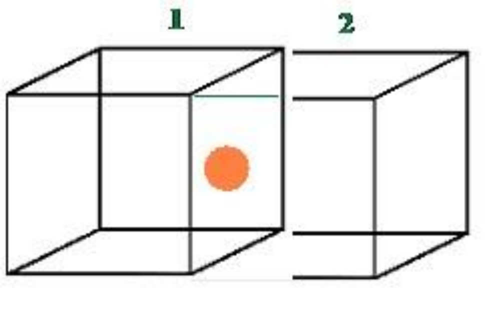
.$r = 1.431 \times 10^{-10}$ m

Number of atoms per unit cell : Face Centered Cubic Unit Cell

- In a face-centered cubic (*fcc*) unit cell the atoms are present in the corners and at the center of all the faces of the cube.



- Each atom present at the face-center is shared between two adjacent unit cells and only a ½ of each atom belongs to a unit cell.



Thus, in a face-centered cubic (*fcc*) unit cell:

8 corners X 1/8 per corner atom = 8 * 1/8 = 1 atom

6 face-centered atoms X 1/2 per unit cell = 6 X 1/2 = 3 atoms

Total number of atoms per unit cell = 4 atoms

In solids, these constituent particles are closely-packed that leaves minimum vacant space.

Question : An element with molar mass 2.7×10^{-2}kg mol^{-1} forms a cubic unit cell with edge length 405 pm. If its density is 2.7×10^{3}kg^{-3}, what is the nature of the cubic unit cell?

Answer : d = 2.7×10^{3}kg^{-3}

M = 2.7×10^{-2} kg mol^{-1}

a= 405 pm = 405 X 10^{-12}

N_A= 6.023 X 10^{23}

Using the formula

$$d = \frac{zM}{(a^3 N_A)}$$

$$2.7\times10^3\,kg^{-3} = \frac{z2.7\times10^{-2}\,kg\ mol^{-1}}{[(405\ X10^{-12})^3\,X6.023\ X\ 10^{23}]}$$

Z=4

Unit cell is fcc unit cell.

Volume of 54 g of the element = 0.054/(2.7X10^{3}) = 2 X 10^{-6}

Number of unit cell in this volume = volume of 554 g of element/volume of each unit cell = 2 X 10^{-6}/(405 X 10^{-12})^{3} = 3.012 X 10^{22}

Question: Copper crystallises into a fcc lattice with edge length 3.61 x 10^{-8}cm. Show that the calculated density is in agreement with its measured value of 8.92 g cm^{-3}

Answer: Given that Copper crystallises into a fcc lattice

Hence Z= 4

M = 63.5

a = 3.61x10^{-8}

N_o = 6.023 x 10^{23}

Using the formula

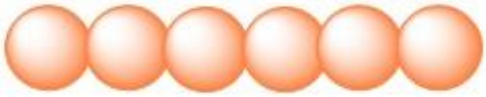
$$d = \frac{zM}{(a^3 N_o)}$$

$$\text{Density} = \frac{4\times\ 63.5}{[(3.61x10^{-8})^3\,X6.023\ X\ 10^{23}]} = 8.96\ gcm^{-3}.$$

Therefore, approximately the value is equal to 8.92.

Close Packing in One Dimension

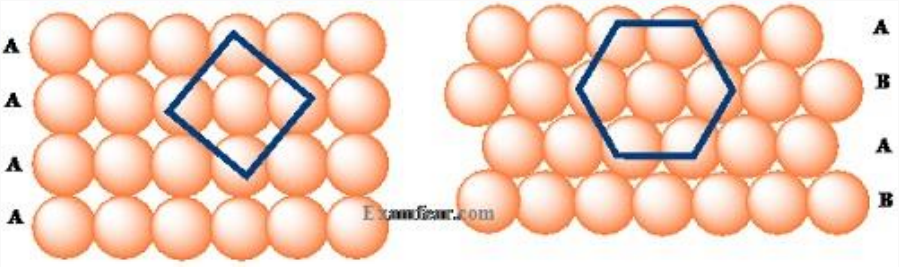
- The only way to arrange spheres in a one dimensional close packed structure is to arrange the spheres in a single row and touching each other.



- Each sphere is in contact with two of its surrounding atom.
- The number of nearest surrounding particles is called its **coordination number**. Therefore in one dimensional close packed arrangement, the coordination number is 2.

Close Packing in Two Dimensions

Two dimensional close packed structure can be generated by stacking (placing) the rows of close packed spheres.

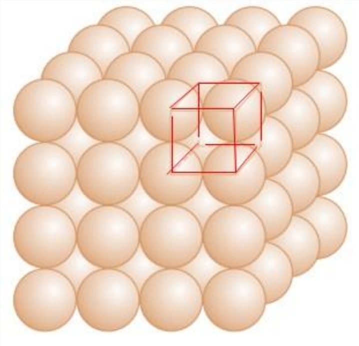


The second row can be placed in contact with the first row in such a way that the spheres of second row are exactly above the first row.

- The spheres of the two rows are aligned horizontally as well as vertically.
- Let the first row be ‘A’ type row and the second row is also of ‘A’ type due to its similarity with the first one.
- Similarly, we may place more rows to obtain AAA type of arrangement.
- Each sphere is in contact with four of its surrounding atom. Thus, the two dimensional coordination numbers is 4.
- If the centers of these 4 immediate surrounding spheres are joined, a square is formed. Due to which this packing is known as square close packing in two dimensions.
- The second row can be placed above the first row in a staggered manner in such a way that the spheres fit in the depressions of the first row.
- Let the first row be ‘A’ type row, and the second row be ‘B’ type row.
- When the third row is placed adjacent to the second in staggered manner, its spheres are aligned with those of the first layer. Hence this layer is also of ‘A’ type.
- The spheres of similarly placed fourth row will be aligned with those of the second row (‘B’ type). Hence this arrangement is of ABAB type.
- This arrangement provides less free space and is more efficient than the square close packing.
- Each sphere in this arrangement is in contact with six of surrounding spheres and the two dimensional coordination numbers is 6.
- The centers of these six spheres are at the corners of a regular hexagon due to which this packing is also known as two dimensional hexagonal close packing**.**
- These are triangular in shape. In one row, the apex of the triangles is pointing upwards and in the next layer the apex of the triangles is pointing downwards.

Close Packing in Three Dimensions

All real structures are three dimensional structures that are obtained by stacking two dimensional layers one above the other in a square close-packed and hexagonal close-packed manner. It can be categorized into two types:



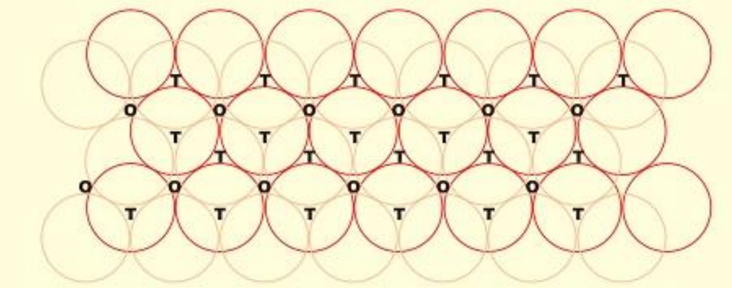
Three dimensional close packing from two dimensional square close-packed layers:

- The second layer is placed over the first layer in such a way that the spheres of the upper layer are exactly above those of the first layer.
- In this arrangement of spheres, both the layers are perfectly aligned horizontally as well as vertically.
- Let the first row be ‘A’ type row, and the second row be ‘B’ type row.
- Thus this lattice has AAA.... type pattern.
- The lattice therefore generated is the simple cubic lattice, and its unit cell is the primitive cubic unit cell.

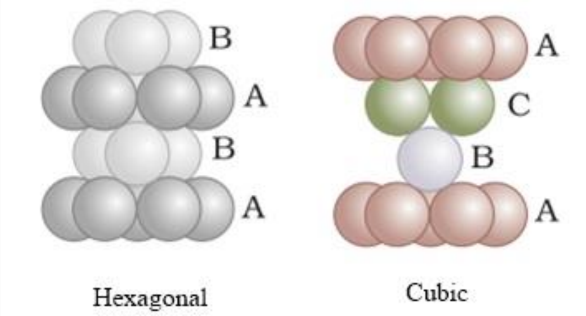
Three dimensional close packing from two dimensional hexagonal close packed layers:

Three dimensional close packed structure can be generated by placing layers one over the other.

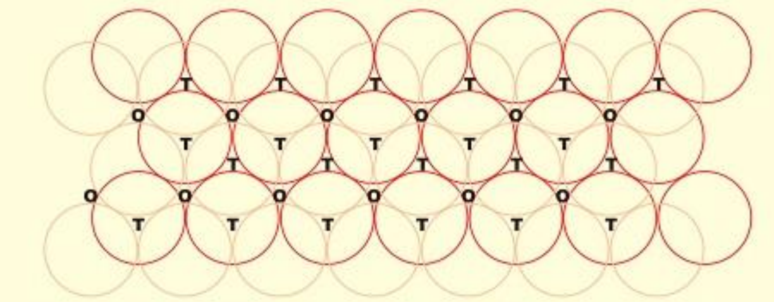
- Placing second layer over the first layer



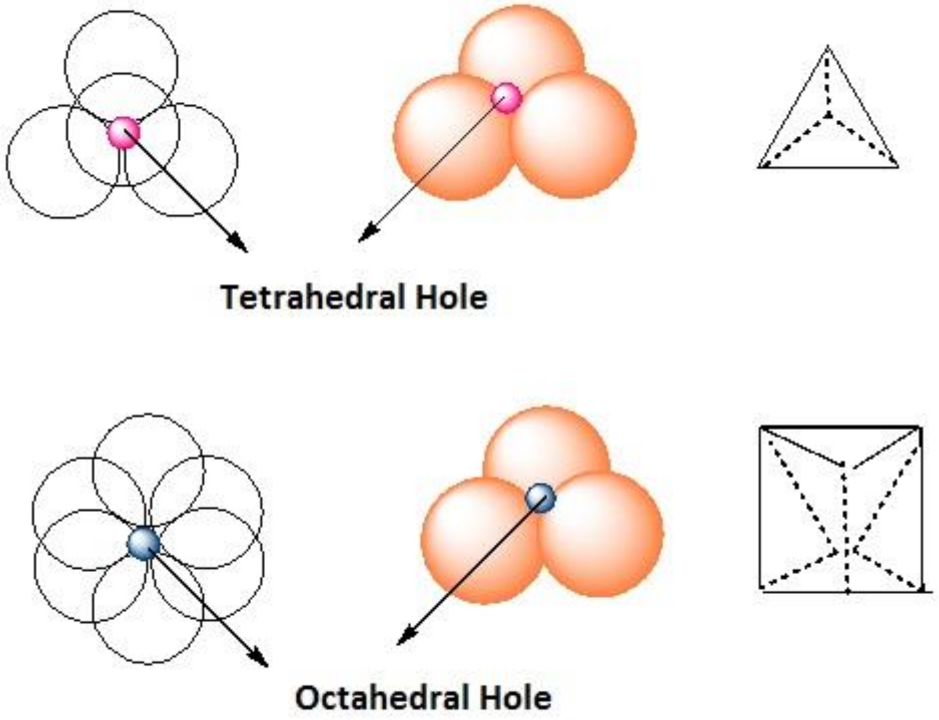
- Placing third layer over the second layer



Placing second layer over the first layer



- Consider a two dimensional hexagonal close packed layer of type 'A' and place a similar layer above it in such a way that the spheres of the second layer lies in the depressions of the first layer.
- Let the second layer be of type 'B' due to its different alignment.
- All the triangular voids of the first layer are not covered by the spheres of the second layer which gives rise to a different arrangement.
- The area where a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed.
- These voids are called tetrahedral voids because a joining of the centers of four spheres gives rise to *tetrahedron*.
- There are areas where the triangular voids in the second layer lies above the triangular voids of the first layer, and the triangular shapes of these do not overlap.
- One of them has the apex of the triangle pointing upwards and the other downwards.



- Such voids are surrounded by six spheres and are called **octahedral voids (O).**

Let the number of close packed spheres be *N*, then:

The number of octahedral voids generated in the structure = *N*.

The number of tetrahedral voids generated in the structure = *2N*.

Question : If the radius of the octachedral void is r and radius of the atoms in close packing is R, derive relation between r and R.

Answer: Given that

Radius of octahedral void in close packing = r

Radius of atom in close packing = R

Using Pythagoras theorem,

$2R^2 = (R+ r)^2 + (R+ r)^2$

$4R^2 = 2(R +r)^2$

$2R^2 = (R+ r)^2$

$R\sqrt{2} = R +r$

$R\sqrt{2} – R = r$

$r = R\sqrt{2} – R$

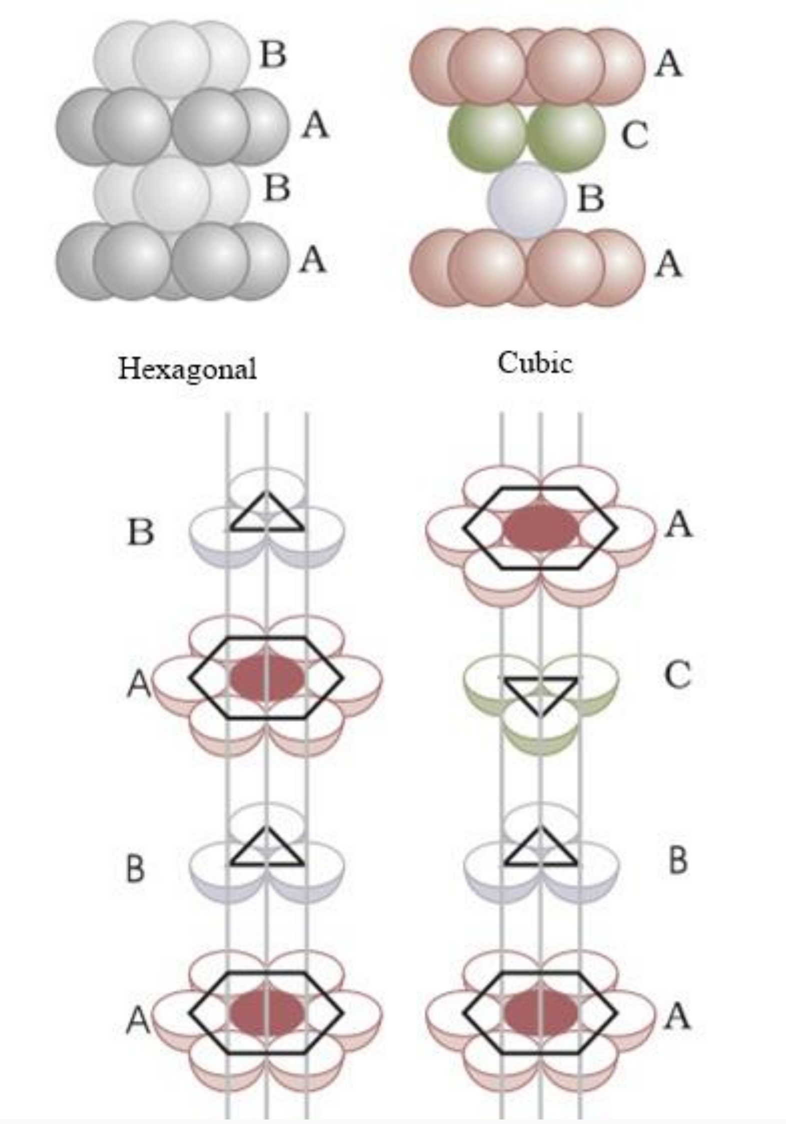
Putting the value of $\sqrt{2}$, we derive

$r = R (1.414-1)$

$r = 0.414R$

<u>Placing third layer over the second layer</u> : **<u>Covering Tetrahedral Voids</u>**

- Tetrahedral voids of the second layer can get covered by the spheres of the third layer.
- Here the spheres of the third layer get exactly aligned with the spheres of the first layer.
- Therefore it can be observed that the pattern of spheres is repeated in alternate layers.
- This pattern is often written as ABAB .... pattern and the structure is called hexagonal close packed (*hcp*) structure found in many metals like magnesium and zinc.



Question : A compound forms hexagonal close-packed structure. What is the total number of voids in 0.5 mol of it? How many of these are tetrahedral voids?

Answer: Number of particles in 1 mol of compound = 6.022×10^{23}

Number of particles in 0.5 mol = $0.5 \times 6.022 \times 10^{23} = 3.011 \times 10^{23}$

Number of octahedral voids = number of atoms or particles.

Number of tetrahedral voids = 2 X number of particles

Therefore number of octahedral in the given compound = 3.011×10^{23}

Number of tetrahedral voids = $2 \times 3.011 \times 10^{23} = 6.022 \times 10^{23}$

The total number of voids = $3.011 \times 10^{23} + 6.022 \times 10^{23}$

= 9.033×10^{23}

Number of tetrahedral voids = 6.022×10^{23}

Question. Atoms of element B form hcp lattice and those of the element A occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by the elements A and B?

Answer: Number of tetrahedral voids = 2 X number of particles of atom B

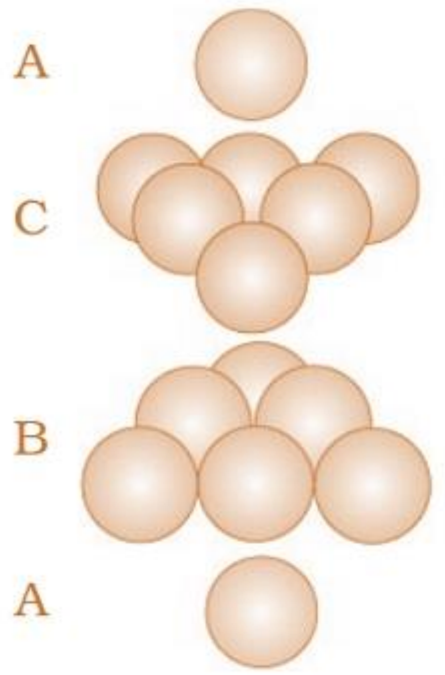
Number of atoms of A is equal to of the number of atoms of B.

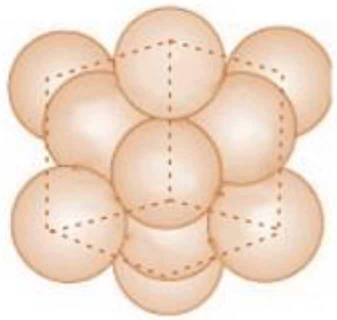
Hence the ratio A:B = (4/3):1 or 4:3

Therefore, the formula of the compound is A_4B_3.

Placing third layer over the second layer : **Covering Octahedral Voids**

- The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids.
- When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called "C'
- Only when fourth layer is placed, its spheres are aligned with those of the first layer.
- This pattern of layers is often written as ABCABC........... This structure is called cubic close packed (*ccp*) or face-centered cubic (*fcc*) structure.





- Metals such as copper and silver crystallize in this structure. Both these types of close packing are highly efficient and 74% space in the crystal is filled. In either of them, each sphere is in contact with twelve spheres. Thus, the coordination number is 12 in either of these two structures.

Question: A compound is formed by two elements M and N. The element N forms *ccp* and atoms of M occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

Answer: The ccp lattice is made by the atoms of the element N.

Here, the Number of tetrahedral voids = 2 X number of particles of the elements N.

According to the question, the atoms of element M occupy = 1/3rd of the tetrahedral voids.

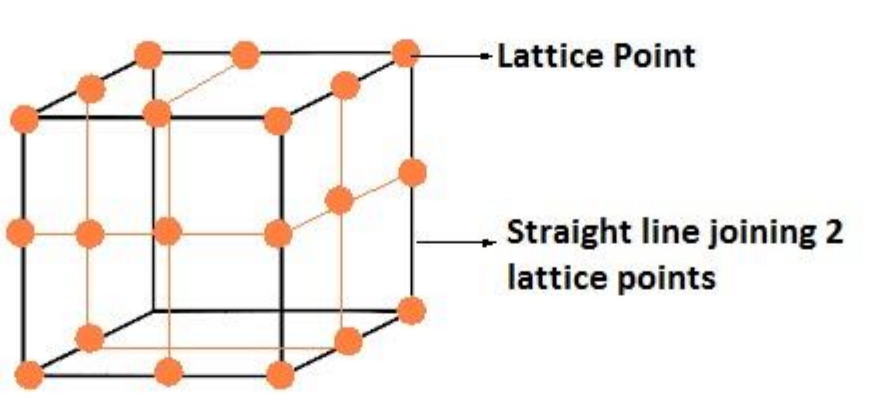
Therefore, the number of atoms of M is equal to

2 x 1/3 = 2/3rd of the number of atoms of N.

Therefore, the ratio M:N = 2/3 :1 = 2:3

Hence formula of the compound is M_2N_3.

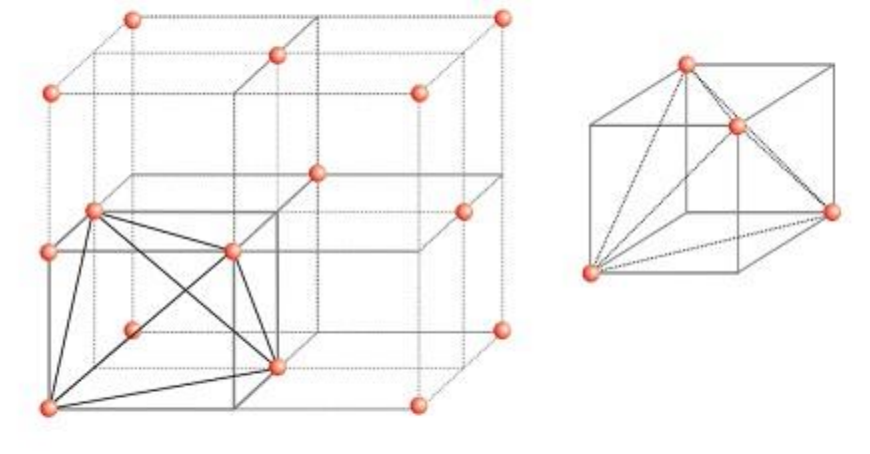
Formula of a Compound and Number of Voids Filled



- The number of octahedral voids present in a lattice = The number of close packed particles.
- The number of tetrahedral voids produced is twice this number.
- In ionic solids, the bigger ions i.e. anions forms close packed structure and the smaller ions i.e. cations occupy the voids.
- If the latter ion is small then tetrahedral voids are occupied, if bigger, then octahedral voids are occupied.
- In a compound, the fraction of octahedral or tetrahedral voids that are occupied depends upon the chemical formula of the compound.
- Close packed structures have both tetrahedral and octahedral voids.

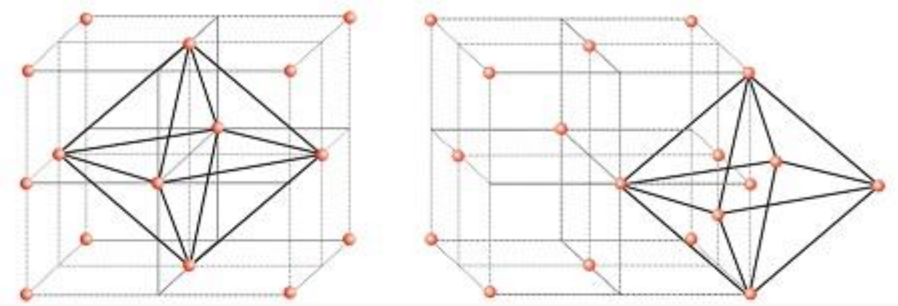
Locating Tetrahedral Voids

- Take a unit cell of ccp or fcc lattice divide into eight small cubes with each small cube having atoms at alternate corners.
- Thus, each small cube has 4 atoms that on joining to each other make a regular tetrahedron.
- Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total.
- Each of the eight small cubes have one void in one unit cell of *ccp*
- *ccp* structure has 4 atoms per unit cell. Thus, the number of tetrahedral voids is twice the number of atoms.



Locating Octahedral Voids

- Take a unit cell of ccp or fcc.
- The body center of the cube, C is not occupied but surrounded by six atoms on face centers.
- Joining the face centers creates a octahedron.
- Thus, this unit cell has one octahedral void at the body centre of the cube.
- There is one octahedral void at the centre of each of the 12 edges.
- It is surrounded by six atoms, three belonging to the same unit cell and three belonging to two adjacent unit cells.
- Each edge of the cube and octahedral void are shared between four adjacent unit cells.
- Only ¼ of each void belongs to a particular unit cell



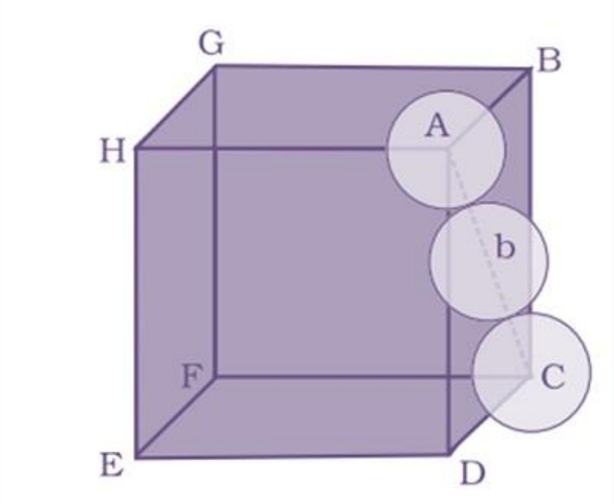
In *cubic close packed structure* octahedral void at the body-center of the cube = 1
12 octahedral voids positioned at each edge and shared between four unit cells =12 x 1/4 =3

Total number of octahedral voids = 4

In ccp structure, each unit cell has 4 atoms. Thus, the number of octahedral voids is equal to this number.

Packing Efficiency in hcp and ccp Structures

let the unit cell edge length be ‘a’ and face diagonal AC = b.



$$\Delta ABC$$
$$AC^2 = b^2 = BC^2 + AB^2$$
$$= a^2 + a^2 = 2a^2$$
$$b = \sqrt{2}a$$

Let r be the radius of the sphere. So we get

$$b = 4r = \sqrt{2a}$$
$$a = \frac{4r}{\sqrt{2}} = 2\sqrt{2r}$$

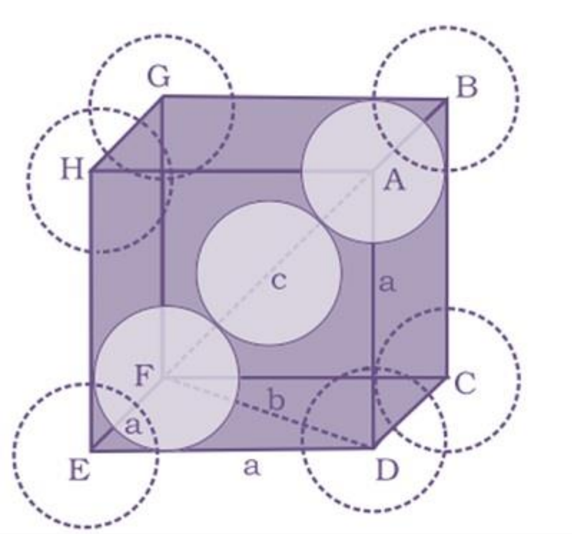
Each unit cell in ccp structure has effectively 4 spheres.

Hence total volume of four spheres is equal to 4 X (4/3)Π r^3 and volume of the cube is a^3 or $(2\sqrt{2}r)^3$.

Therefore, Packing efficiency = (Volume occupied by four spheres in the unit cell X 100)/(Total volume of the unit cell)

$$= \frac{4X\frac{4}{3}\pi r^3 X100}{(2\sqrt{2r})^3}\%$$
$$= \frac{\frac{16}{3}\pi r^3 X100}{16\sqrt{2r}^3}\% = 74\%$$

Efficiency of Packing in Body Centered Cubic Structures



$$\Delta EFD$$
$$b^2 = a^2 + a^2 = 2a^2$$
$$\Delta AFD$$
$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$
$$c = \sqrt{3}a$$

The length of the body diagonal c = 4r, where r is the radius of the sphere as all the spheres along the diagonal touch each other. Therefore,

$$\sqrt{3}a = 4r$$
$$a = \frac{4r}{\sqrt{3}}$$
$$r = \frac{\sqrt{3}}{4}a$$

This type of structure has 2 atoms and their volume is $2X(\frac{4}{3})\pi r^3$.

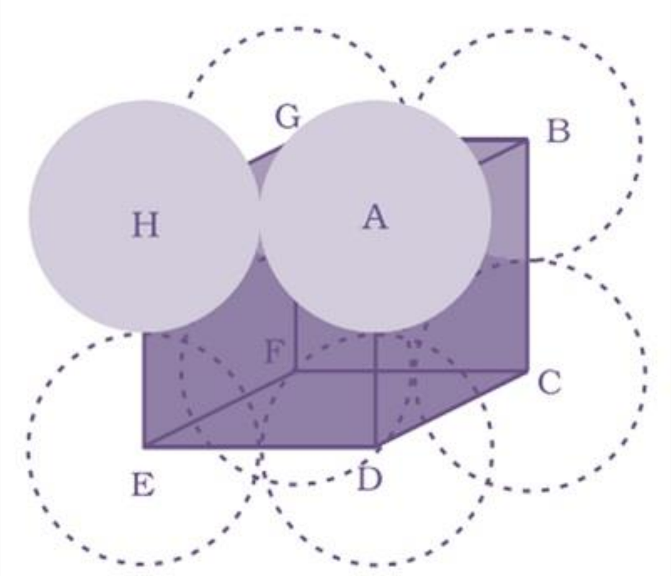
Volume of the cube = $a^3 = (\frac{4r}{\sqrt{3}})^3$

Packing efficiency = (Volume occupied by two spheres in the unit cell X 100)/(Total volume of the unit cell)

$$= \frac{2X\frac{4}{3}\pi r^3 X100}{(4\sqrt{3}r)^3}\%$$

$$= \frac{\frac{8}{3}\pi r^3 X100}{64/(3\sqrt{3})r^3}\% = 68\%$$

Packing Efficiency in Simple Cubic Lattice



a = 2r

Where a = Edge length or side of the cube

r = radius of each particle,

The volume of the cubic unit cell = a3 = $(2r)^3 = 8r^3$

A simple cubic unit cell contains only 1 atom. The volume of the occupied space =4/3 Π r^3

Packing efficiency = (Volume of one atom X 100)/(Volume of cubic unit cell)

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} X100 = \frac{\pi}{6} X100 = 52.4\%$$

Therefore it can be concluded that ccp and hcp has maximum packing efficiency.

Calculations Involving Unit Cell Dimensions

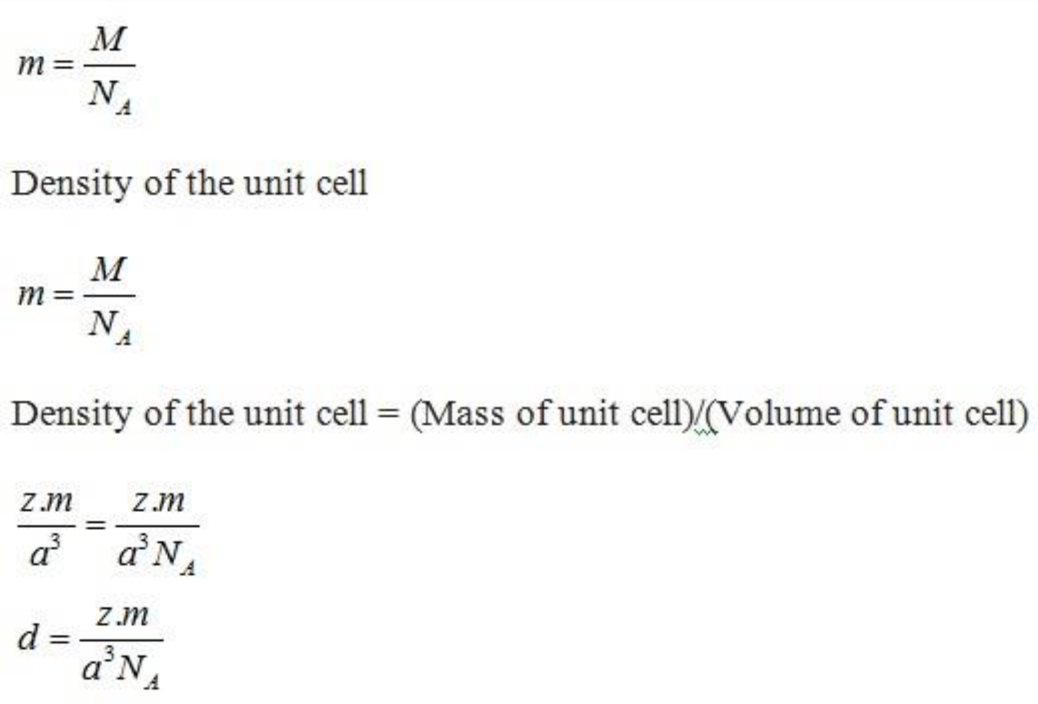
Edge length of a unit cell of a cubic crystal = *a*,

Density of the solid substance = *d*

Molar mass = M

Volume of a unit cell = *a3*

Mass of the unit cell = number of atoms in unit cell × mass of each atom = number of atoms present in one unit cell *(z)* × mass of a single atom *(m)*



$$m = \frac{M}{N_A}$$

Density of the unit cell

$$m = \frac{M}{N_A}$$

Density of the unit cell = (Mass of unit cell)/(Volume of unit cell)

$$\frac{z.m}{a^3} = \frac{z.m}{a^3 N_A}$$

$$d = \frac{z.m}{a^3 N_A}$$

Imperfections in Solids

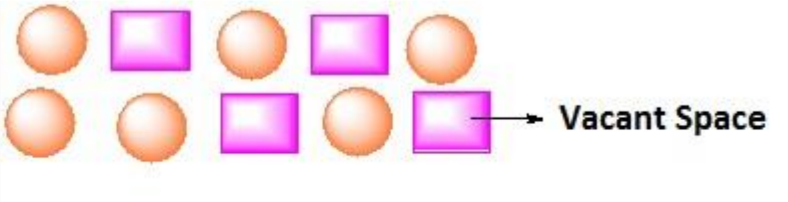
- Constituent particles in crystalline solids are arranged in a short range as well as long range order yet crystals are not perfect.
- They possess small crystals have defects that are irregularities in the arrangement of constituent particles in them when crystallization process occurs at fast or moderate rate.
- These defects are of two types- point defects and line defects.
- The irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance.
- The irregularities or deviations from ideal arrangement in entire rows of lattice points are known as line defects.
- These irregularities are called *crystal defects*.
- Point defects can be classified into three types: (i) stoichiometric defects (ii) impurity defects and (iii) non-stoichiometric defects

Stoichiometric Defects

- These ranges of point defects do not disturb the stoichiometry of the solid.
- They are also called *intrinsic* or **thermodynamic defects.**
- Non-ionic solids exhibit their defects as vacancy defects and interstitial defects.

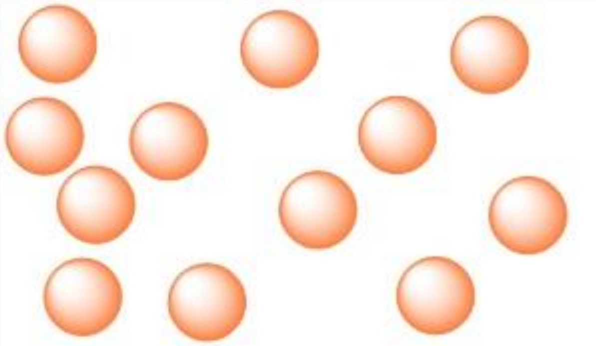
***Vacancy Defect*:**

A crystal containing vacant lattice sites is said to have **vacancy defect.** This defect can also develop due to heating up of a substance.



***Interstitial Defect*:**

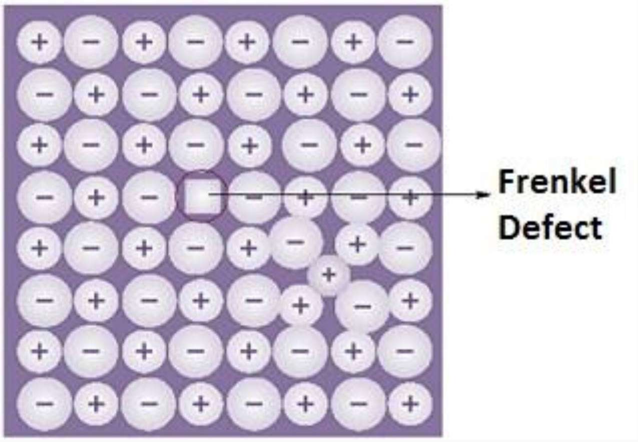
A crystal in which some constituent particles occupy an **interstitial** site, are said to have **interstitial defect** which increases the density of the substance.



Ionic solids exhibit their defects as **Frenkel and Schottky defects.**

Frenkel Defect:

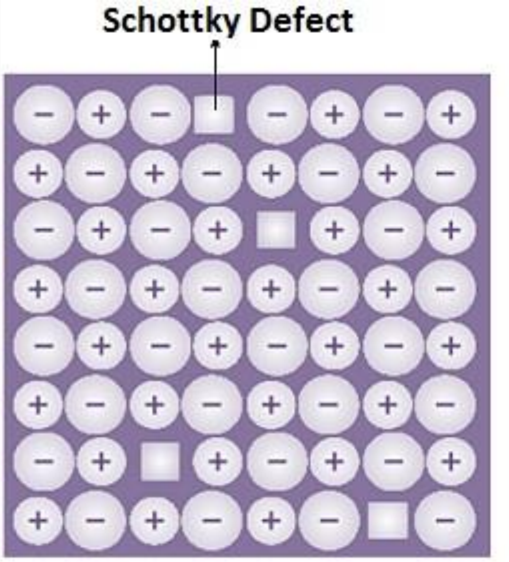
- This defect is exhibited by the ionic substances due to the large difference in size of ions.
- The smaller ion (cation) is displaced from its normal site to an interstitial site which creates a vacancy defect at its original site and an interstitial defect at the new location.
- It is also called dislocation defect.
- It does not alter the density of the solid.
- For example, ZnS, AgCl, AgBr and AgI due to small size of Zn^{2+} and Ag^+ ions.



Schottky Defect:

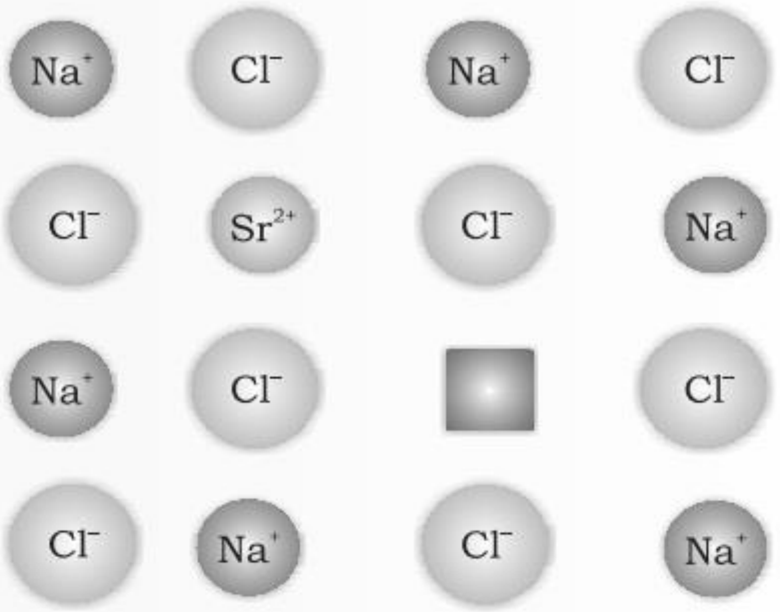
- This defect in ionic solids is equivalent to the vacancy defect in non-ionic solids.
- In order to maintain electrical neutrality, the number of missing cations and anions are equal
- Schottky defect also decreases the density of the substance.
- This defect is shown by ionic substances in which the cation and anion are of almost similar sizes.

- In NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In 1 cm^3 there are about 10^{22} Thus, there is one Schottky defect per 10^{16} ions.
- For example, NaCl, KCl, CsCl and AgBr.
- Out of these AgBr shows both, Frenkel as well as Schottky defects.



Impurity defect

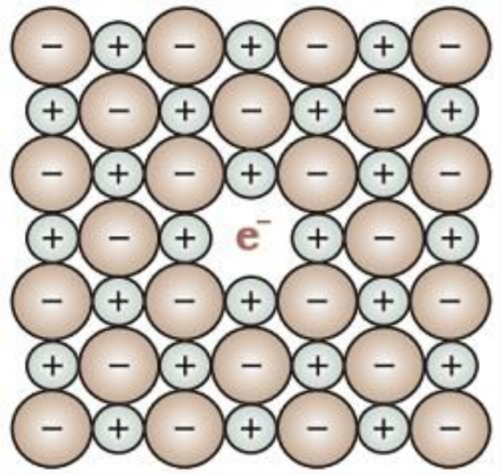
- Crystallization of molten NaCl with little amount of $SrCl_2$ results in Sr^{2+} occupying some of the sites of Na^+
- Each Sr^{2+} replaces two Na+ ions.
- It occupies the site of one ion and the other site remains vacant.
- The cationic vacancies thereby produced are equal in number to that of Sr^{2+}
- Solid solution of $CdCl_2$ and AgCl.



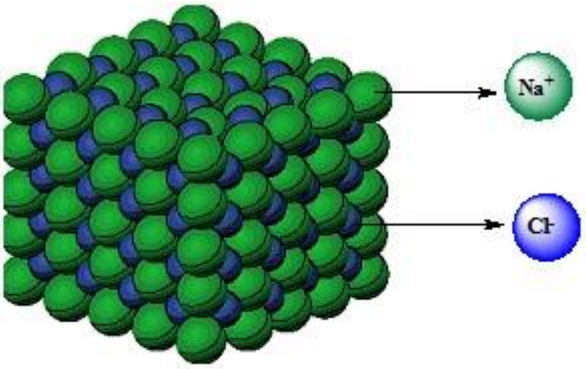
Non-Stoichiometric Defects

- Nonstoichiometric inorganic solids contain the constituent elements in a non-stoichiometric ratio due to defects in their crystal structures.
- These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

(i) Metal Excess Defect.



- Metal excess defect due to anionic vacancies:
- This type of defect is exhibited by alkali halides like NaCl and KCl.
- Application of heat to NaCl in an atmosphere of sodium vapour results in deposition of the sodium atoms on the surface of the crystal.
- The sodium atoms lose electron to form Na^+
- The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl.



- The released electrons diffuse into the crystal and occupy anionic sites.
- The anionic sites occupied by unpaired electrons are called F-centres that imparts yellow colour to the crystals of NaCl due to the excitation of the electrons on absorption of energy from the visible light falling on the crystals.
- Excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet.
- Metal excess defect due to the presence of extra cations at interstitial sites:
- Heating Zinc oxide that exists in white colour at room temperature loses oxygen and turns yellow.

$$ZnO \xrightarrow{\text{Heating}} Zn^{2+} + 1/2\ O_2 + 2e^-$$

- This results in excess of zinc in the crystal and its formula becomes Zn1+xO.
- The excess Zn^{2+} ions move to interstitial sites and the electrons to neighbouring interstitial sites.
- Metal Deficiency Defect:
- Many solids possess less amount of the metal as compared to the stoichiometric proportion.
- For example, FeO is mostly found with a composition ranging from $Fe_{93}O$ to $Fe_{0.96}O$.
- In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+}

Electrical Properties of soilds

Solids exhibit electrical conductivities that extend from 27 orders of magnitude ranging from 10^{-20} to 10^{7} ohm^{-1} m^{-1}.

Conductors:

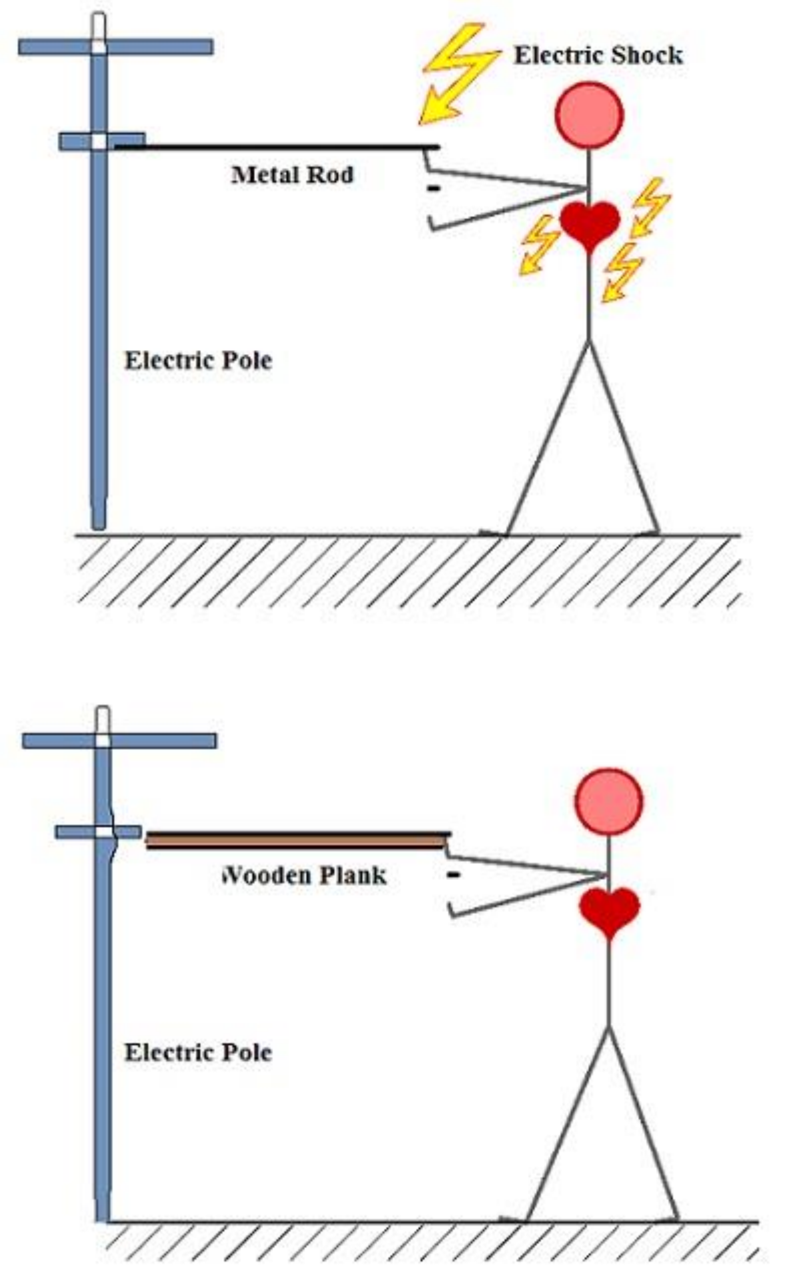
- Solids with conductivities ranging between 10^{4} to 10^{7} ohm^{-1}m^{-1} are conductors.
- Metals have conductivities in the order of 10^{7} ohm^{-1}m^{-1} are good conductors.
- For example, Iron, Copper, Aluminum.

Fig. Metal is used at the tip of the plug that is inserted into the socket

Insulators:

- Solids with very low conductivities ranging between 10^{-20} to 10^{-10} ohm^{-1}m^{-1}.
- For example, Wood, plastic, cloth, glass.

Fig. Wood and plastics are also solids but are insulators

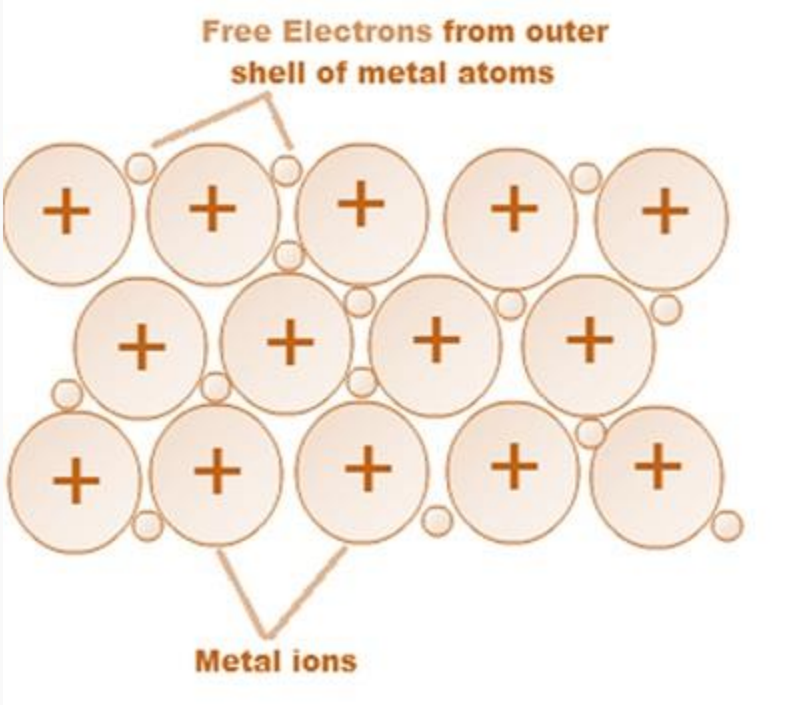


A man touching the electric pole with a metal rod will get an electric shock because metal rod is a conductor whereas a man touching the same with a wooden plank will be safe because wood is an insulator.

- Semiconductors:
- Solids with conductivities in the intermediate range from 10–6 to 104 ohm^{-1} m^{-1}.
- For example, Gallium, Germanium, Silicon

<u>Conduction of Electricity in Metals</u>

- A conductor conducts electricity due to the movement of electrons or ions.



- Metals conduct electricity both in solid state as well as molten state.
- The conductivity of metals depends upon the number of valence electrons available per atom.
- The atomic orbitals of metal atoms form molecular orbitals that are close in energy to each other as to form a band.
- Partial filling or overlapping with a higher energy unoccupied conduction band enables the electrons to flow easily under an applied electric field.
- This results in conductivity of metals.

If the gap between valence band and the conduction band is large, electrons cannot jump to it and such a substance has very low conductivity that makes it behave like an insulator

Conduction of Electricity in Semiconductors

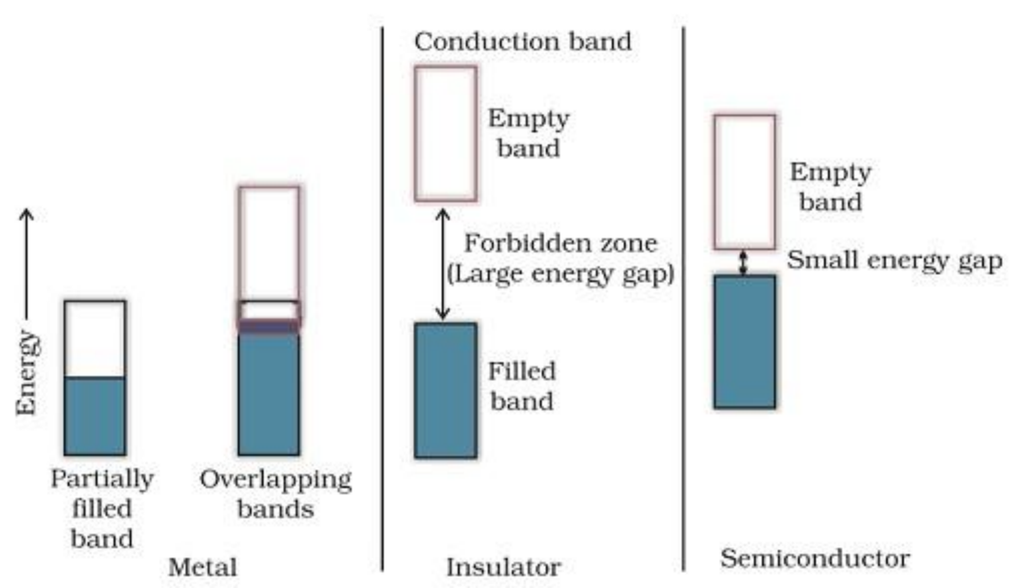
In semiconductors, the gap between the valence band and conduction band is small.

This enables some electrons to jump to conduction band and exhibit their conductivity.

Electrical conductivity of semiconductors increases with increase in temperature, since more electrons can jump to the conduction band due to small gap between the valence band and conduction band.

Silicon and germanium exhibit this behavior and are called intrinsic semiconductors.

The conductivity of these intrinsic semiconductors is too low to be practically used.



Doping

- The conductivity of metal is increased by adding an appropriate amount of suitable impurity.
- This process is known as doping.
- It can be performed with an impurity which is electron rich or electron deficient than the intrinsic semiconductor silicon or germanium.

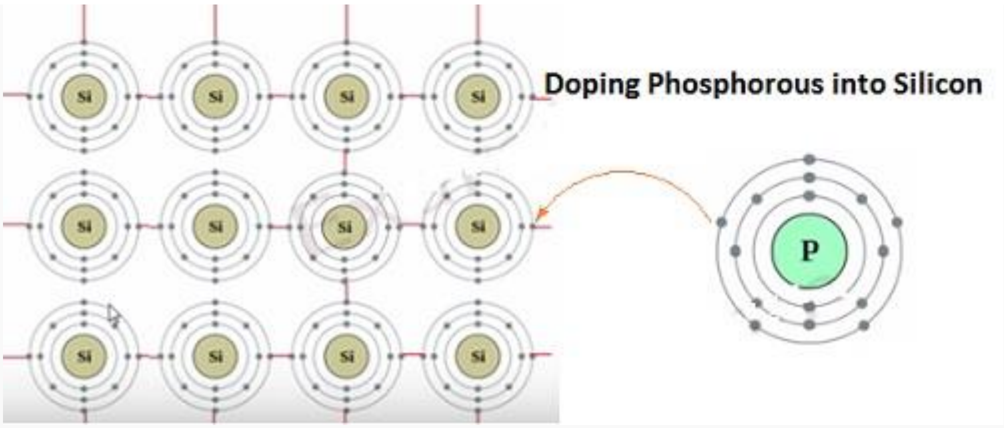


Fig. Doping electron rich impurity into an intrinsic conductor

- Such impurities introduce electronic defects in them.

1. If NaCl is doped with 10-3mol % of $SrCl_2$, what is the concentration of cation vacancies?
2. 1 Cation of Sr^{2+} = 1 cation vacancy in NaCl.

Number of cation vacancies in lattice of NaCl = Number of divalent Sr^{2+} ions added.

Concentration of cation vacancy on doping with 10^{-3} mol% of $SrCl_2$. = 10^{-3} mol% = $10^{-3} / 100 = 10^{-5}$ mol.

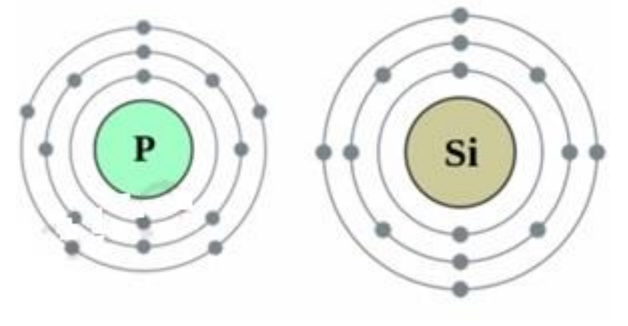
Number of Sr^{2+} ion in 10^{-5} mol = $10^{-5} \times 6.023 \times 10^{23} = 6.023 \times 10^{18}$

Hence number of cationic vacancies = 6.023×10^{18}

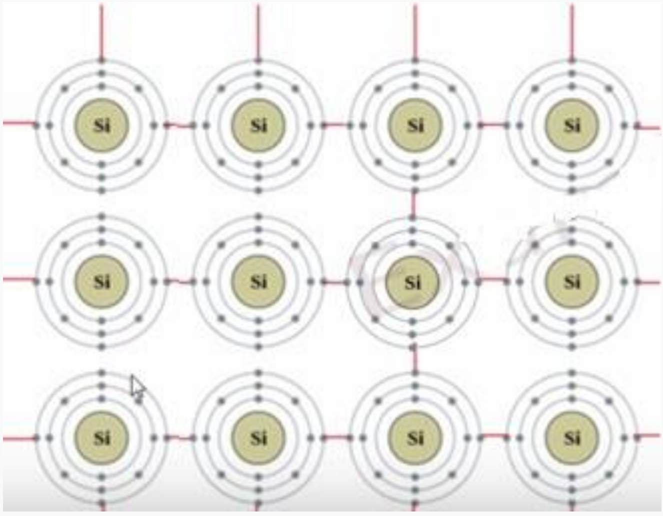
Electron – rich impurities

In a periodic table Silicon and germanium belongs to group 14 with four valence electrons each. In their crystals each atom forms four covalent bonds with surrounding atom.

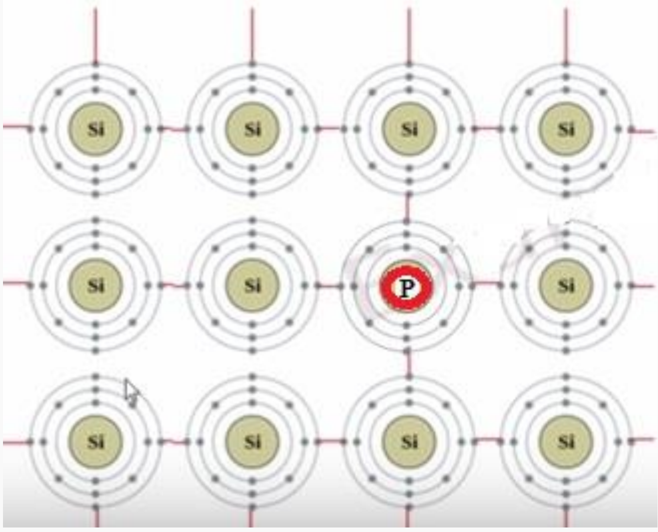
When doped with a group 15 element like P or As, which contains five valence electrons,



They occupy some of the lattice sites in silicon or germanium crystal.



Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring silicon atoms. The fifth electron in P is extra and becomes delocalized.

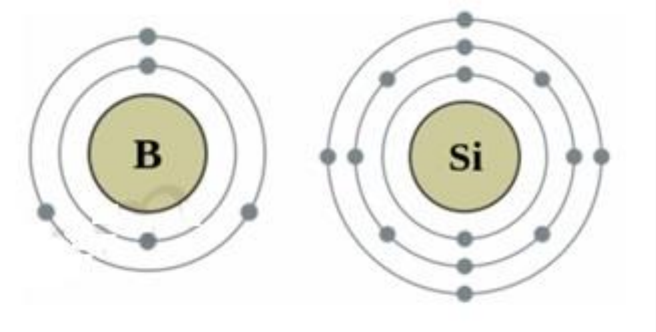


These delocalized electrons increase the conductivity of doped silicon (or germanium).

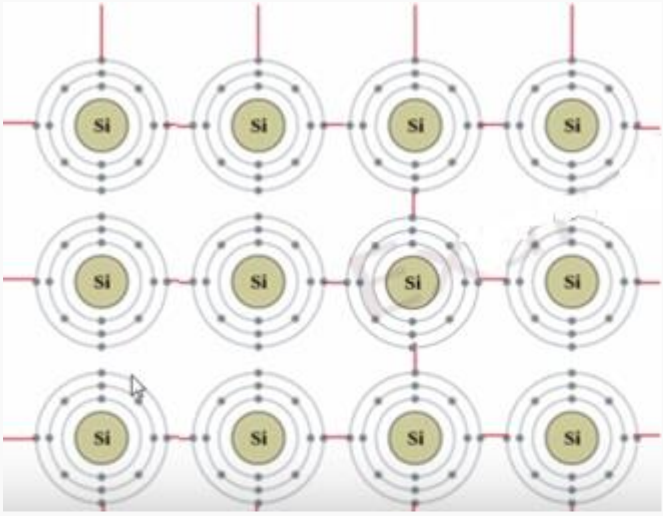
This type of semiconductor is known as n-type semiconductor because the increase in conductivity is due to the negatively charged electron.

Electron – deficit impurities

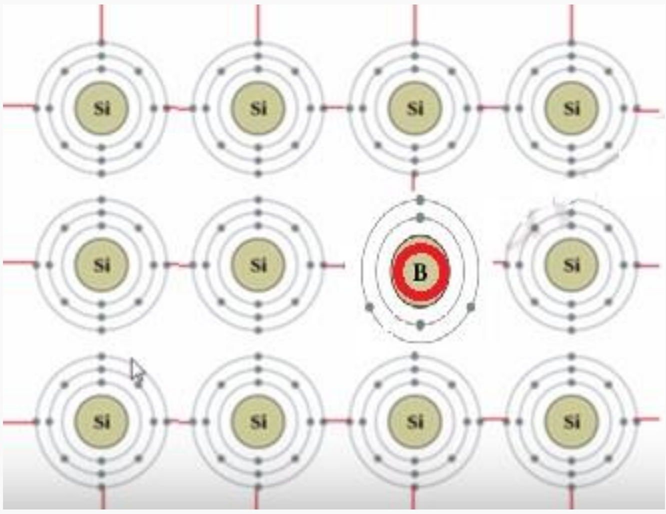
Silicon or germanium of group 14 can also be doped with elements of group 13 element like B, Al or Ga which contains only three valence electrons.



Three electrons of B form covalent bonds with three electrons of Si.



The fourth electron in Si is extra that remains isolated and creates an electron hole or electron vacancy.



An electron from a neighbouring atom can come and fill the electron hole, but leave an electron hole at its original position resulting in displacement of the electron hole in the direction opposite to that of the electron that filled it.

Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate.

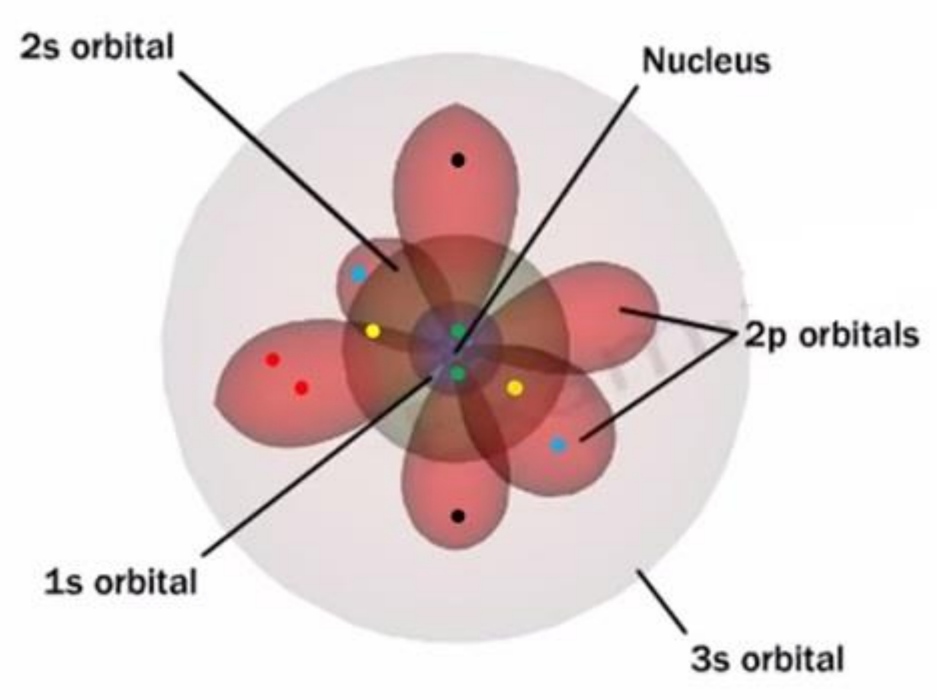
These types of semiconductors are called p-type semiconductors.

Applications of n-type and p-type semiconductors

- n-type and p-type semiconductors finds a great use in manufacturing electronic components.
- Diode is a combination of n-type and p-type semiconductors extensively used as a rectifier.
- Transistors are manufactured by keeping a layer of one type of semiconductor between two layers of another type of semiconductor.
- npn and pnp type of transistors are used to detect or amplify radio or audio signals.
- The solar cell is an efficient photo-diode used for conversion of light energy into electrical energy.
- Gallium arsenide (GaAs) semiconductors have very fast response and have transformed the design of semiconductor devices.
- Transition metal oxides show marked differences in electrical properties.
- TiO, CrO_2 and ReO_3 behave like metals.
- Rhenium oxide, ReO_3 resembles metallic copper in terms of its conductivity and appearance.
- Certain other oxides like VO, VO_2, VO_3 and TiO_3 exhibit metallic or insulating properties depending on temperature.

agnetic Properties

- Every substance possesses magnetic properties originated from the electrons present in them.



- Each electron in an atom behaves like a tiny magnet.
- The magnetic moment of these substances originates from two types of motions
    - its orbital motion around the nucleus and
- its spin around its own axis.
- Electron being a charged particle undergoes these motions and can be considered as a small loop of current possessing a magnetic moment.
- Therefore, each electron has a permanent spin and an orbital magnetic moment associated with it.

- Magnitude of this magnetic moment is very small and is measured in the unit called Bohr magneton, μ B and is equal to 9.27 × 10–24A m^2.

On the basis of their magnetic properties, substances can be classified into five categories:

- Paramagnetic
- Diamagnetic
- Ferromagnetic
- Antiferromagnetic
- Ferrimagnetic.

Paramagnetism

- Paramagnetic substances are weakly attracted on application of magnetic field.
- It is due to presence of one or more unpaired electrons that gets attracted by the magnetic field.
- Application of a magnetic field magnetizes the paramagnetic substances in the same direction.
- They lose their magnetism in the absence of magnetic field.
- O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} are some examples of such substances.

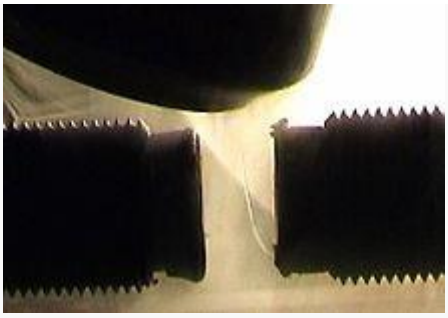
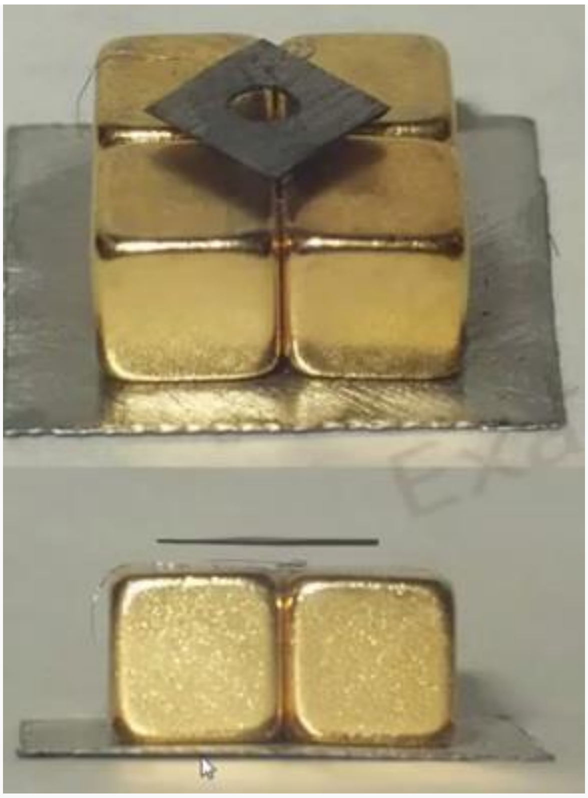


Fig. A trickle of liquid oxygen is deflected by a magnetic field, illustrating its paramagnetism.

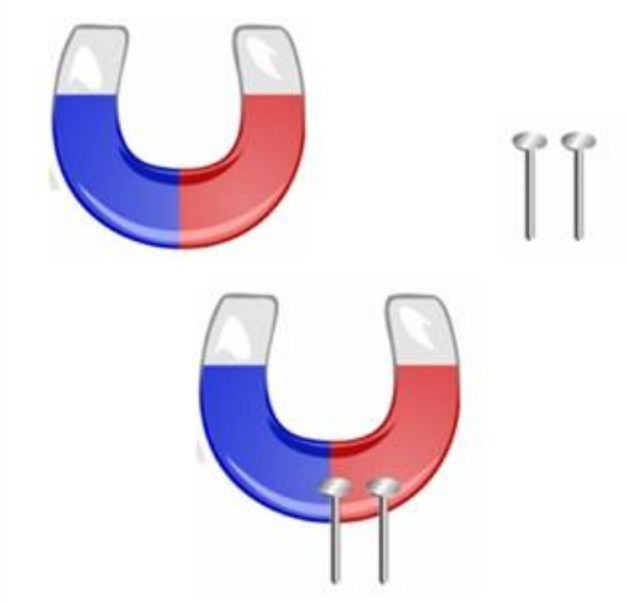
Diamagnetism

- Diamagnetic substances are weakly repelled by a magnetic field.
- This property is represented by the substances in which all the electrons are paired and there are no unpaired electrons.
- They are weakly magnetized on application of magnetic field in opposite direction.
- Pairing of electrons cancel out their magnetic moments and they lose their magnetic character.
- For example, H_2O, NaCl and C_6H_6 are some examples of such substances.



Ferromagnetism

- Ferromagnetic substances get strongly attracted towards magnetic field.
- They can be permanently magnetized.
- In solid state, the metal ions of ferromagnetic substances are grouped together into small regions and are known as domains that act as a tiny magnet.
- In an unmagnetised ferromagnetic substance the domains are randomly oriented that cancels out their magnetic moments.
- When placed in a magnetic field all the domains of the substance get oriented in the direction of the magnetic field producing a strong magnetic effect which persists even on removal of the magnetic field and the ferromagnetic substance becomes a permanent magnet.
- For example, iron, cobalt, nickel, gadolinium and CrO2 are ferromagnetic substances.



- Whereas in case of Antiferromagnetism domains are oppositely oriented thereby cancel out each other's magnetic moment. For example, MnO.

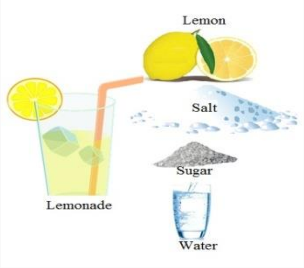
Ferrimagnetism

- Magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers.
- They are weakly attracted by magnetic field as compared to ferromagnetic substances.
- For example, Fe_3O_4 (magnetite) and ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$.
- These substances also lose ferrimagnetism on heating and become paramagnetic.

Fig. A magnet made of ferrite which is a ferromagnetic substance

Introduction

During summer after returning home from outside it feels refreshing to drink a glass lemon water. What is it actually?? It is nothing just a mixture of salt, sugar, lemon juice in water. This a rehydrating solution. Solution can be defined as a liquid mixture with minor component (salt, sugar, lemon juice) uniformly distributed within the major component (water).



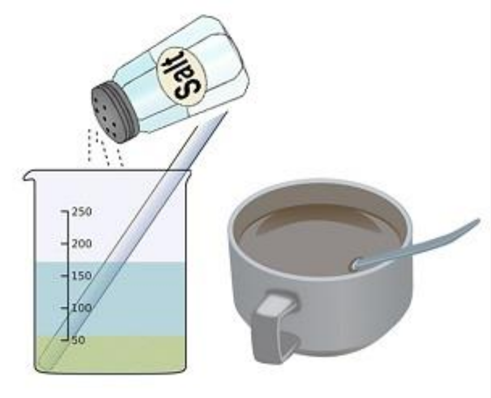
The component of a solution present in the huge quantity is referred to as solvent which determines the physical state of the solution whereas the components of a solution present in the lesser amount is referred to as solute.

In the case of lemonade Water is the solvent whereas salt/sugar are the solute.

Types of solutions

Solutions can be broadly categorized into two types:

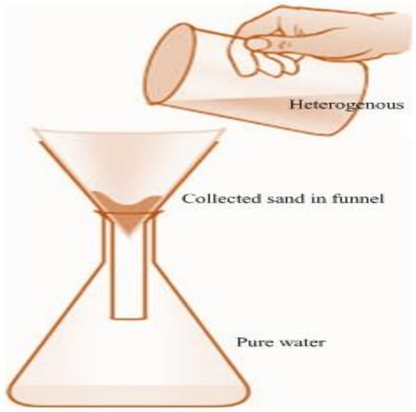
Homogeneous **solutions:** Solutions with uniform composition and properties throughout the solution are known as homogenous solution. E.g. solution of salt or sugar in water, cough syrup, cup of coffee, Mouthwash, perfume are homogeneous mixture of chemicals and dyes, etc.



Homogenous solution of salt dissolved in water (left), a cup of coffee (right)

Heterogeneous **solutions:** Solutions with non-uniform composition and properties throughout the solution are known as heterogeneous solution. E.g. solution of water and sand, solution of oil and water, water and chalk powder, etc.

Heterogeneous solution of oil and water

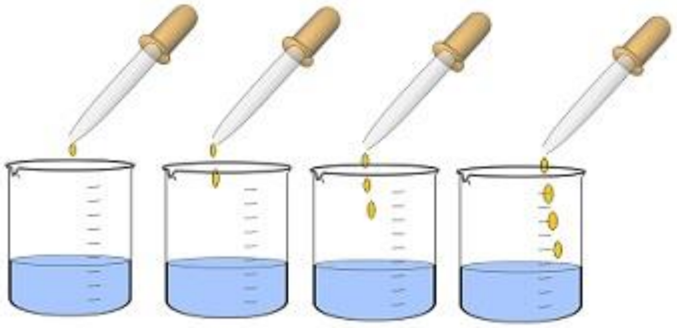


Heterogeneous solution of sand & water

Type of solution	Solute	Solvent	Example
Gaseous	Gas	Gas	Oxygen and nitrogen mixture
	Liquid	Gas	Chloroform with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid	Gas	Liquid	Oxygen in water
	Liquid	Liquid	Ethanol in water
	Solid	Liquid	Glucose in water
Solid	Gas	Solid	Hydrogen solution in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Dissolved copper in gold

Concentration of solution

- Concentration of a solution is the measure of the composition of a solution.
- A solution with relatively very large quantity of solute is called concentrated solution.
- A solution with relatively very small quantity of solute is called a dilute solution.



- These four beakers are not same. In 1st beaker there is one drop of solute.

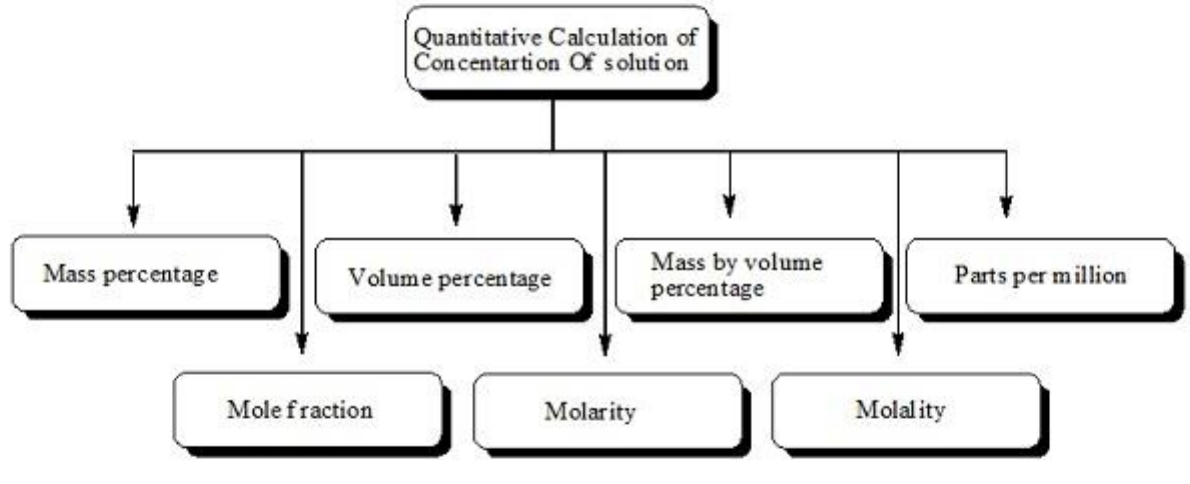
In 2nd beaker there are two drops.

In 3rd there are three drops of solute.

Whereas in 4th beaker there are four drops of solute.

They are different from one another because they differ in their concentration.

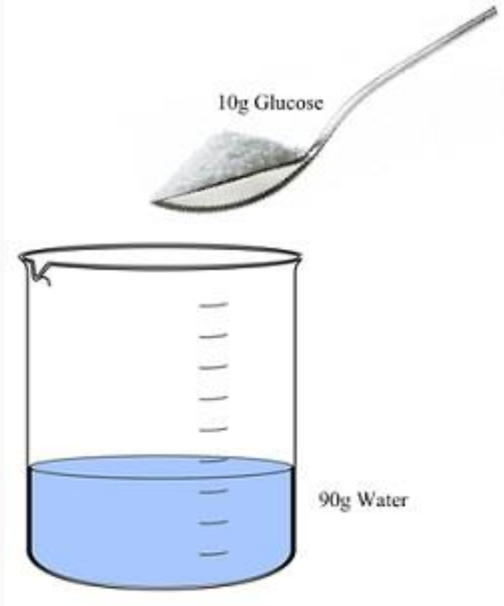
- There are several ways to calculate the concentrationof a solution quantitatively.



Mass percentage

- Mass percentage can be defined as the ratio of Mass of the component of the solution and total mass of the solution multiplied by 100%.
- Mathematically, Mass % of a component $\frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100$
- Mass percentage of glucose in a 100g solution containing 10 g of glucose dissolved in 90 g ofwater is 10%.

Mass % of glucose $= \frac{\text{Mass of glucose in the solution}}{\text{Total mass of the solution}} \times 100 = \frac{10}{100} \times 100 = 10\%$



- Commercial bleaching solution contains62 mass percentage of sodium hypochlorite in water.

Problem: Calculate the mass percentage of benzene (C_6H_6) and carbon tetrachloride (CCl_4) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

Solution:

$$\text{Mass percentage of } C_6H_6 = \frac{\text{Mass of } C_6H_6}{\text{Total mass of the solution}} \times 100\%$$

$$= \frac{\text{Mass of } C_6H_6}{\text{Mass of } C_6H_6 + \text{Mass of } CCl_4} \times 100\%$$

$$= \frac{22}{22+122} \times 100\% = 15.28\%$$

And we also know that:

$$\text{Mass percentage of } CCl_4 = \frac{\text{Mass of } CCl_4}{\text{Total mass of the solution}} \times 100\%$$

$$= \frac{\text{Mass of } CCl_4}{\text{Mass of } C_6H_6 + \text{Mass of } CCl_4} \times 100\%$$

$$= \frac{122}{22+122} \times 100\% = 84.72\%$$

Alternatively, Mass percentage of CCl_4= (100 - 15.28)% = 84.72%

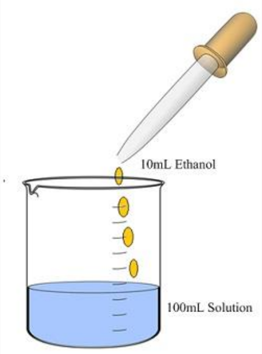
Volume percentage

- Volume percentage can be defined as the ratio of Volume of the component of the solution and total mass of the solution multiplied by 100%.
- Mathematically,

Volume% of a component = $\dfrac{\text{Volume of the component in the solution}}{\text{Total volume of the solution}} \times 100$

- Volume percentage of ethanol in a 100 mL solution containing 10 mL of ethanol dissolved in water is 10%.

Mass % of ethanol = $\dfrac{\text{Volume of ethanol in the solution}}{\text{Total volume of the solution}} \times 100 = \dfrac{10}{100} \times 100 = 10\%$



At this concentration the antifreeze lowers the freezing point of water to 255.4K or –17.6°C.

Problem:

Ami took a 20 cm^3 mixture of CO, CH_4 and He gases and exploded it by an electric discharge at room temperature with excess of oxygen. The volume initially contracted to 13.0 cm^3. Then it further contracted to 14.0 cm^3 when the residual gas is treated with KOH solution. Find out the consumption of gaseous mixture in terms of volume percentage.

Solution:

Take V_1= Partial volumes of CO

V_2= Partial volumes of CH_4

V_3 = Partial volumes of He

$V_1+V_2+V_3 = 20.0$ **cm^3**

The equation for combustion is as follows:

$CO + \frac{1}{2} O_2 \text{-->} CO_2$

$CH_4 + 2O_2 \text{-->} CO_2 + 2H_2O$

V_1 volume of CO = ½ V_1 volume of O_2 = V_1 volume of CO_2

V_2 volume of CH_4 = $2V_2$ volume O_2 = V_2 volume of CO_2

$V1/2 + 2V_2 = 13.0$ **cm^3**

Treating of residual gases with KOH solution would cause the absorption of CO2

$V_1 + V_2 = 14.0$ **cm^3**

$V_1 = 10$ **cm^3**

$V_2 = 4.0$ **cm^3**

$V_3 = 6.0$ **cm^3**

Volume % of CO = 10/20 x 100 = 50

Volume % of CH_4 = 4/20 X 100 = 20

Volume % of He = 100 - (50 + 20) = 30

Mass by volume percentage

- Mass by volume percentage can be defined as the mass of solute dissolved in 100 mL of the solution.
- For instance, mass by volume percent of a solution with 1 g of solute dissolved in 100 mL of **solution** will be 1% or 1% (**mass/volume**).
- Mathematically, Mass by volume% =

$$\frac{\text{Mass of solute (g)}}{\text{Volume of solution (mL)}} \times 100$$

Problem:

Rashida dissolved 40g of sugar in 600 mL of sugar solution. Calculate the mass by volume percentage.

Solution:

Mass by volume% = $$\frac{\text{Mass of solute (g)}}{\text{Volume of solution (mL)}} \times 100 = \frac{40\text{g}}{600} \times 100 = 6.66\%$$

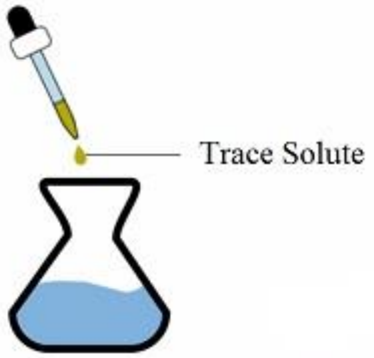
Parts per million

- Parts per million can be defined as the ratio of number of parts of the component to the total number of parts of all components of the solution multiplied by 10^6.
- It is denoted by ppm.
- It is used to express concentration of a solution where solute is present in trace For instance, concentration of pollutants in water or atmosphere is expressed in terms of g mL–1 or ppm.
- Mathematically,

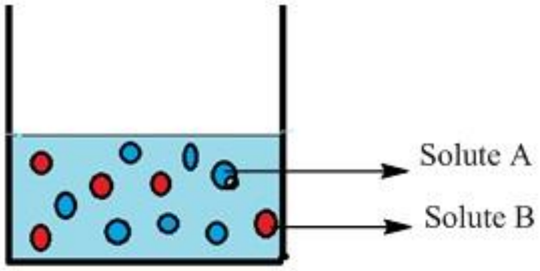
$$\text{Parts per million} = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

- For example, let 0.0005g of NaCl be dissolved in 100mL of water then parts per million =

$$= \frac{0.0005}{100\text{g}} \times 10^6 = 0.000005 \times 10^6 = 5\,ppm$$



Mole fraction



- Mole fraction can be defined as the ratio of number of moles of the component in the solution to the total number of moles of all components in the solution.
- It is denoted by the alphabet *x* and subscript written on the right hand side of *x* denotes the component of which mole fraction is being calculated.
- Mathematically, Mole fraction of a component = $\frac{\text{Number of moles of the component}}{\text{Total number of moles of all components}}$
- Let us consider a binary mixture of A and B. let the number of moles of A and B bee n_A and n_B respectively, then

$$\text{Mole fraction of A} = x_A = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of B} = x_B = \frac{n_B}{n_A + n_B}$$

- For solution where number of components = i

$$\text{Mole fraction} = x_i = \frac{n_i}{n_1 + n_2 + \ldots\ldots + n_i} = \frac{n_i}{\sum n_i}$$

- In a given solution sum of the mole fractions of all the components is unity. Mathematically, $x_1 + x_2 + x_3 \ldots. + x_i = 1$

Problem: Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

Solution:

Total mass of the solution = 100 g

Mass of benzene = 30 g.

∴ Mass of carbon tetrachloride = (100 - 30)g = 70 g

Molar mass of benzene (C_6H_6) = (6 × 12 + 6 × 1) g mol^{-1} = 78 g mol^{-1}

∴ Number of moles of C_6H_6 =30/78 mol

= 0.3846 mol

Molar mass of carbon tetrachloride (CCl_4) = 1 × 12 + 4 × 355 = 154 g mol^{-1}

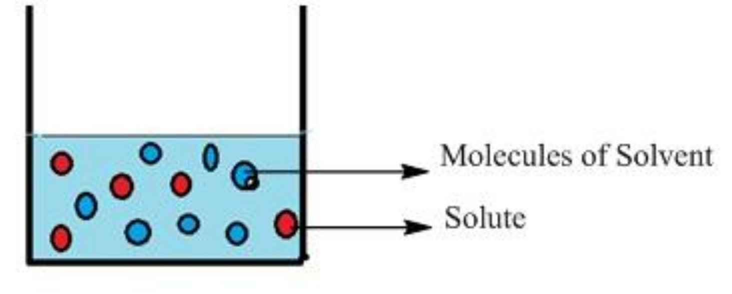
∴ Number of moles of CCl_4 = 70/154 mol = 0.4545 mol

Mole fraction of C_6H_6 =

$$= \frac{\text{Number of moles of } C_6H_6}{\text{Number of moles of } C_6H_6 + \text{Number of moles of } CCl_4} \times 100\%$$

$$= \frac{0.3846}{0.3846 + 0.4545} = 0.458$$

Molality



- *Molality* (*m*) can be defined as the ratio of number of moles of solute to the mass of solvent in kg.
- It can also be defined as the number of moles of solute present in unit kilogram of solvent.
- Mathematically, Molality (m) = Moles of Solute / Mass of Solvent in Kg
- For instance, molality of a solution containing 74.5 g (1 mol) of KCl dissolved in 1 kg of water is 1.00 m or 1.00 mol kg^{-1}.

Problem: Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution.

Solution:

Molar mass of urea (NH_2CONH_2) = 2 (1 × 14 + 2 × 1) + 1 × 12 + 1 × 16 = 60 g mol^{-1}

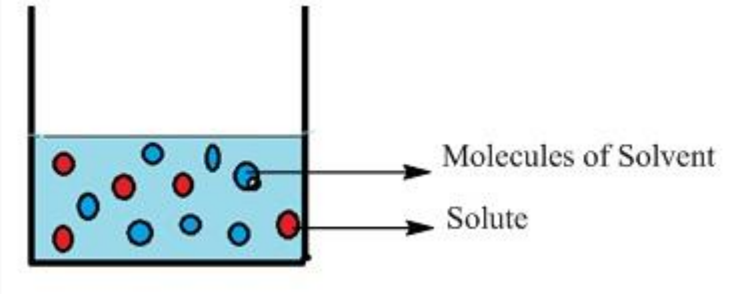
0.25 Molar aqueous solution of urea means 1000 g of water contains 0.25 mol = (0.25 × 60) g of urea = 15 g of urea

(1000 + 15) g of solution contains 15 g of urea.

Therefore, 2.5 kg (2500 g) of solution contains = (15 X 2500) / (1000+15) g = 36.95 g = 37 g of urea (approximately).

Mass of urea required = 37 g

Molarity



- Molarity (*M*) can be defined as the ratio of number of moles of solute to the volume of solution in liter.
- It can also be defined as the number of moles of solute present in unit litre or cubic decimeter of solution.
- It is function of temperature due to the dependence of volume on temperature whereas Mass %, ppm, mole fraction and molality are independent of temperature because mass does not depend on temperature.
- Mathematically, Molarity = Moles of Solute / Volume of Solution in Litre
- For instance, molarity of a solution containing 0.25 mol of NaOH dissolved in one litre or one cubic decimeter is 0.25 M or 0.25 mol L^{-1}.

Problem: Calculate the molarity of each of the following solutions:

(a) 30 g of $Co(NO_3)_2 \cdot 6H_2O$ in 4.3 L of solution

(b) 30 mL of 0.5 M H_2SO_4 diluted to 500 mL.

Solution:

Molarity = Moles of Solute / Volume of Solution in Litre

(a) Molar mass of $Co(NO_3)_2 \cdot 6H_2O$ (solute)

= 59 + 2 (14 + 3 × 16) + 6 × 18 = 291 g mol^{-1}

∴Moles of $Co(NO_3)_2 \cdot 6H_2O$ = 30 / 291 mol = 0.103 mol

Therefore, molarity = 0.103 mol / 4.3 L = 0.023 M

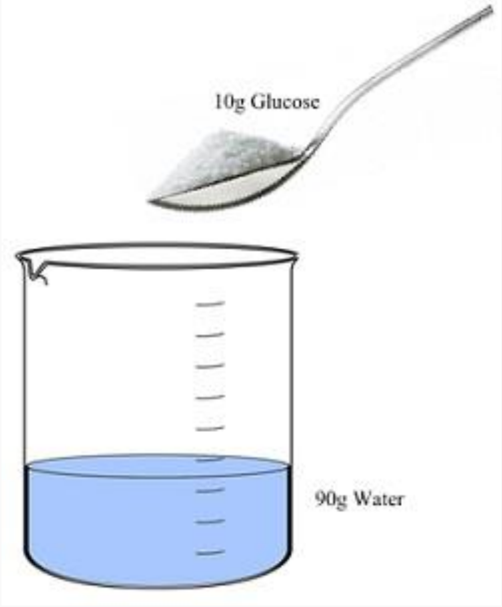
(b) Number of moles present in 1000 mL (Solvent) of 0.5 M H_2SO_4 (Solute) = 0.5 mol

∴ Number of moles present in 30 mL of 0.5 M H_2SO_4 = (0.5 X 30) / 1000 mol = 0.015 mol

Therefore, molarity = 0.015 mol / 0.5 L = 0.03 M

Solubility

Solubility is a physical property of a solution. It can be defined as the measure of maximum amount of solute that can be dissolved in a quantified amount of solvent.



10g of glucose powder soluble in 90 g of water

This property of solution depends upon the factors like:

- **The nature of soluteand solvent and the interaction between them** :The stronger the attractions between solute and solvent molecules, the greater will be the solubility.

- **Molecular size of solute** :Larger molecules are more difficult to dissolve in solvents whereas the smaller molecules dissolve easily and are more soluble in solvents.

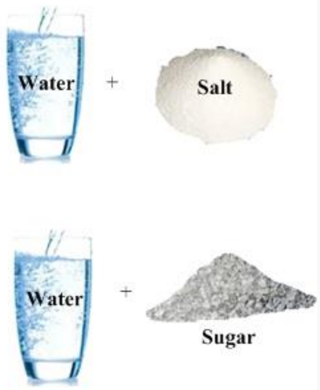
- **Polarity** :Polar solvents (having bonds with different electro negativities) like Water, ethanol, formaldehyde dissolve polar solutes whereas nonpolar solvents (having bonds with similar electro negativities) like pyridine, toluene, and hexane dissolve nonpolar solutes.

- **Temperature** : Rise in temperature increases the solubility.

- **Pressure** : Rise in pressure increases the solubility.

Solubility of a solid in a liquid

- Solution of sugar or salt dissolved is a common example of solubility of a solid in liquid. But it is not necessary that all solids will dissolve in liquid.



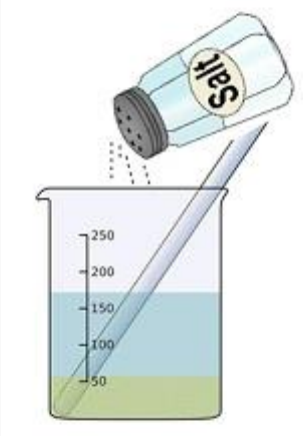
- For instance, solids like naphthalene and anthracene do not dissolve in water but dissolves easily in benzene but sugar and salt does not dissolves in benzene.

- This is because it is property of solution that polar solutes dissolve in polar solvents like Water, ethanol, formaldehyde and chloroform whereas non polar solutes in nonpolar solvents like pyridine, toluene, and hexane. This phenomenon can be easily defined as like dissolves like.
- The phenomenon of increase in the concentration of solution due to dissolving of solid solute to the solvent is known as **dissolution**.
- The phenomenon of collision of solute particles in a solution resulting in the separation of the solute particles from the solution is known as **crystallization**.
- A phase when number of solute particles going into solution is equal to the solute particles separating out of the solution is known as **equilibrium**. The concentration of solute remains constant at this stage.
- A solution in which no more solute can be dissolved into the solvent at the same temperature and pressure is known as saturated solution.
- Whereas a solution in which more solute can be dissolved in the solvent at the same temperature and pressure is known as unsaturated solution.
- According to **Le Chateliers Principle** in a saturated solution, if the dissolution process is endothermic ($\Delta_{sol} H > 0$), the solubility should increase with rise in temperature but if the dissolution process is exothermic ($\Delta_{sol} H > 0$) the solubility should decrease.
- Pressure does not have crucial effect on solubility of solids in liquids because they remain unaffected to pressure due to the high incompressibility of solids and liquids.

Solubility of a gas in a liquid

- Aerated drinks, Dissolved oxygen in water bodies that supports the aquatic life are natural instance of solubility of gas in a liquid. Hydrogen chloride gas (HCl) is also highly soluble in water.

- The phenomenon of increase in the concentration of solution due to dissolving of solid solute to the solvent is known as **dissolution**.

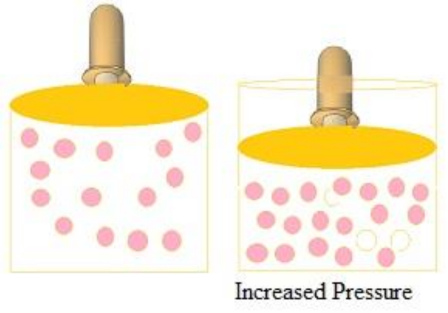


Dissolution of Salt in Water

- The phenomenon of collision of solute particles in a solution resulting in the separation of the solute particles from the solution is known as **crystallization**.

Crystal of copper Sulfate obtained by the crystallization of Copper Sulfate solution

- A phase when number of solute particles going into solution is equal to the solute particles separating out of the solution is known as **equilibrium**. The concentration of solute remains constant at this stage of dynamic equilibrium.
- Solubility of gas in liquid is highly affected by temperature and pressure.
- Increase in temperature reduces the solubility of gases in liquids because on dissolving gas molecules in liquid the process of dissolution is similar to condensation leading to the evolution of heat. Therefore, dissolution is an exothermic process, due to which the solubility decreases with increase of temperature.
- Increase in pressure by compressing the gas to a smaller volume increase the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of solution to enter it leading to the increase in the solubility of gases.



Henry's law

- Henry's Law establishes aquantitative relation betweenpressure and solubility of a gasin a solvent.
- This law is for gas-liquid solution.
- According to the law at a constant temperature, thesolubility of a gas in a liquid is directly proportional to thepressure of the gas.
- It can also be stated as - The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.
- Mathematically,

$p = K_H x$ where K_H = Henry's law constant.

- At same temperature different gasses have different K_H
- It is a function of the nature of the gas. At a given pressure increasing value of K_H implies lower solubility of the gas in the liquid.
- Value of K_H increases with the increase in temperature therefore solubility of gases increases with decreasing temperature. Due to this reason cold water is more sustainable for aquatic life than warm water.

Problem: H_2S, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

Solution:

It is given that the solubility of H_2S in water at STP is 0.195 m, i.e., 0.195 mol of H_2S is dissolved in 1000 g of water.

Moles of water = 1000g / 18g mol^{-1} = 55.56 mol

∴Mole fraction of H_2S, x = Moles of H_2S / Moles of H_2S+Moles of water 0.195 / (0.195+55.56)= 0.0035

At STP, pressure (p) = 0.987 bar

According to Henry's law:

$p = K_H x \Rightarrow K_H = p / x$

= 0.0987 / 0.0035 bar

= 282 bar

Applications of Henry's law

- Sealing of soft drink bottles at high pressure increases the solubility of CO_2 in soft drinks and soda water.

- When a diver goes underwater his body is subjected to high pressure. Due to this the body tissues absorbs more gases. The breathed in oxygen is required for cellular respiration to provide energy to the diver. But the nitrogen gets absorbed into the body tissues.

The pressure increases with the increase in depth. Therefore as the diver approaches the bottom of the water body the pressure increases. With this increase in pressure more nitrogen gets absorbed by the body tissues.

But as he approaches upward to come out of the water body the pressure starts decreasing with the decrease in depth. This in turn decreases the amount of nitrogen getting absorbed by the body tissues.

This causes bubbles of nitrogen in the body which in turn causes bends in the body of the diver.

They are difficult and can even cause threat to their life. To protect the divers from such situation the water utilized by scuba jumpers are loaded with diluted air containing 11.7% helium, 56.2% nitrogen and 32.1% oxygen.

- At high heights the fractional weight of oxygen is not as much as that at the ground level. This stimulates low concentrations of oxygen in the blood and tissues of individuals living at high heights or climbers. Low blood oxygen causes climbers to feel feeble and not able to think plainly, indications of a condition known as anoxia.

Raoult's law

- Raoult's law establishes a quantitative relationship between the partial vapour pressure and mole fraction of a solution.
- This law is only for liquid-liquid solution.
- The law states that for a solution of volatile liquids, the partial vapour pressure (p) of each component in the solution is directly proportional to its mole fraction (x).
- Mathematically, $p \propto x$

Or $p = p^0 x$

Where p^0 is the vapour pressure of pure component at the same temperature.

- Thus, for component 1, $\mathbf{p_1 = p_1{}^0 x_1}$ and for component 2 $\mathbf{p_2 = p_2{}^0 x}$
- Let the solvent be represented by 1 and solute be represented by 2. At the point when the solute is non-volatile, just the solvent molecules are present in vapour phase and add to vapour pressure.

Let p_1 = vapour pressure of the solvent,

x_1 = mole fraction,

$p_i{}^0$ = vapour pressure in the pure state.

According to Raoult's law

$\mathbf{p_1 \propto x_1}$

And $\mathbf{p_1 = p_1{}^0 x_1}$

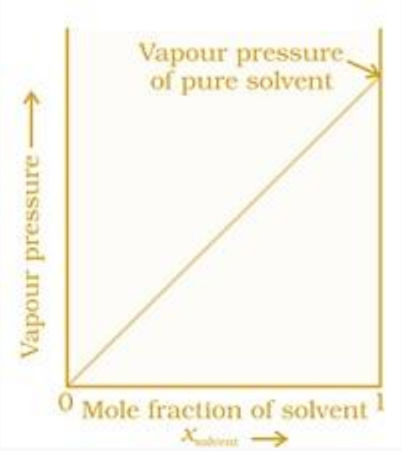
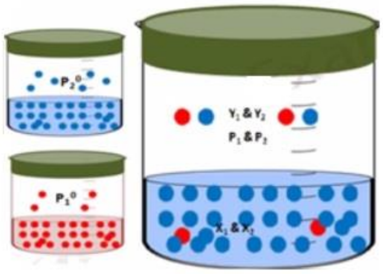


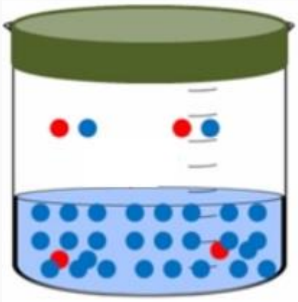
Fig. a plot between the vapour pressure and the mole fraction of the solvent is linear

Raoult's law as special case of Henry's law



- At a given temperature liquids vaporize. At equilibrium the pressure exertedby the vapour of the liquid over the liquidphase is referred to as vapour pressure.
- According to Raoult's law, vapour pressure of a volatile component in a given solution ca be defined by $\mathbf{p_i = p_i^0 x_i}$
- In an answer of a gas in a fluid one of the segments is volatile to the point that it exists as a gas and solvency is given by Henry's law which expresses that $\boldsymbol{p = K_H x}$
- Comparing both the equations we get that partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution. Proportionality constant K_H differs from p_1^0
- Therefore, Raoult's law turns into a unique instance of Henry's law in which K_H get to be equivalent to p_1^0.

Vapour pressure of a liquid-liquid solution



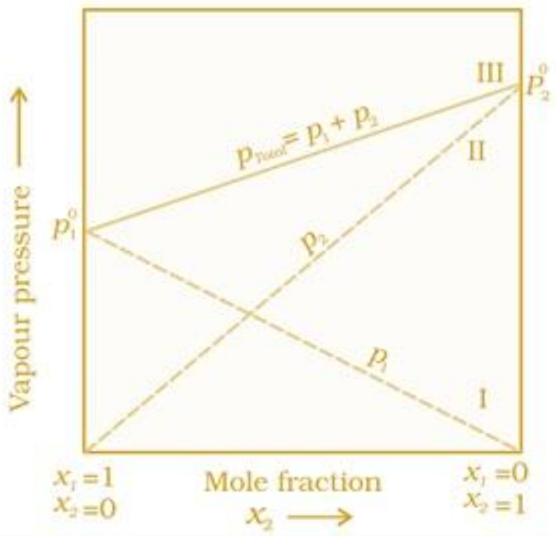
- Acetic acid in water is a liquid-liquid solution. Similarly lemon juice added to water for making lemonade is a liquid-liquid solution.
- Let two volatile components of a binary solution be expressed as 1 and 2.
- In a closed vessel both the components of the solution would evaporate and establish an equilibrium state between the vapour phase and the liquid phase.
- Let p_{total} = Total vapour pressure

p_1 = Partial vapour pressures of component 1

p_2= Partial vapour pressures of component 2
x_1 = Mole fractions of component 1.
x_2 = Mole fractions of component 2

- Dalton's law of partial pressures states that the total pressure (p_{total}) of the solution is the sum of the partial pressures of the components of the solution.
- Mathematically, $P_{total} = P_1 + P_2$
- Substituting the values of p_1 and p_2 we get

$$\begin{aligned} P_{total} &= x_1 P_1^0 + x_2 P_2^0 \\ &= (1 - x_2) P_1^0 + (1 - x_1) P_2^0 \\ &= P_1^0 + (P_2^0 - P_1^0) x_2 \end{aligned}$$



- The minimum value of p_{total} is p_1^0 and the maximum value is p_2^0, assuming that $p_1^0 < p_2^0$.
- Let y_1 = Mole fractions of the component 1

y_2 = Mole fractions of the component 2

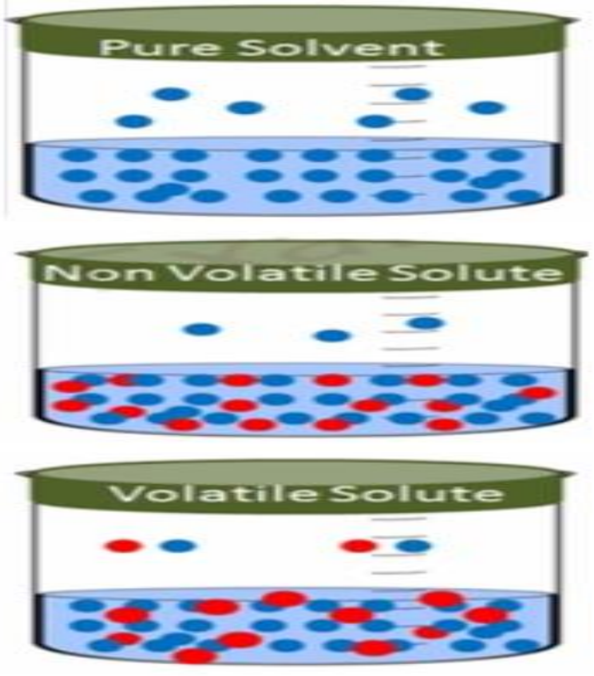
According to Dalton's law of partial pressures:

$P_1 = y_1 P_{total}$

$P_2 = y_2 P_{total}$

Vapour pressure of solution of solids in liquids

- Solution of salt, sugar or glucose dissolved in water is solutions of solids in liquids.
- Similarly iodine and sulphur dissolved in carbon disulphide are also solutions of solids in liquids
- Addition of anon-volatile solute to a solvent togive a solution results in the exertion of the vapourpressure of the solution uniquely from the solvent.



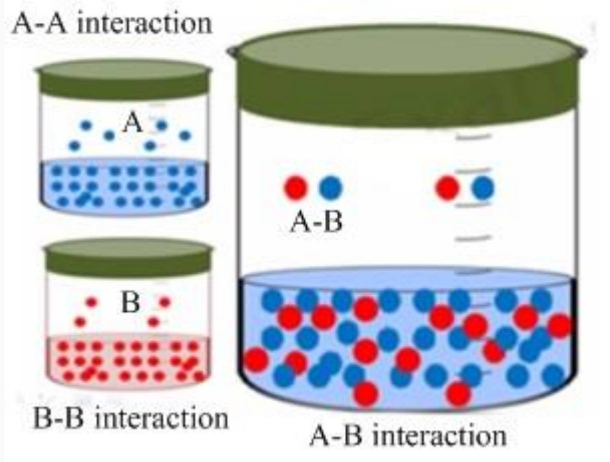
- This vapour pressure is lower than the vapour pressure of the pure solvent at a given temperature.

- The surface of the solution is occupied by both solute andsolvent molecules which results in the reduction of the surface for the solvent molecules. As a result the apparent number ofsolvent molecules escaping from the surface is reduced. This in turn reduces the vapour pressure.
- The reduction of vapour pressure of solvent depends on thequantity of non-volatile solute present in the solution not on its nature.

Ideal solutions and Non- ideal solutions

- The solutions that obey Raoult's law over the whole collection of concentration are known as ideal solutions.

- The enthalpy of mixing of the pure components for the formation of the solution is zero. Mathematically, $\Delta_{mix} H = 0$.
- This implies that heat is neither absorbed nor evolved during the mixing of components in a solution.
- The volume of mixing of the pure components for the formation of the solution is also zero. Mathematically, $\Delta_{mix} V = 0$
- Volume of the entire solution = Sum ofvolumes of the components.



- In case of pure components the intermolecular attractive interactions is of A-A and B-B type.
- In case of binary solutions the intermolecular attractive interactions is of A-A, B-B and A-B type.
- When the intermolecular attractive forces between the A-A and B-B type arenearly equivalent to the intermolecular attractive forces between A-B it results in the formation of ideal
- No solution is perfectly ideal but some solutions are nearlyideal in behaviour. For instance, solution of n-hexane and n-heptane, Bromoethaneand chloroethane, benzene and toluene, etc. exhibits ideal behaviour.
- The solutions that do not obey Raoult's law over the whole collection of concentration are known as non-ideal solutions.
- The vapour pressure of a non-ideal solution is either higher or lower than predicted by Raoult's law.

Positive deviation from Raoult's Law

- The solute- solute and solvent-solvent interaction are stronger than solute-solvent interaction.
- Let p_A = Partial vapour pressures of component A

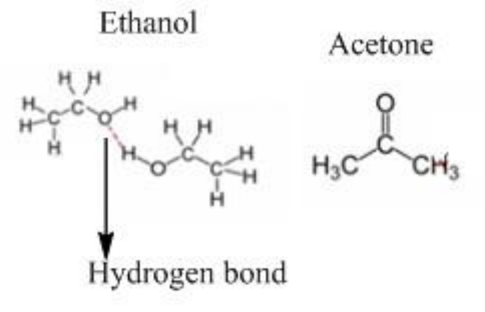
P_B = Partial vapour pressures of component B

H_{mix} = Change in enthalpy of mixing.

V_{mix} =Change in volume of mixing.

- $p_A > p_A^o x_A$

- $p_B > p_B^o x_B$
- $\Delta H_{mix} > 0$
- $\Delta V_{mix} > 0$
- Total vapor pressure is more than as expected from Raoult's law.
- Solution of ethanol and acetonebehaves in the same manner. Molecules of pure ethanol are hydrogen bonded. The molecules of acetone get in between the molecules of ethanol on addition of acetone and break some of the hydrogen bonds between them.



Negative deviation from Raoult's Law

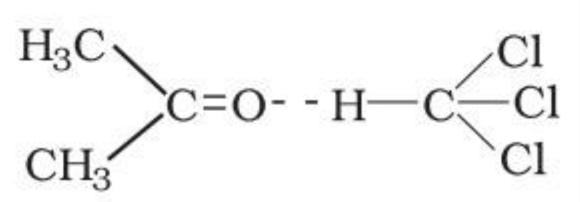
- The solute-solute and solvent –solvent interactions are weaker than solute-solvent interaction.
- Let p_A = Partial vapour pressures of component A

P_B = Partial vapour pressures of component B

H_{mix} = Change in enthalpy of mixing.

V_{mix} =Change in volume of mixing.

- $p_A < p_A^o x_A$
- $p_B < p_B^o x_B$
- $\Delta H_{mix} < 0$
- $\Delta V_{mix} < 0$
- Total vapor pressure is less than as expected from Raoult's law.
- Solution of phenol and aniline. It has strong intermolecular hydrogen bonding between phenolicproton and lone pair of nitrogen atom of aniline than the intermolecular hydrogen bonding between similar molecules.
- A solution of chloroform and acetone shows negative deviation from Raoult's law due to the formation of hydrogen bond with acetone molecule by chloroform molecule. This decreases the chances of molecules of component to escape leading to the decrease in vapour pressure. And hence the solution exhibits negative deviation from Raoult's law



Azeotropes

- Azeotropes are binary mixturespossessing the same synthesis in fluid, vapor stage and boiling stage at a steady temperature.
- The components of azeotropic mixtures are separated by fractional distillation.
- Azeotropes can be broadly categorized into two types-

1. ***Minimum boiling azeotrope***

The solutions showing positive deviation from Raoult’s law. For instance, solution of ethanol and water on fractional distillation results in a solution containing approximately 95% by volume of ethanol.

2. ***Maximum boiling azeotrope.***

The solutions showing negative deviation from Raoult’s law. For instance, solution of nitric acid and water has the approximate arrangement, 68% nitric corrosive and 32% water by mass, with a breaking point of 393.5 K.

Properties of solution affected by vapour pressure

- Vapour pressure of solution decreases on addition of a non-volatile solute to a volatile solvent.
- Properties of solutions affected by the decrease of vapour pressure includes-

1. Relative lowering of vapour pressure of the solvent
2. Depression of freezing point of the solvent
3. Elevation of boiling point of the solvent and
4. Osmotic pressure of the solution.

- These properties of solution depend on the number of solute particles present in the solution regardless of their nature relative to the total number of particles present in the solution. These properties are termed as colligative properties derived from a Latin word with co meaning together ligare meaning to bind.

Relative lowering of vapour pressure

- Vapour pressure of a solvent present insolution is less than the vapour pressure of the pure solvent.
- According to Raoult lowering of vapour pressure of a solution depends only on the concentration of thesolute particles and remains independent of their identity.
- $p_1 = x_1 p_1^0$
- The reduction in the vapour pressure of solvent (p_1) is given as:

$$\Delta p_1 = p_1^0 - p_1 = p_1^0 - p_1^0 x_1$$
$$= p_1^0(1 - x_1)$$

As $x_2 = 1 - x_1$ the above equation reduces to $\Delta p_1 = x_2 p_1^0$

- Lowering of the vapour pressure of a solution with several non-volatile solutes depends upon the sum of the mole fraction of different solutes which makes the above equation as-

$$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2$$

$$\frac{p_1^0 - p_1}{p_1^0} = \text{Relative lowering of vapour pressure}$$

$$x_2 = \text{mole fraction of the solute} = \frac{n_2}{n_1 + n_2}$$

Where n_1 and n_2 are the number of moles of solvent and solute respectively present in the solution.

- The above equation can be written as:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

- For dilute solutions $n_2 << n_1$, hence ignoring n_2 in the denominator we get

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1}$$

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 + w_1}$$

w_1 and M_1 = Masses and molar masses of solvent.

w_2 and M_2 = Masses and molar masses of solute.

Elevation of boiling point

- Increase in temperature increases the vapour pressure of a
- A liquid boils at atemperature where the vapour pressure is equal to the atmospheric
- Vapourpressure of the solvent decreases in the presence of non-volatile solute.
- The boilingpoint of a solution is always higher than that ofthe boiling point of the pure solvent in which thesolution is prepared as.
- The elevation ofboiling point also depends on the number ofsolute molecules rather than their nature.
- The increase in the boiling point = $\Delta T_b = T_b - T_b^0$. This is known as elevation of boiling point.

T_b^0 = boiling point of pure solvent

T_b^0 = boiling point of solution

- In dilute solutions the elevation of boiling point *T*b is directly proportional to the molal concentration of the solute in a solution. Mathematically,

$\Delta T\text{b} \propto m$

$\Delta T\text{b} = k_b m$

m = Molality = number of moles of solute dissolved in 1 kg of solvent

K_b = constant of proportionality. It is also known as Boiling Point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant). The unit of K_b is K kg mol^{-1}.

- Let w_2 and M_2 = Masses and molar masses of solute

w_1= Mass of solvent

$$\text{Molality of the solution} = m = \frac{w_2/M_2}{w_1/1000} = \frac{1000 \times w_2}{M_2 \times w_1}$$

Substituting the value of molality in $\Delta Tb = k_b m$

$$\Delta T_b = \frac{k_b \times 1000 \times w_2}{M_2 \times w_1}$$

Hence M_2 can be determined by the following equation:

$$M_2 = \frac{1000 \times w_2 \times k_b}{\Delta T_b \times w_1}$$

Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C.Molal elevation constant for water is 0.52 K kg mol^{-1}.

Sol. Elevation of boiling point ΔT_b= (100 + 273) - (99.63 + 273) = 0.37 K

Mass of water, w_1 = 500 g

Molar mass of sucrose ($C_{12}H_{22}O_{11}$),

M_2= 11 × 12 + 22 × 1 + 11 × 16 = 342 g mol $^{-1}$

Molal elevation constant, K_b= 0.52 K kg mol $^{-1}$

We know that:

$$\Delta T_b = \frac{k_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$w_2 = \frac{\Delta T_b \times M_2 \times w_1}{1000 \times k_b}$$

= (0.37 x 342 x 500) / (0.52 x 1000)

= 121.67 g (approximately)

Hence, 121.67 g of sucrose is to be added.

Depression of freezing point

- Freezing point of a substance is the temperature at which the vapour pressure of the substance in its liquid phase is equal to the vapour pressure in the solid phase.
- If the vapour pressure of the solution is equal to the vapour pressure of the pure solid solvent then the solution freezes.
- According to Raoult's law, addition of non-volatile solute decreases the vapour pressure of the solvent and would be equal to that of solid solvent at lower This decreases the freezing point of thesolvent.
- The decrease in the freezing point = $\Delta T_f = T_f - T_f^0$. This is known as depression in freezing point.

T_f^0 = freezing point of pure solvent

T_f^0 = freezing point when non-volatile solute is dissolved

- In a dilute solution the depression of freezing point T_f is directly proportional to molality of the solution. Mathematically,

$\Delta T_f \propto m$

$\Delta T_f = K_f m$

K_f = Proportionality constant depending upon the nature of the solvent. This is known as Freezing Point Depression Constant or Molal Depression Constant or Cryoscopic Constant**.** The unit of K_f is K kg mol^{-1}.

- Let w_2 and M_2 = Masses and molar masses of solute

w_1= Mass of solvent

$$\text{Molality of the solute} = m = \frac{w_2 / M_2}{w_1 / 1000}$$

Putting this value of molality in the equation $\Delta T_f = K_{f\,m}$

$$\Delta T_f = \frac{k_f \times w_2 / M_2}{w_1 / 1000}$$

$$\Delta T_f = \frac{k_f \times w_2 \times 1000}{M_2 \times w_1}$$

- M_2 can be determined by the equation

$$M_2 = \frac{k_f \times w_2 \times 1000}{\Delta T_f \times w_1}$$

- The values of K_f and K_b can be determined from the following relations.

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus} H}$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap} H}$$

R= gas constant

M_1 = molar mass of the solvent

$\Delta_{fus}H$= enthalpies for the fusion of the solvent.

$\Delta_{vap}H$= enthalpies for the vaporization of the solvent.

Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. K_f= 3.9 K kg mol^{-1}.

Sol. Mass of acetic acid, w_1= 75 g Molar mass of ascorbic acid ($C_6H_8O_6$),

M_2= 6 × 12 + 8 × 1 + 6 × 16 = 176 g mol^{-1}

Lowering of melting point, ΔT_f = 1.5 K

$$\Delta T_b = \frac{k_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$w_2 = \frac{\Delta T_b \times M_2 \times w_1}{1000 \times k_b}$$

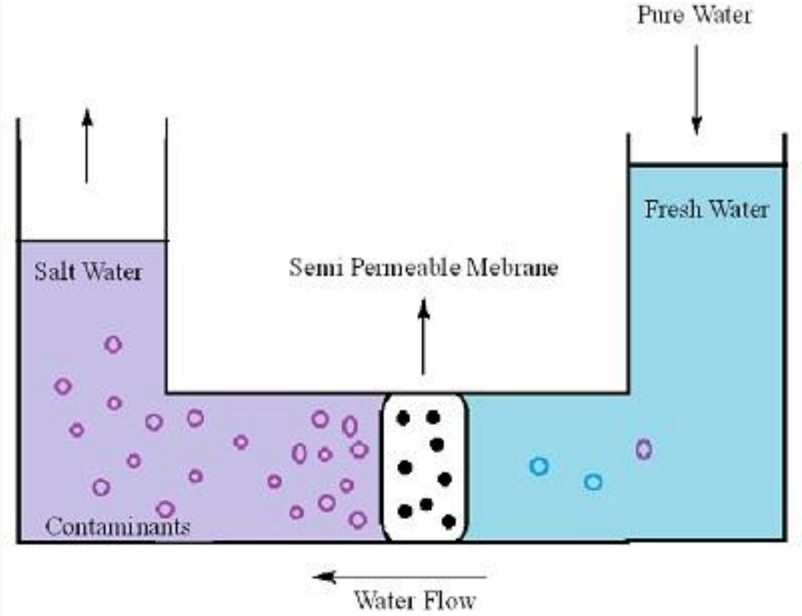
= (1.5 x 176 x 75) / (3.9 x 1000)

= 5.08 g (approx)

Hence, 5.08 g of ascorbic acid is needed to be dissolved.

Osmosis and Osmotic pressure

- We have often observed that raw mangoes shrink when kept in salt water (brine solution), flowers remain fresh for longer time when kept in water.
- This is due to the fact that small solvent molecules such as water are capable of passing through the pores present in every cell. These pores allows small solvents like water to pass through but hinders the passing of larger molecules. This membrane possessing such pore is known as semipermeable membranes.
- The process of flow of solvents from the pure solvent to the solution through a semipermeable membrane is termed as osmosis.
- This flow of solvents to the solution continues until the stage of equilibrium is reached.
- Application of extra pressure on the solution can terminate the flow of solvents from the pure solvent to the solution. This pressure is called osmotic pressure of the solution. It is a colligative property that depends upon the concentration of the solution and is basically meant to stop the passage of solvent molecules through a semipermeable membrane into the solution.
- Solvent molecules generally flows from lower concentration to higher concentration. This flow of solvent from dilute solution to the concentrated solution through a semipermeable membrane is due to the phenomenon of osmosis.



Calculate the osmotic pressure in Pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

Sol. Volume of water, V= 450 mL = 0.45 L

Temperature, T = (37 + 273) K = 310 K

Number of moles of the polymer, *n* = 1 / 185000 mol

Osmotic pressure ð (n/V)RT

= 1/185000 mol **X** 1/0.45L **X** 8.314 **X** 10^3 Pa L $K^{-1}mol^{-1}$ **X** 310K

= 30.98 Pa = 31 Pa

Calculation of Molar Mass from Osmotic Pressure

In dilute solutions the osmotic pressure is proportional to the molarity, *C* of the solution at a given temperature *T*. Mathematically,

ð = *C R T*

R= gas constant

ð = osmotic pressure = (n_2/V) RT

V = Volume of a solution in litres

n_2 = Moles of solute.

w_2 = Grams of solute

M_2 = Molar mass

Now, $n_2 = w_2/M_2$

$$\text{Osmotic pressure } \eth = \frac{w_2RT}{VM_2}$$

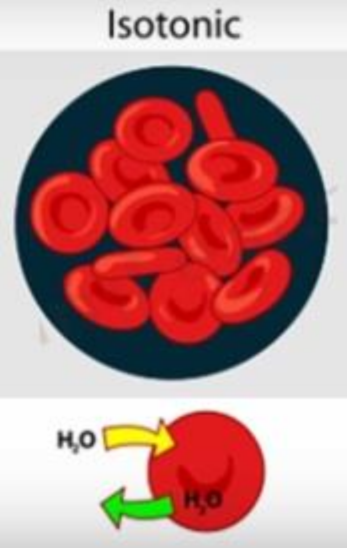
$$\text{Or } \eth V = \frac{w_2RT}{M_2}$$

$$\text{Or } M_2 = \frac{w_2RT}{\eth V}$$

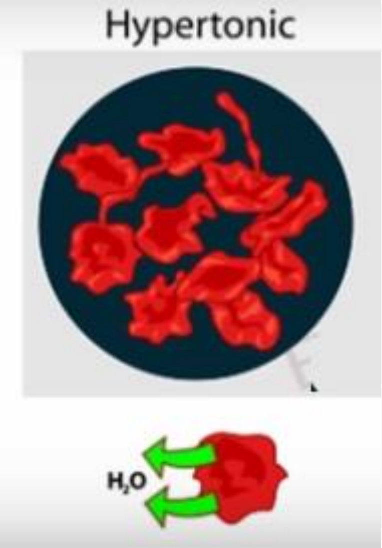
Classification of solutions on the basis of osmotic pressure

On the basis of osmotic pressure solution can be classified into three broad categories.

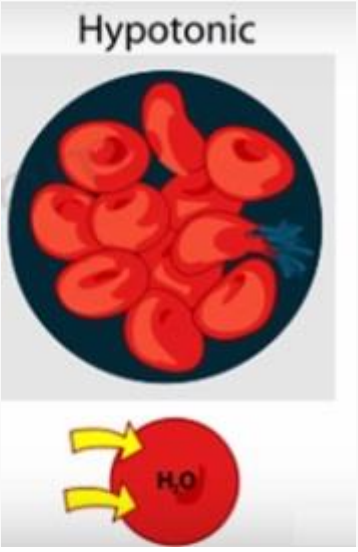
1. **Isotonic solutions :** Two solutions possessing same osmotic pressure at a given temperature are termed as isotonic solution. No osmosis occurs on isolation of these solutions when isolated through a semipermeable membrane.



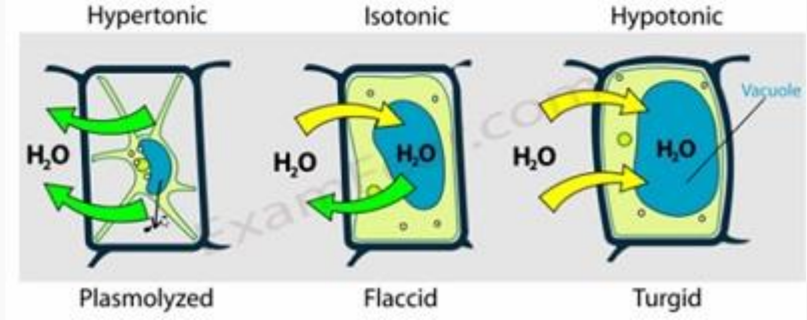
2. **Hypertonic solutions :** In the event that the medium has a lower convergence of water than the cell, implying that it is a concentrated solution, the cell will lose water by osmosis. . Such a solution is known as a hypertonic solution. Once more, water crosses the cell layer in both directions, yet this time more water leaves the cell than enters it. In this manner the cell will shrink.



3. **Hypotonic solutions :** In the event that the medium encompassing the cell has a higher water concentration than the cell, implying that the outside solution is extremely weaken, the cell will pick up water by osmosis. Such a solution is known as a hypotonic solution. Water particles are allowed to go over the cell layer in both directions, yet more water will come into the cell than will clear out. The net (general) result is that water enters the cell. The cell is prone to swell up.



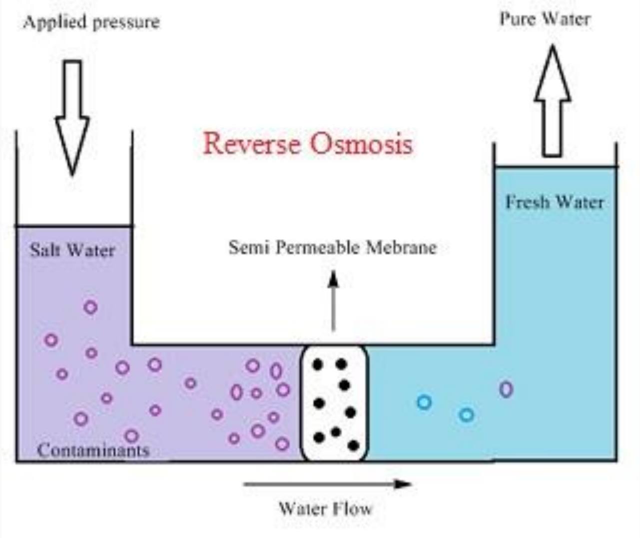
- In case of cells with vacuoles



- Due to this reason people consuming more salty food suffer from water retention in their cell tissues and intercellular spaces resulting in swelling. This is known as edema.
- Movement of water from soil to the top of the tree is also due to the phenomenon of osmosis.
- Adding salt preserves the food from getting spoilt. Due to osmosis bacterium germinating on the food loses water and shrinks down. This kills the bacteria.

Reverse osmosis

- As the name suggests Reverse Osmosis is just the reverse process of Osmosis. Osmosis can occur naturally whenever there is a difference in concentration between the two solutions. But reverse osmosis takes place only when external energy is applied to the more saline solution.
- Application of larger osmotic pressure to the solution side reverses the direction of osmosis.
- This phenomenon makes the pure solvent flow out of the solution through the semi permeable
- Reverse osmosis is extensively used in desalination of sea



Use of Reverse osmosis in water purification

Reverse osmosis is extensively used in the desalination of sea water.

A porous film of cellulose acetate is used as a membrane which is permeable to water but impermeable to impurities and ions is placed over a support.

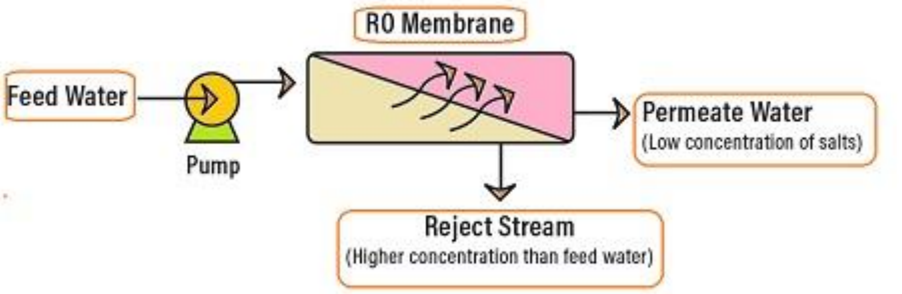
Pressure larger than the osmotic pressure is applied on the sea water solution which allows the passing out of the pure water holding back the bulk of contaminants through the membrane made of polymer.

The measure of pressure required relies upon the salt grouping of the food water. Greater concentration of feed water requires more pressure to defeat the osmotic pressure.

As the water enters the RO membrane under great pressure the water molecules pass through the semi-permeable membrane.

The membrane is impermeable to salts and other contaminants and hence is not allowed to pass through it.

These leftover contaminated water is then discharged through the reject stream and finally drained out or is fed back into the feed water supply. This water will again undergo same procedure and will be purified in some way.



Abnormal molar mass

- Some molecules of solvents with low dielectric constant like molecules of ethanoic acid dimerize into benzene due to the presence of hydrogen bond.
- Association of all the molecules of ethanoic acid into benzene means T_b or T_f for ethanoic acid will be half of the normal value.
- The molar mass calculated on the basis of this ΔT_b or ΔT_f will be twice the expected molar mass.
- This value of molar mass is either lower or higher compared to expected or normal value and is known as abnormal molar mass.
- In 1880 van't Hoff introduced a factor *i* and was named as the van't Hoff factor.
- The van't Hoff factor account for the degree of dissociation or association.
- The van't Hoff factor *i* can be defined as the ratio of Normal molar mass to the abnormal molar mass. Mathematically,

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/ dissociation}}$$

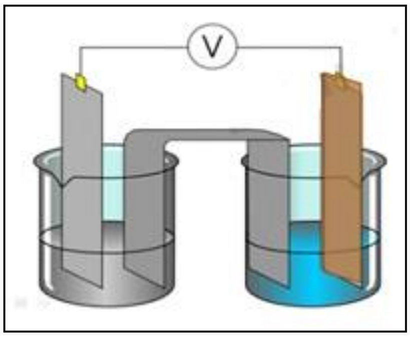
- In case of association, value of i is less than unity.
- In case of dissociation value of i is greater than unity.
- Relative lowering of vapour pressure of solvent =

$$\frac{p_1^0 - p_1}{p_1^0} = i\,\frac{n_2}{n_1}$$

- Elevation of Boiling point, $\Delta T_b = i\,K_b\,m$
  Depression of Freezing point, $\Delta T_f = i\,K_f\,m$
  Osmotic pressure of solution, ð = $i\,n_2RT/V$

Introduction

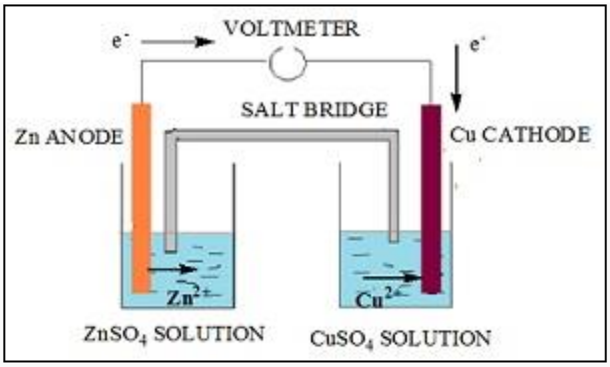
- Electrochemistry refers to the conversion of chemical energy to electrical energy and vice versa. It is basically the study of Production of electricity from energy released during spontaneous reaction and use of electrical energy to bring about non-spontaneous chemical transformation.
- A spontaneous chemical reaction is a reaction which happens on its own and releases free energy. This reaction produces electric energy from chemical reaction. For example, burning of coal, rusting of iron, melting of ice, etc.
- On the other hand non-spontaneous reaction occurs by providing an external source like electricity. For example, Hydrolysis of water.
- Electrochemistry is used for the following purposes.



- Production of metals like sodium hydroxide, chlorine, fluorine and many other chemicals.
- It is also used for purification of metals.
- The process is used in batteries as well as fuel cells which converts the chemical energy into electrical energy and is used in several instruments and devices.
- This process is used in electroplating.
- The reactions carried out using the process of electrochemistry are energy effective and less polluting.

Daniel cell

- The cell that converts the chemical energy liberatedas a result of redox reaction to electrical energy is called a Daniel cell.
- It has anelectrical potential of 1.1 V.



- The setup for Daniel cell is as follows:
    - In a beaker a plate of zinc is dipped in a solution of zinc sulfate ($ZnSO_4$).
    - In another beaker a plate of copper is dipped in a solution of copper (II) sulfate in another container. These plates of metal are called the *electrodes* of the cell.
    - These electrodes behave as terminal to hold the electrons.
    - The two electrodes are connected via wire.

- A salt bridge is placed between the two beakers. This provides a path for the movement of ions from one beaker to the other in order to maintain electrical neutrality.
- Zinc electrode gets oxidized and hence releases electrons that flow through the wire towards the copper electrode.
- The copper (II) sulfate solution releases copper ions Cu^{2+}.
- **At the anode:**

  Oxidation ---------------- loss of electrons.
  $Zn \rightarrow Zn^{2+} + 2e^-$

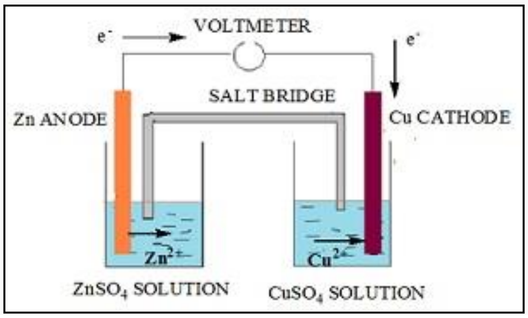
  At cathode,

  Reduction -------------gain of electrons.

  $Cu^{2+} + 2e^- \rightarrow Cu$
- Zinc atoms being more reactive have a greater tendency to lose electrons than that of copper.
  The electrons in this cell moves from zinc anode to copper cathode through the wire connecting the two electrodes in the external circuit
- A bulb placed within this circuit will glow and a voltmeter connected within this circuit will show deflection.
- The net reaction of this cell is the sum of two half-cell reactions.
  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

In a Daniel cell a salt bridge is placed between the two beakers containing a solution of zinc sulfate ($ZnSO_4$) and a solution of copper (II) sulfate respectively. This provides a path for the movement of ions from one beaker to the other in order to maintain electrical neutrality.

Salt Bridge

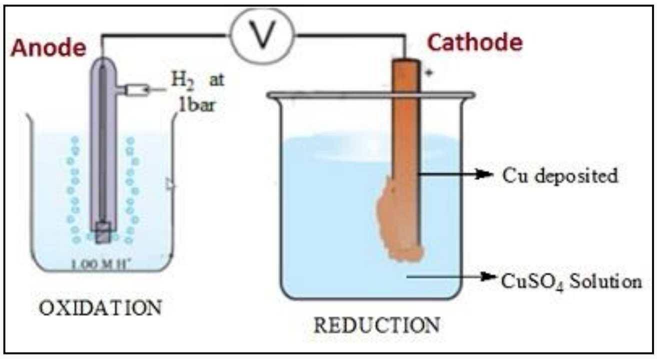


- Salt bridge is an inverted U-tube like structure.
- The tube is filled with concentrated solution of an inert electrolyte.
- The electrolyte does not undergo any sort of chemical reaction nor does it reacts with concentrated solution in the two half cells.
- Most of the time salts like KCl, KNO_3, NH_4NO_3 are used as electrolyte.
- Salt bridge is constructed by filing the U-tube with a mixture prepared by mixing agar-agar or gelatin with a hot concentrated solution of the electrolyte.
- The apparatus is then cooled and consequently the solution fixes within the U-tube in the form of gel.
- This prevents the intermixing of fluids.
- The either ends of the tube are then sealed using cotton wool in order to reduce diffusion.

- The main advantage of suing this bridge is that it prevents the arousal of potential difference (also called liquid junction potential) when two solutions are in contact with each other.
- It completes the electrical circuit as it connects the electrolytes in the two half cells.
- It avoids the chances of diffusion of solutions between the half cells.
- It maintains electrical neutrality by providing a path for the movement of ions.

Measurement of electrode potential in a cell

- The electrode is connected to a **standard hydrogen electrode (SHE)** to constitute a cell.
- The electrode forming the negative terminal of the cell is allotted negative value of electrode potential whereas the electrode forming the positive terminal of the cell is allotted a positive value of electrode potential.
- The potential difference developed between the two terminals is measured using a potentiometer.
- The direction of the flow of electric current in the external circuit is identified using a galvanometer.
- This enables us to identify the positive and the negative terminal of the set up as the current flows from positive terminal to negative terminal.
- This in turn will help us mark the anode and the cathode electrodes due to the fact that the electrons will flow from anode to cathode.



$E_{cell} = E_{cathode} – E_{anode}$

- In case of Daniel cell

At the anode:

Oxidation ---------------- loss of electrons.

$Zn \text{ --> } Zn^{2+} + 2e^-$

At cathode,

Reduction -------------gain of electrons.

$Cu^{2+} + 2e^- \text{ --> } Cu$

The net reaction of this cell is the sum of two half-cell reactions.
$Zn(s) + Cu^{2+}(aq) \text{ --> } Zn^{2+}(aq) + Cu(s)$

Emf of the cell = $E_{cell} = E_{cathode} – E_{anode}$

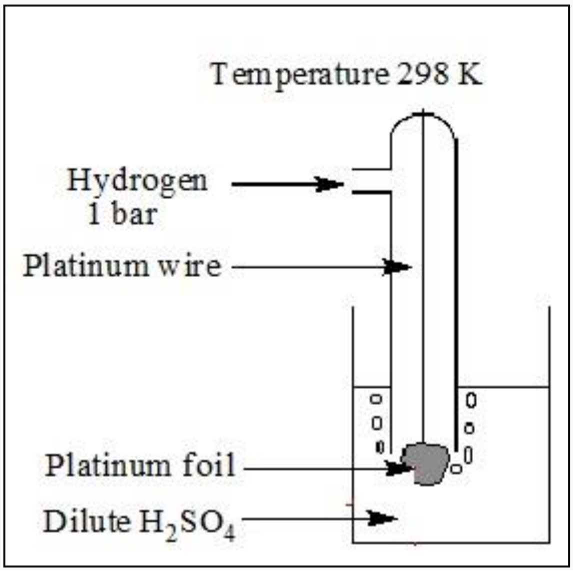
$= 0.34\ V – (-0.76)\ V = 1.10\ V$

(Measured Emf of Cu is 0.34 V and that of Zn is 0.76 V).

Standard hydrogen electrode

- The electrode is connected to a **standard hydrogen electrode (SHE)** to constitute a cell
- It consists of a platinum electrodecoated with a layer of platinum black.

$$\boxed{H^{+}\,(aq) + e^{-} \rightarrow \frac{1}{2}H_2(g)}$$



- The electrode is immersed in an acidicsolution and the pure hydrogen gas is bubbled through it.
- Theconcentration of the reduced form and the oxidized form of hydrogen issustained at unity with following conditions:
- Pressure of hydrogen gas = 1 bar
- Concentration of hydrogen ion in the solution = 1 molar

$E_{cell} = E_{cathode} – E_{anode}$

$E_{cell} = E_{cathode} – 0 = E_{cathode}$

- The measured Emf of the cell:

Pt| H_2 (1 bar)| H^+ (1M) || Cu^{2+}(1M)| Cu is 0.34 V.

The positive value of the standard electrode potential signifies the easy reduction of Cu^{2+} ions than H^+ ions.

- The measured Emf of the cell

Pt| H_2 (1 bar)| H^+ (1M) || Zn^{2+}(1M)| Zn is -0.76 V.

The negative value of the standard electrode potential signifies that the hydrogen ions oxidizes the zinc (or it can be said that zinc can reduce hydrogen ions).

- An electrode with standard electrode potential greater than zero is stable in its reduced form compared tohydrogen gas.
- Whereas an electrode with negative standard electrode potential is less stable in its reduced form compared to hydrogen gas.

- This decreases the standard electrodepotential which in turn decreases the oxidizing power ofthe specific electrode on the left and increases the reducing power of the electrodeto the right of the reaction.

Nernst Equation

- This equation was named after a German physicist Walther Nernst.

- The Nernst Equation empowers the assurance of cell potential under non-standard conditions and relates the measured cell potential to the reaction quotient and permits the exact measurement of equilibrium constants.
- Let us consider an electrochemical reaction of the following type:

aA +bB --> cC + dD

- Nernst equation for this can be written as follows:

$$E_{Cell} = E^{-}_{Cell} - \frac{RT}{nF}\ln Q$$
$$= E^{-}_{Cell} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- In case of daniel cell Nerst equation is as follows:

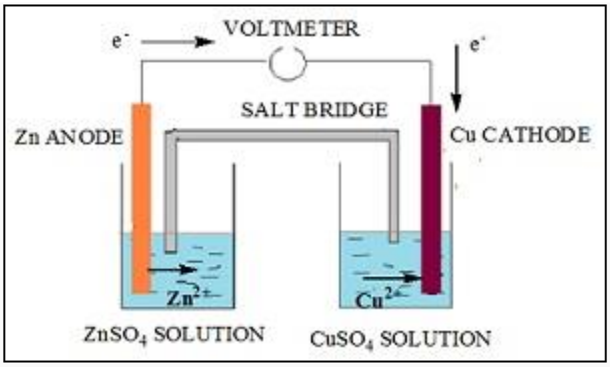
$$E_{Cell} = E^{-}_{Cell} - \frac{RT}{nF}\ln Q$$
$$= E^{-}_{Cell} - \frac{RT}{2F}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

- The above equation implis that the value of increases with the increase in the concentartion of Cu^{2+} ion increases and decrease in the concentration Zn^{2+}
- Putting the values of R, F at T= 298 K. the equation becomes

$$E^{-}_{Cell} - \frac{0.059}{2}\ln\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

- If the circuit in Daniel cell is closed:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$



- With time the concentration of Zn^{2+}
- The concentration of Cu^{2+}
- Voltage reading of the cell on the voltmeter decreases.
- After some time there is no alteration in the concentration of Cu^{2+} and Zn^{2+} ions and the voltmeter gives zero reading. At this point of time equilibrium has been reach
- The Nernst equation for the reaction is:

$$E_{cell} = E^{o}_{cell} - \frac{2.303RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\text{Or } E^{o}_{cell} = \frac{2.303RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

- But at equilibrium,

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c$$

At T = 298 K.

The equation can be rewritten as

$$E^{o}_{cell} = \frac{0.059V}{2}\log K_c$$

$$E^{o}_{cell} = \log K_c = \frac{1.1\times 2}{0.059V} = 37.288$$

$$K_c = 2\times 10^{37} \text{ at } 298\text{K}$$

$$E^{o}_{cell} = \frac{0.059V}{2}\log K_c$$

Problem:

Calculate the emf of the cell in which the following reaction takes place: $Ni_{(s)} + 2Ag^{+}$ (0.002 M) → Ni^{2+} (0.160 M) + $2Ag_{(s)}$. Given that E^{0}_{cell} = 1.05 V.

Solution:

By using Nernst equation

$$E^{-}_{Cell} - \frac{0.059}{2}\log\frac{[Ni^{2+}]}{[Ag^{+}]^{2}}$$
$$= 1.05 - \frac{0.059}{2}\log\frac{[0.160]}{[0.002]^{2}}$$
$$= 1.05 - 0.02955\log\frac{0.160}{0.000004}$$

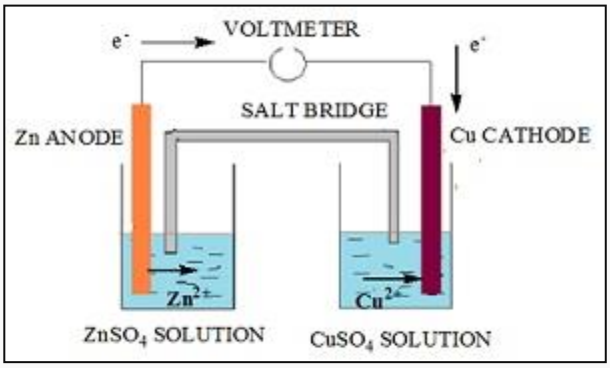
= 1.05 - 0.02955 log 4 × 10^{4}

= 1.05 - 0.02955 (log 10000 + log 4)

= 1.05 - 0.02955 (4 + 0.6021)

= 0.914 V

Electrochemical Cell and Gibbs Energy of the Reaction



- Electrical work done (1 second) = Electrical potentialX Total charge passed
- Passing the charges reversibly through the galvanic cell results in maximum work.
- Reversible work done by galvanic cell = Decrease in Gibbs energy
- Let E = Emf of the cell

nF = Amount of charge passed

$\Delta_r G$ = Gibbs energy of the reaction

$\Delta_r G = -nFE_{cell}$

For the reaction,

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

[$\Delta_r G = -2FE_{cell}$]

But when the equation becomes

$2Zn(s) + 2Cu^{2+}(aq) \dashrightarrow 2Zn^{2+}(aq) + 2Cu(s)$

[$\Delta_r G = -4FE_{cell}$]

Problem:

The cell in which the following reactions occurs:

$$2Fe^{3+} + 2I^{-} \rightarrow 2Fe^{2+} + I_2$$

has E^{θ}_{cell} = 0.236 V at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Solution:

By using the formula,

$\Delta_r G = -nFE_{cell}$

= -2 X 96487 X 0.236

= - 45541.864 J mol^{-1}

= - 45.54 KJ mol^{-1}

Now,

$$\Delta_r G = -2.303RT\log K_c$$

$$\log K_c = -\frac{\Delta_r G}{2.303RT} = \frac{-45.54X10^3}{2.303X8,314X298}$$

$$= 7.981$$

$$K_c = Anti\log(7.981)$$

$$9.57\,X10^7$$

Electrical resistance

- It is denoted by the symbol ‘***R***’.
- It is measured in a unit called ohm (**Ω**) with the help of a Wheatstone bridge
- The electrical resistance is:

1. Directly proportional to its length, ***l***
2. Inversely proportional to its area of cross section, ***A***.

$$R \propto \frac{1}{A}$$

$$R = \rho \frac{1}{A}$$

- In the equation the constant of proportionality denoted by called rho is called **resistivity.**
- It is measured in units called ohm metre.
- When length = 1m.

Cross sectional area = 1m^2

- Then resistivitybecomes the resistance.

1 Ω m = 100 Ω cm

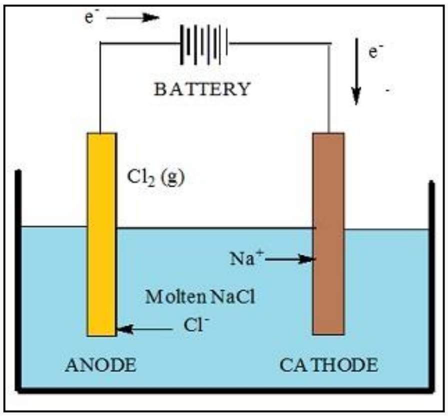
1 Ω cm = 0.01 Ω m

Electrical conductance

- The inverse of resistance is known as conductance.

$$G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$$

- It is measured in a unit called Siemens represented by the symbol ‘S’
- It is equal to ohm^{-1} also known as mho or Ω^{-1}.
- The electricalconductance depends on:
  Nature and structure of the metal
  2. Number of valence electrons per atom
  3. Electrical conductance decreases with increase of temperature and vice versa.



- The free ions Na^+ and Cl^- present in the solution are responsible for the conductance in a solution.
- The inverse of resistivity is termed as conductivity.
- **Ω = 1/k**
- It is represented by the symbol (Greek, kappa).
- It is measured in a unit called Sm^{-1}.
- When length = 1m.

Cross sectional area = $1 m^2$

Then conductivity becomes the conductance.

The conductivity of an electrolytic solution depends on:

1.Nature of the electrolyte added
2.Size of the ions produced and their solvation
3.Nature of the solvent and its viscosity
4.Concentration of the electrolyte
5.It increases with the increase of temperature.
6.Pressure

- Matters can be classified into conductors, insulators andsemiconductors depending on the magnitude of their conductivity.

Conductors:

- Solids with conductivities ranging between 10^4 to 10^7 $ohm^{-1}m^{-1}$ are conductors.
- Metals have conductivities in the order of 10^7 $ohm^{-1}m^{-1}$ is good conductors.
- For example, Iron, Copper, Aluminum.

Fig. Metal is used at the tip of the plug that is inserted into the socket

Insulators:

- Solids with very low conductivities ranging between 10^{-20} to 10^{-10} $ohm^{-1}m^{-1}$.
- For example, Wood, plastic, cloth, glass.

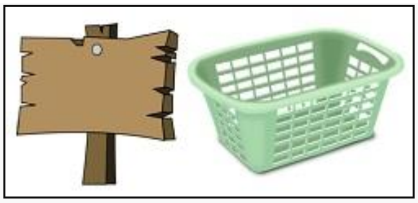
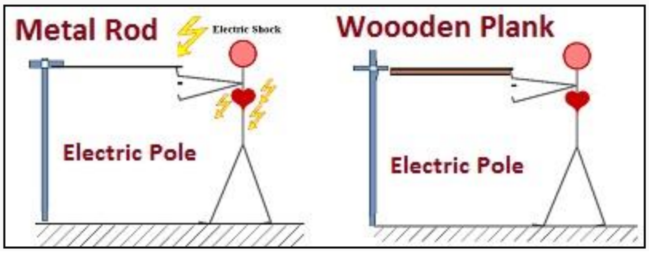


Fig. Wood and plastics are also solids but are insulators



A man touching the electric pole with a metal rod will get an electric shock because metal rod is a conductor whereas a man touching the same with a wooden plank will be safe because wood is an insulator.

Semiconductors:

- Solids with conductivities in the intermediate range from 10–6 to 104 ohm^{-1} m^{-1}.
- For example, Gallium, Germanium, Silicon

Measurement of resistance of a solution of an electrolyte

- In the formula

- *l*/*A* is called cell constant denoted by the symbol, *G*’.
- The cell constant depends on the distance between the electrodes (l) and their area of cross-section (A).
- It is determined by measuringthe resistance of the cell containing a solution of known conductivity.

Problem:

The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}.

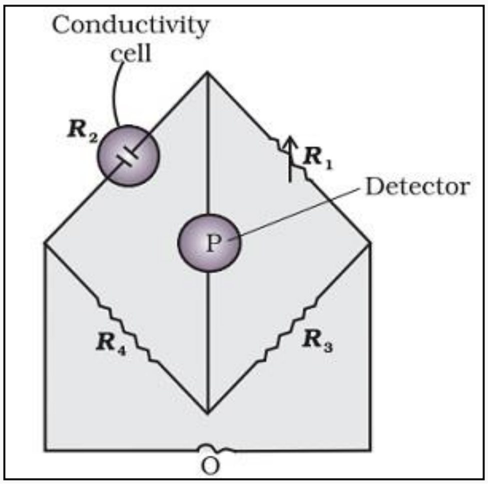
Solution:

Conductivity, $k = 0.146 \times 10^{-3}$ S cm^{-1}

Resistance, R = 1500 Ω

Cell constant = $k \times R = 0.146 \times 10^{-3} \times 1500 = 0.219$ cm^{-1}

Arrangement for measurement of Resistance



- The arrangement consists of two resistances R_3 and R_4.
- There is a variable resistance R_1 and a conductivity cell with unknown resistance R_2.
- The Wheatstone bridge is provided with an oscillator O that acts as source of a.c. power.

- The arrangement has a suitable detector P.
- The Wheatstone bridge is balanced when there is no flow of current through the detector.

Unknown resistance = $R_2 = R_1R_4 / R_3$

- After calculating the resistance the conductiviry can be easily calculated using the formula:
- $\kappa = G' / R$

Molar conductivity

- It is denoted by the symbol. It is related to the conductivity of the solution by the following equation:
- The units of is S m^2 mol^{-1}.

Problem:

The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 Scm^{-1}. Calculate its molar conductivity.

Solution:

$k = 0.0248$ S cm^{-1}

c = 0.20 M

Molar conductivity,Λ_m = $(k \times 1000) / c$

= 0.0248 x1000 / 0.20

= 124 $Scm^2 mol^{-1}$

Variation of Conductivity and Molar Conductivity with Concentration

- They depend on the concentration of the electrolyte. The Conductivity and Molar Conductivity of both weak and strong electrolytes decreases withdecrease in concentration as the number of ions per unitvolume carrying the current in a solution decreases on dilution.

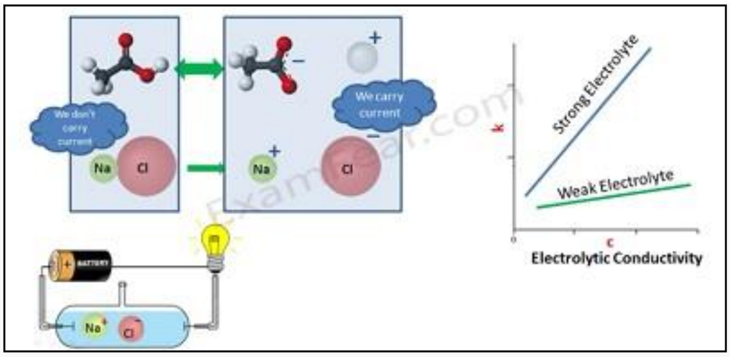


Fig. Variation of electrolytic conductivity

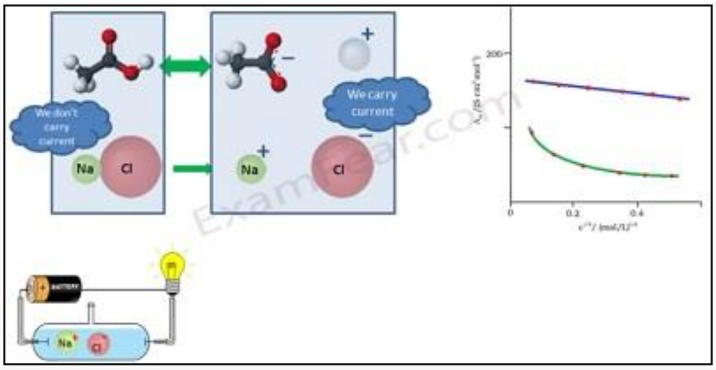


Fig. Variation of Molar conductivity

- Conductivity of a solution at a specific concentration = Conductance of solution placed in between the two platinum electrodes where
- Volume of solution = 1 unit

Cross sectional area of electrodes = 1unit

Distance = 1unit

$$\boxed{G = \frac{\kappa A}{l} = \kappa}$$

- Molar conductivity of a solution at a specific concentration = Conductance of solution where

Volume of solution = V

Concentration of electrolyte = 1 mole
Cross sectional area of electrodes = A

Distance = 1unit

$$\boxed{\wedge_m = \frac{\kappa A}{l} = \kappa}$$

- When the concentration approaches to zero, the molar conductivity is referred to as limiting molar conductivity. It is represented by the symbol $\ddot{E}^{o}{}_{m}$.

<u>Strong electrolytes</u>

- A solute or substances that completely ionize or dissociates in a solution are known as strong electrolyte. These ions are good conductors of electricity in the solution.
- For example, HCl, HBr, HI, HNO_3, NaOH, KOH, etc.
- For strong electrolytes, Λ_m increases slowly with dilution and can berepresented by the equation:

$$\wedge_m = E^o{}_m - Ac^{\frac{1}{2}}$$

- It dissociates completely at moderate concentrations.
- The conductance of the solution increases with dilution of solution.

- There exist strong interionic forces of attraction at moderate concentrations.
- The slope for Λ_m vs $c^{1/2}$ is linear at low concentrations.

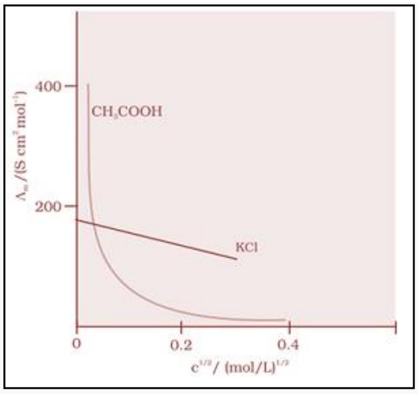
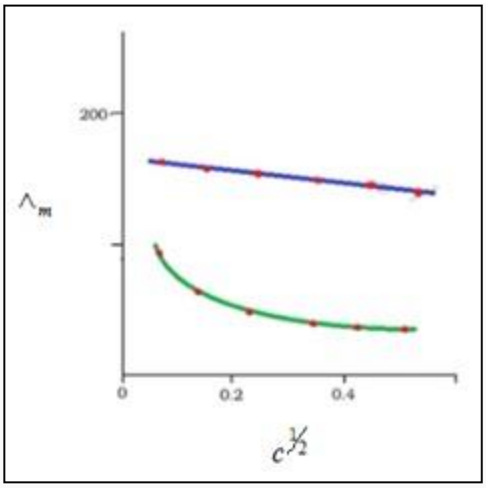


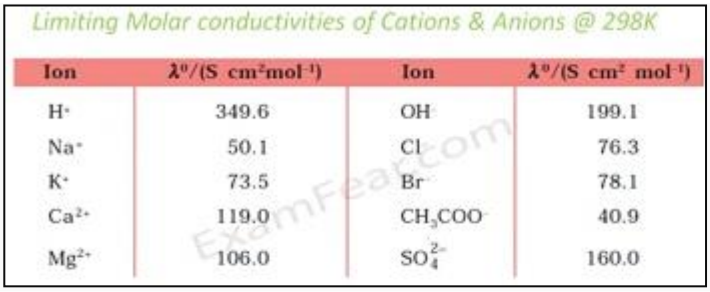
Fig. Molar conductivity Λ_m Vs. $c^{1/2}$ for acetic acid and potassium chloride

<u>Kohlrausch law of independent migration of ions</u>

- The Kohlrausch law of independent migration of ions states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.



- Limiting equivalent molar conductivity of an electrolyte is the algebraic sum of limiting molar equivalent conductivities of its constituent ions.



Limiting Molar conductivities of Cations & Anions @ 298K

Ion	$\lambda^0/(S\ cm^2 mol^{-1})$	Ion	$\lambda^0/(S\ cm^2\ mol^{-1})$
H^+	349.6	OH^-	199.1
Na^+	50.1	Cl^-	76.3
K^+	73.5	Br^-	78.1
Ca^{2+}	119.0	CH_3COO^-	40.9
Mg^{2+}	106.0	SO_4^{2-}	160.0

- Mathematically,

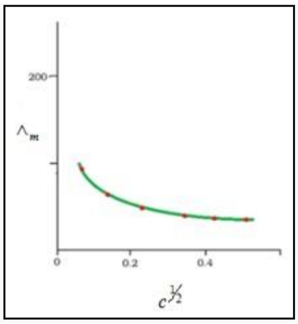
$$\wedge_o^{electrolyte} = \lambda_o^{+} + \lambda_o^{-}$$

Where λ_o^+ = limiting equivalent conductivities of cation

λ_o^- = limiting equivalent conductivities of anion.

Weak electrolytes

- A substance which forms ions in an aqueous solution do not dissociate completely at moderate concentrations **is known as weak electrolyte**.
- For example, $HC_2H_3O_2$ (acetic acid), H_2CO_3 (carbonic acid), etc.
- The conductance of the solution increases with dilution of solution.
- The interionic forces of attraction are not strong at a low concentration.
- The slope for Λ_m vs $c^{1/2}$ is not linear even at a lower concentrations.



- These electrolytes have lower degree of dissociation at higher concentrations.
- The value of Λ_m changes with dilution due to increase in the degree of dissociation.
- $\ddot{E}_m$ increases sharply on dilution exclusively at lower concentrations.
- At infinite dilutionwhen concentration approaches to zero, the electrolyte dissociates completely. But at lower concentration the conductivity of a solution is low to an extent that cannot be even measured.

Electrolysis

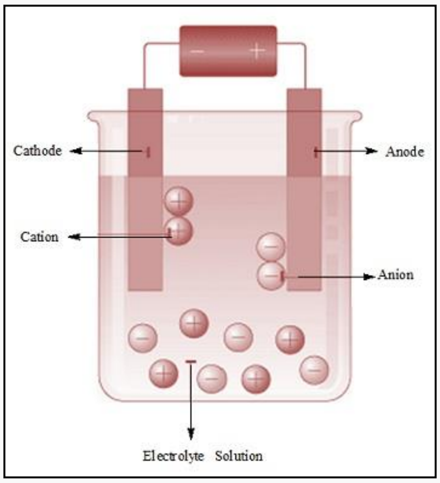


Fig. Electrolysis

- Two copper strips are dipped in an aqueous solution ofcopper sulphate ($CuSO_4$).
- A DC voltage is applied to both the electrodes.
- Cu^{2+} ions discharge at the cathode

$Cu^{2+}(aq) + 2e^{-}$ --> Cu (s)

- Copper metal is deposited on the cathode and copper is converted into Cu^{2+} ions at the anode by the following reaction:

$Cu \text{ --> } Cu^{2+}(aq) + 2e^{-}$

- The impure copper is the anode that dissolves on passing current whereas the pure copper gets deposited at the cathode. Metals like Na, Mg, Al, etc. are produced using electrochemical reduction of their respective cations.

Faraday’s Laws of Electrolysis

- Michael Faraday described the quantitative aspects of electrolysis and came forward with two laws of electrolysis:
- 1st Law: The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).

- 2nd Law: The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights

- Mathematically, Atomic Mass of Metal ÷ Number of electrons required to reduce the cation.

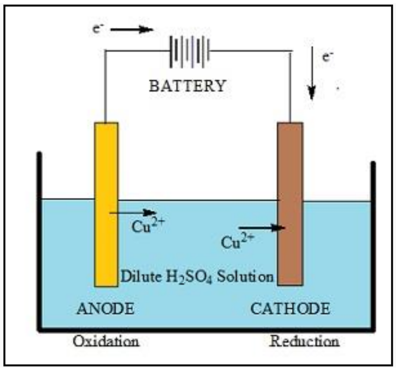
$Q = It$

where Q is in coloumb

I is in ampere and

t is in second.

- This quantity of electricity is known as **Faraday** and is represented by the symbol **F**.



- In the above example application of more current results in the deposition of more amount of copper from the anode to the cathode.

Problem:

If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

Solution:

$I = 0.5$ A

t = 2 hours = 7200 s

By using the formula, $Q = It$

= 0.5 A × 7200 s

= 3600 C

We know that 96487C = 6.023×10^{23} number of electrons.

Now, 3600 C = $\boxed{\frac{6.023\times10^{23}\times3600}{96487} = 2.25\times10^{22}}$ number of electrons. Hence, 2.25×10^{22}number of electrons will flow through the wire.

Problem:

Consider the reaction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow Cr^{3+} + 8H_2O$. What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$?

Solution:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow Cr^{3+} + 8H_2O$

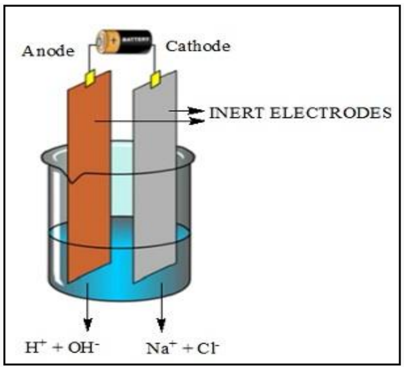
Therefore, quantity of electricity required to reduce 1 mole of $Cr_2O_7^{2-}$ = 6 F

= 6 × 96487 C

= 578922 C

Products of Electrolysis

- The product of electrolysis produced depends on the nature of material being that is being electrolyzed as well as the type of electrodes that is being used.
- An inert electrode e.g., platinum or gold does not participate in chemicalreaction and acts as a source or sink for electrons.
- Whereas a reactive electrode participates in the electrode reaction.
- It also depends on the different oxidizingas well as reducing species that are present in the electrolytic cell and their standardelectrode potentials.
- Electrolysis of molten NaCl results in the production of sodium metal and Cl_2



- Net reactions may be summarized as:
  $NaCl (aq) \rightarrow Na^+ (aq) + Cl^- (aq)$
  Cathode: $H_2O(l) + e^- \rightarrow \frac{1}{2} H_2(g) + OH^- (aq)$
  Anode: $Cl^- (aq) \rightarrow \frac{1}{2} Cl_2(g) + e^-$
  Net reaction:
  $NaCl(aq) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$

Problem:

Given the standard electrode potentials,

$K^+/ K = - 2.93V$,

$Ag^+/ Ag = 0.80V$,

$Hg^{2+} / Hg = 0.79V$

$Mg^{2+} / Mg = - 2.37 V$,

$Cr^{3+} / Cr = - 0.74V$

Arrange these metals in their increasing order of reducing power.

Solution:

Lower the reduction potential leads to higher reducing power. The given standard electrode potentials increases in the following order:

$K^+/ K < Mg^{2+} / Mg < Cr^{3+} / Cr < Hg^{2+} / Hg < Ag^+ / Ag$.

Hence, reducing power of the given metals increases in the following order:

Ag < Hg < Cr < Mg < K

Battery:

Battery is a collection of two or more batteries connected in series.

It is of two types:

1. Primary battery
2. Secondary battery

Primary battery:

- The reaction in a primary battery occurs only once.
- The battery becomes dead after used onceand cannot be reused
- Example of primary cell is dry cell and mercury cell.

- The dry cell consists of a zincanode and the carbon (graphite) cathode surrounded by powdered manganesedioxide and carbon.

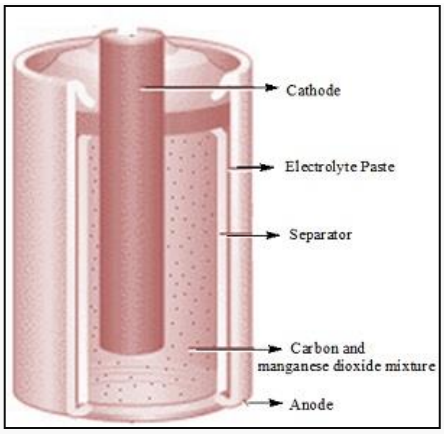


Fig. Dry cell

- The space between the two electrodes is filled by a soaking paste of ammonium chloride(NH_4Cl) and zinc chloride ($ZnCl_2$).

Anode: Zn(s) $^{-}$ -->Zn^{2+} + $2e^-$
Cathode: MnO_2+ NH_4^++ e^{--} -->MnO (OH) + NH_3

- At the cathode manganese is reduced from + 4 oxidation state to +3 oxidation state.
- As per the equation, Ammonia producedforms a complex with Zn^{2+} giving rise to $[Zn(NH_3)_4]^{2+}$.
- The cell has a potential of nearly 1.5 V.
- Mercury cell consists of zinc – mercuryamalgam as the anode and a paste of HgO and carbon as the

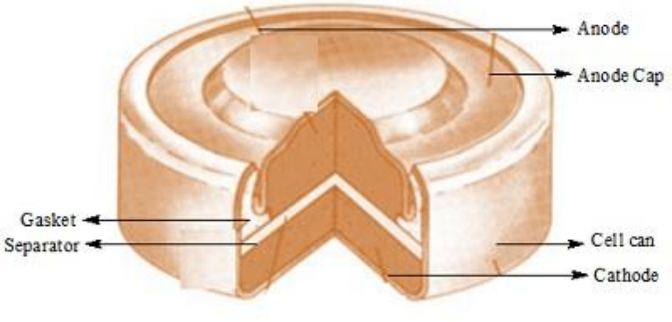


Fig. Mercury cell

- A paste of KOH and ZnO electrolyte used as an electrolyte.
- Theelectrode reactions for the cell are given below:
  Anode: Zn(Hg) + $2OH^-$ -->ZnO(s) + H_2O + $2e^-$
  Cathode: HgO + H_2O + $2e^-$ --> Hg(l) + $2OH^-$
- The overall reaction is represented by
  Zn (Hg) + HgO(s) --> ZnO(s) + Hg(l)
- The cell potential is approximately 1.35 V that remains constant throughout its lifetime.

<u>Secondary Battery</u>

- The reaction in a secondary battery occurs many times.
- Once it exhausts it can be recharged and used again.

- They are recharged by passing electric current through it in opposite direction.
- Example of secondary cell is lead and nickel cadmium cell.

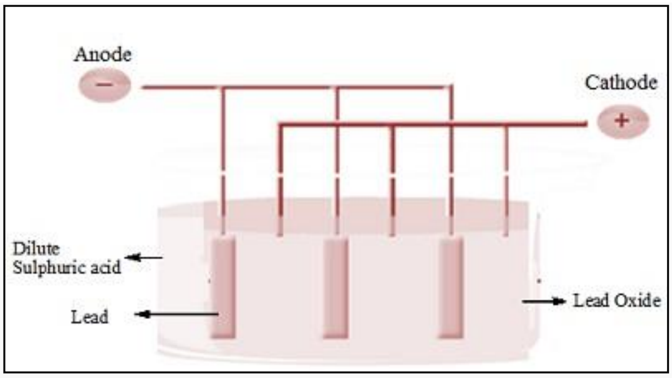


Fig. Lead storage battery

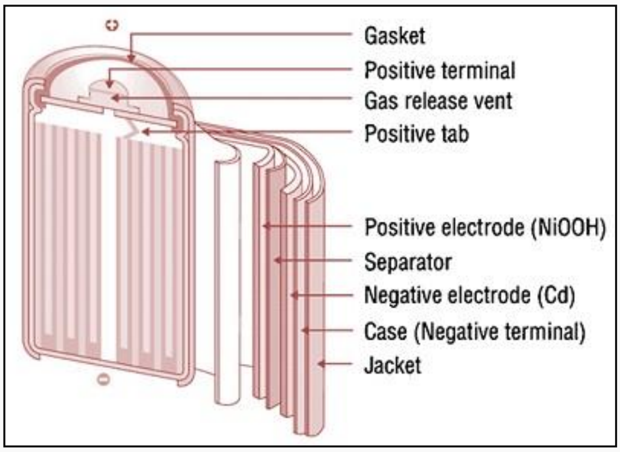


Fig. Nickel-Cadmium cell

- It is used extensively in automobiles and invertors.
- The lead cell contains a lead anode and a lead dioxide (PbO2) cathode and sulphuric acid is used as an electrolyte.
  Anode: $Pb(s) + SO_4^{2-}(aq) \dashrightarrow PbSO_4(s) + 2e^-$
  Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \dashrightarrow PbSO_4\,(s) + 2H_2O\,(l)$
- The net cell reaction is:
  $Pb(s)+PbO_2(s)+2H_2SO_4(aq) \dashrightarrow 2PbSO_4(s) + 2H_2O(l)$
- While charging, the reaction within the battery is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively.
- It has a longer life thanlead storage cell and it requires more expenses to
- The net reaction is:
  $Cd\,(s)+2Ni(OH)_3\,(s) \dashrightarrow CdO\,(s) +2Ni(OH)_2\,(s) +H_2O(l)$

Fuel cells

- In this kind of cell the chemical energyof fossil fuels like coal,gas or oil is initially used to convertwater into high pressure steam and is used to run a turbine to generate

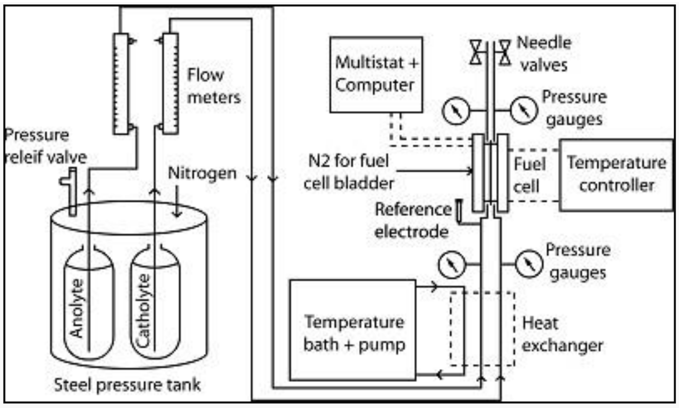


Fig. Diagrammatic representation of fuel cell

- Hydrogen and oxygenare bubbled using porous carbon electrodes into concentrated aqueoussodium hydroxide solution.
- Finely splitted platinum orpalladium metal are added to the electrodes for increasing the rateof electrode reactions.

Cathode: O_2 (g) + $2H_2O$ (l) + $4e^-$ --> $4OH^-$(aq)
Anode: $2H_2$ (g) + $4OH^-$(aq) – --> $4H_2O$(l) + $4e^-$

- The net reaction is:
  $2H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$

Corrosion

We all must have observed newly bought iron, silver or coper articles appears very shiny but with passage of time they get dull. This is due to the layer of metal oxide that develops on their surface. Rusting of iron, silver jewellery getting tarnished or copper articles getting covered by green layer. Metals react with atmospheric oxygen and produces metal oxides that are basic in nature because they react with water to form bases.

- In case of rusting of iron, the iron reacts with the oxygen present in air and moisture and develops rust (hydrated iron (III) oxide).

$$\underset{\text{Iron}}{4Fe} + \underset{\text{Oxygen}}{3O_2} + \underset{\text{Water}}{2H_2O} \longrightarrow \underset{\text{Rust}}{2Fe_2O_3.H_2O}$$

Fig. Iron chain left in moist air got rusted

Corrosion causes damage to car bodies, bridges, iron railings, ships and to all objects made of metals, especially those of iron.

- In case of rusting of copper, the metallic copper reacts with oxygen, carbon-dioxide and atmospheric moisture and develops a green coloured coating of copper hydroxide and copper carbonate.

$$2Cu + H_2O + CO_2 + O_2 \longrightarrow Cu(OH)_2 + CuCO_3$$

Fig. Copper developing green coloured rust on exposure to moist air

- In case of tarnishing of silver articles, the metallic silver reacts with hydrogen sulphide or sulphur present in air and gets tarnished.

$$4Ag + 2H_2S + O_2 \longrightarrow 2Ag_2S + 2H_2O$$

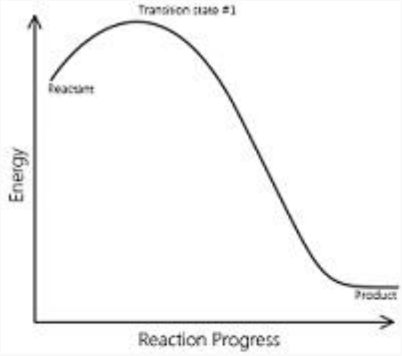
Fig. Tarnished silver Vs polished silver

Introduction

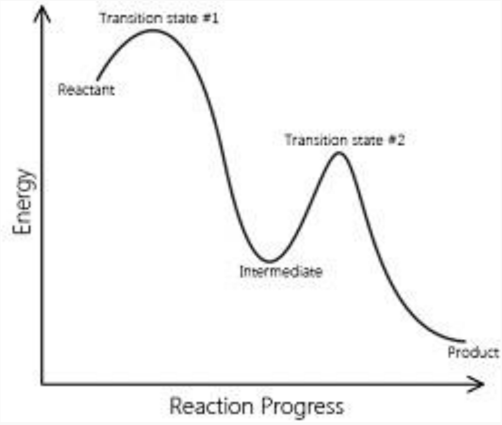
The stream of chemistry that governs the rate of reactions along with their mechanisms is termed as Chemical kinetics derived from a Greek word meaning chemical movement.

Combination of two or more reactants to produce a new product is called reaction**.**

Elementary Reaction: The reaction that occurs in a single step to give the product is called an elementary reactions**.**



Complex reaction: The reactions that occur as a result of sequence of elementary reactions to give the product is called complex reactions.



Rate of reaction

The rate at which the concentration of reactant or product participating in a chemical reaction alters is called rate of reaction.

Rate of reaction = change in concentration/ time = (mol/litre)/time

Reactant (R) --> Product.

Rate [R]

Rate = k[R]

k = rate constant or velocity constant.

Let one mole of the reactant A produce one mole of the product B.

Let at time t1

$[A]_1$ and $[B]_1$ = Concentrations of A and B

Let at time t2

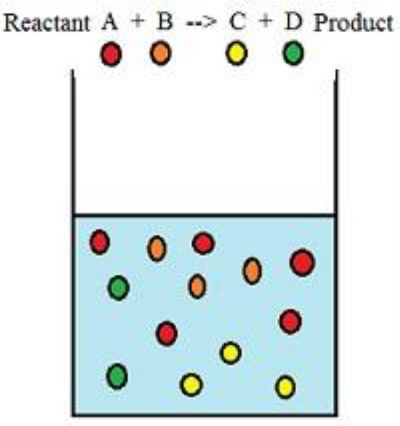
$[R]_2$ and $[P]_2$ = Concentrations of A and B

Rate of disappearance of A = Decrease in concentration of R / Time taken = $-\Delta[A]/\Delta t$

Rate of appearance of B = Increase in concentration of P / Time taken = $+\Delta[B]/\Delta t$

When two or more reactants combine with each other the molecules of the respective reactants collide with each other to form the product. The collision between the molecules increases with the increase in concentration of the reactants and thereby increases the rate of reaction.

A + B --> C + D



Here molecules of reactant A and B collide to produce molecules of product C and D.

Therefore we can conclude that rate of reaction is directly proportional to the concentration of the participating reactants.

Rate $\propto [A]^x [B]^y$

Or Rate = $k[A]^x [B]^y$

Hg(l) + Cl2 (g) --> HgCl2(s)

Rate of reaction= $-\Delta[Hg]/\Delta t = \Delta[Cl_2]/\Delta t = \Delta[HgCl_2]/\Delta t$

Factors affecting rate of reaction

Nature of reactant

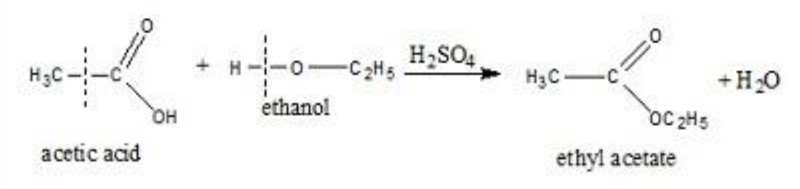
Nature of bonding in the reactants determines the rate of a reaction. The ionic compounds react faster compared to covalent compounds due to requirement of energy in covalent compounds to cleave the existing binds.

The reaction between ionic compounds:

Precipitation of AgCl

$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

The reactions between covalent compounds:



Temperature

Rate of reaction increases with the rise in temperature due to increase in average kinetic energy which in turn increases the number of molecules having greater energy than threshold energy and consequently increasing the number of effective collisions. The rate of a reaction is doubled (i.e., increased by 100%) with 10 °C rise in temperature.

Pressure

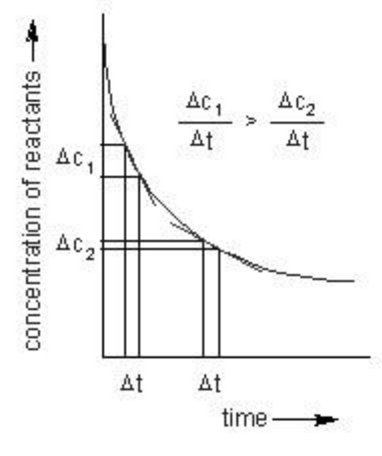
Increase in partial pressure increases the number of collisions. Therefore, the rate of reactions involving gaseous reactants increases with the increase in partial pressures.

Catalyst

A catalyst increases the rate of reaction by giving an alternative path with lower activation energy (E_a') for the reaction to proceed.

Concentration of reactants

Increase in concentration increases the number of collisions and the activated collisions between the reactant molecules. According to the collision theory, rate is directly proportional to the collision frequency. Consequently, the rate of a reaction increases with the rise in the concentration of reactant.



Surface area

The rate of a reaction increases with increase in the surface area of solid reactant.

PROBLEM. For the reaction: $2A + B \rightarrow A_2B$, The rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6} mol^{-2}L^2s^{-1}$. Calculate the initial rate of the reaction when [A] = 0.1 mol L^{-1}, [B] = 0.2 mol L^{-1}. Calculate the rate of reaction after [A] is reduced to 0.06 mol L^{-1}.

SOLUTION. Rate = k $[A][B]^2$

= $(2.0 \times 10^{-6} mol^{-2}L^2s^{-1})$ $(0.1 mol L^{-1})$ $(0.2 mol L^{-1})^2$

= $8.0 \times 10^{-9} mol^{-2}L^2s^{-1}$

Reduction of [A] from 0.1 mol L^{-1} to 0.06 mol^{-1}

The concentration of A reacted = (0.1 - 0.06) mol L^{-1} = 0.04 mol L^{-1}

The concentration of B reacted= 1/2 x 0.04 mol L^{-1} = 0.02 mol L^{-1}

The concentration of B available, [B] = (0.2 - 0.02) mol L^{-1}

= 0.18 mol L^{-1}

After reduction of [A] to 0.06 mol L^{-1}

The rate of the reaction

Rate = k $[A][B]^2$

= $(2.0 \times 10^{-6} mol^{-2}L^2s^{-1})$ $(0.06 mol L^{-1})$ $(0.18 mol L^{-1})^2$

= 3.89 mol $L^{-1}s^{-1}$

<u>Average rate of reaction</u>

The average rate of the reaction is the ratio of change in concentration of reactants to the change in time. It is determined by the change in concentration of reactants or products and the time taken for the change as well. As the reaction precedes forward the collisions between the molecules of the participating reactants reduces thereby decreasing the average rate of the reaction.

Mathematically, Average rate of reaction = Change in concentration / Time = (mol/litre)/time

PROBLEM. For the reaction R → P, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

SOLUTION. R_2= 0.02 M

R_1= 0.03M

$t_2 - t_1$= 25 minutes

$\Delta[R]/\Delta t = \Delta[R_2-R_1]/ t_2- t_1 =- (0.02-0.03)/25 = 6.67 \times 10^{-6} Ms^{-1}$

$=0.005ML^{-1} min^{-1}$

PROBLEM. In a reaction, 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval?

SOLUTION. $-1/2 (\Delta[A]/\Delta t) =-1/2(\Delta[A_2-A_1]/\Delta t) =-1/2 (0.4-0.5/10)$

$=0.005ML^{-1} min^{-1}$

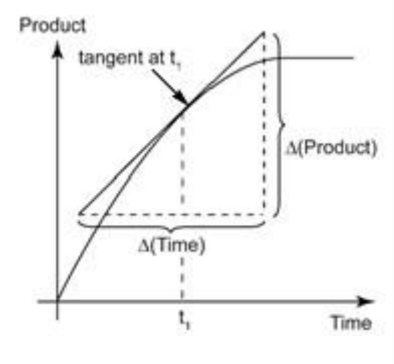
$= 5 \times 10^{-3}M min^{-1}$

Instantaneous rate of reaction

The ratio of change in concentration in chemical reaction to the time period is termed as instantaneous rate of the reaction.

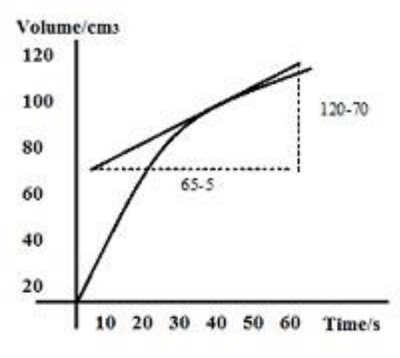
-d[R]/dt = change in chemical concentration over short period of time/ the short time elapsed = (mol/litre) / time

It can be calculated from the slope of the tangent on a concentration- time graph.



For example, consider the following graph.

The rate of reaction at t = 40s in the above graph can be calculated by following method:



Rate of reaction = gradient of the tangent at 40s = (120-70)/(65-5) = 50/60= 0.83 cm^3s^{-1}

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Rate expression

The representation of rate of reaction in terms of concentration of the reactants is called rate equation or rate expression.

For example, in the reaction

2NO(g) + O2(g) --> 2NO2

The rate expression is given as

Rate =$k[NO]^2[O_2]$

Let us consider another reaction

$BrO_3^- + 5Br^- + 6H^+$ --> $3Br + 3\ H_2O$

Rate expression for this reaction is given as

$k[BrO_3^-][Br^-][H^+]^2$

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Order of a reaction

The addition of power of the concentration of reactant in a rate law expression gives the order of reaction.

Let A + 2B --> C + D be a chemical reaction.

From rate law $R = k\ [A]^x\ [B]^y$

Now Order of reaction is defined as addition of the order of all the reactants participating in a chemical reaction.

order w.r.t. A = x

Order w.r.t. B = y

Overall order of the given reaction = (x + y).

Units of order of reaction:

$k = rate / [A]^n = (mol.L^{-1}s^{-1}/molL^{-1})^n$

For 1st order reaction , n=1

$k = rate / [A]^1 = (mol.L^{-1}s^{-1}/molL^{-1})^1 = s^{-1}$

For 2nd order reaction, n=2

$k = rate / [A]^2 = (mol.L^{-1}s^{-1}/molL^{-1})^2 = L.mol^{-1}s^{-1}$

PROBLEM. From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

(i) $3\ NO(g) \rightarrow N_2O(g)$ Rate = $k[NO]^2$

(ii) $H_2O_2\ (aq) + 3\ I^-(aq) + 2\ H^+ \rightarrow 2\ H_2O\ (l) + I_3^-$ Rate = $k[H_2O_2][I^-]$

(iii) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ Rate = $k\ [CH_3CHO]^{3/2}$

(iv) $C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$ Rate = $k\ [C_2H_5Cl]$

SOLUTION. (i) Rate = $k[NO]^2$

Order of the reaction = 2

Dimension of k = Rate / $[NO]^2$

$= mol\ L^{-1}\ s^{-1}\ /\ (mol\ L^{-1})^2$

= mol L^{-1} s^{-1} **/** mol^2 L^{-2}

= L mol^{-1} s^{-1}

(ii) Rate = $k[H_2O_2][I^-]$

Order of the reaction = 2

Dimension of k = Rate / $[H_2O_2][I^-]$

= mol L^{-1} s^{-1} / (mol L^{-1}) (mol L^{-1})

= L mol^{-1} s^{-1}

(iii) Rate =k $[CH_3CHO]^{3/2}$

Order of reaction = 3/2

Dimension of k = Rate / $[CH_3CHO]^{3/2}$

= mol L^{-1} s^{-1} / $(mol\ L^{-1})^{3/2}$

= mol L^{-1} s^{-1} / $mol^{3/2}$ $L^{-3/2}$

= $L^{½}$ $mol^{-½}$ s^{-1}

(iv) Rate = k $[C_2H_5Cl]$

Order of the reaction = 1

Dimension of k = Rate / $[C_2H_5Cl]$

= mol L^{-1} s^{-1} / mol L^{-1}

= s^{-1}

PROBLEM. For a reaction, A + B → Product; the rate law is given by, r = k $[A]^{½}$ $[B]^2$. What is the order of the reaction?

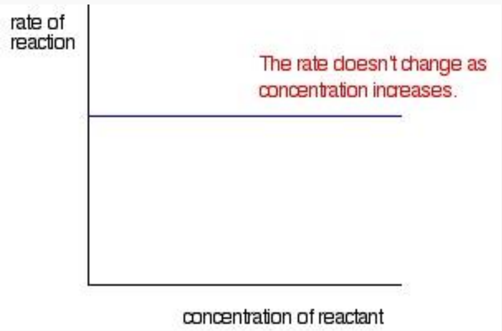
SOLUTION. The order of the reaction = 1/2 + 2

= 2 1/2

= 2.5

Zeroth order reaction

If the rate of reaction is independent of concentration of the reactant participating in the reaction then the reaction is called Zeroth order reaction.



A --> B

At time t = 0 concentration of A (reactant) is a and B (product) is 0. At time t = t the concentration of A (reactant) is (a-x) and that of B (product) is x.

$-d[A]/dt = k_0[A]^0 => dx/dt = k_0(a-x)^0$

$dx/dt = k_0$

$\int_0^x dx = k_0 \int_0^x dt$

X = k0t

PROBLEM. The decomposition of NH3on platinum surface is zero order reaction. What are the rates of production of N2and H2if k = 2.5 x 10-4mol-1L s-1?

SOLUTION. $2NH_3$ --> $N_2 + 3H_2$

Rate of zero order reaction

$-1/2 (d[NH_3]/dt) = d[N_2]/dt = 1/3 (d[H_2]/dt)$

$-1/2 (d[NH_3]/dt) = d[N_2]/dt = 1/3 (d[H_2]/dt)= k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

Rate of production of N_2

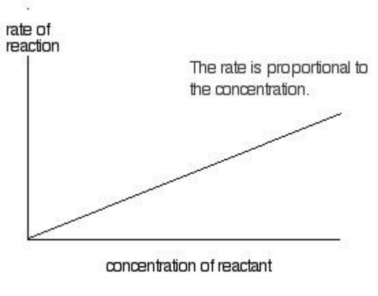
$d[N_2]/dt = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

Rate of production of H_2

$d[H_2]/dt = 3 \times 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

First order reaction

If the rate of reaction depends on the concentration of single reactant participating in chemical reaction raised to the first power then it is called a first order reaction.



A --> B

At time t = 0 concentration of A (reactant) is a and B (product) is 0. At time t = t the concentration of A (reactant) is (a-x) and that of B (product) is x.

-dx/dt ∝ (a-x) = dx/dt = k1(a-x)

∫ 0x dx/(a-x) = k1∫ 0t dt

dx/dt = k0(a-x)0

dx/dt = k0

∫0 x dx = k0∫ 0t dt

ln (a/a-x) = k1t => t = 1/ k1 ln (a/a-x) = 2.303/ k1 log (a/a-x)

k1 = 2.303 log (a/a-x)

PROBLEM. A first order reaction has a rate constant 1.15 10-3s-1. How long will 5 g of this reactant take to reduce to 3 g?

SOLUTION. From the question, we can write down the following information:

Initial amount = 5 g

Final concentration = 3 g

Rate constant = 1.15 10 - 3s - 1

We know that for a 1st order reaction,

t = (2.303/k)log[R0]/[R]

(2.303/1.15X10-3)log[5]/[3]

(2.303/1.15X10-3) X 0.2219 = 444.38 s = 444 s

Pseudo order reaction

The reaction that appears to be an n^{th} order reaction but belongs to some different order is called Pseudo order reaction.

For example, a pseudo first order reaction is a chemical reaction between two reactants participating in a chemical reaction and therefore should be a second order reaction. But it resembles to be a first order reaction due to the presence of reactants in negligible quantity.

Let R` + R`` --> P

Rate = $k[A]^1[B]^1$

Order of reaction = 2.

Let us consider another reaction,

$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

Rate law for this reaction is

Rate = $k [OH^-][CH_3Br]$

Rate = $k [OH^-][CH_3Br] = k(constant)[CH_3Br]=k'[CH_3Br]$

As only the concentration of CH_3Br would change during the reaction, the rate would solely depend upon the changes in the CH_3Br reaction.

Molecularity

- As we know that molecules need to collide to bring about a chemical reaction, so the number of molecules participating in an elementary chemical reaction that collides to bring about the chemical reaction is called molecularity of a reaction.
- The value of molecularity of a reaction is always a positive value.
- Let us consider a following reaction:

A + 2B --> C + D

Here reactants are: 1 molecule of A ,2 molecules of B

Products are: 1 molecule of C , 1 molecule of D.

Therefore we can conclude that reaction is trimolecular.

A reaction with molecularity =1 is called unimolecular.

Example, $PCl_5 \text{-->} PCl_3 + Cl_2$

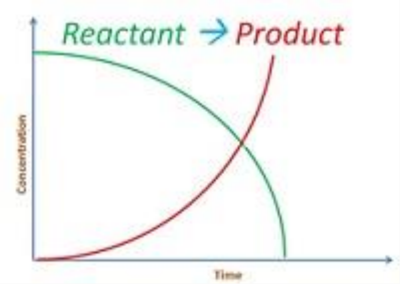
- A reaction with molecularity =2 is called bimolecular.

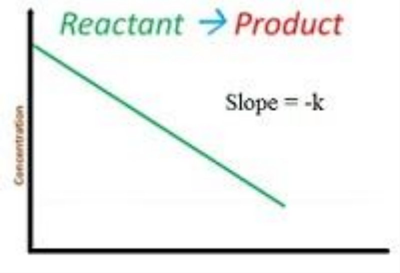
Example, $Cl + CH_4 \text{-->} HCl + CH_3$

- A reaction with molecularity =3 is called trimolecular.

$2FeCl_3 + SnCl_2 \text{-->} 2FeCl_2 + SnCl_4$

- It is theoretical value and does not determine the rate of reaction. Nor does it depend upon external factors like temperature or pressure, etc.
- **Integrated rate equation**

- 

- Consider the reaction
- aA + bB --> cC + dD
- Rate = k $[A]^x[B]^y$
- -dR/dt = k$[A]^x[B]^y$
- dR/dt is instantaneous rate.
- Integrated rate equation for zero order reaction
- -dR/dt = k$[R]^0$=k
- dR/dt = -k
- ∫ dR = -k ∫ dt
- [R]=-kt +I
- At t = 0
- R_0= -k .0 + I
- I = R_0
- So the equation becomes R = -kt + R_0
- Graph for this is as follows:
- 

- Integrated rate equation for first order reaction
- Rate = -dR/dt = k$[R]^2$
- ∫ dR/R= - ∫ kt
- ln R = -kt + I
- At t = 0
- R = R_0
- ln R_0=-k X 0 +I
- I = ln R_0
- So equation becomes
- ln R = -kt + ln R_0
- ln [R_0/ R]=-kt

Rate law

- The representation of rate of reaction in terms of molar concentration of the reactants participating in a reaction raised to some power is called rate law.
- It is also called rate expression or rate equation.
- Consider a reaction:

$2NO (g) + O_2 (g) \rightarrow 2NO_2$

Rate $\propto [NO]^2$

Rate $\propto [O_2]$

Combining these two rates we derive

Rate $\propto [NO]^2 [O_2]$

Rate $=k [NO]^2 [O_2]$

- Where k is the proportionality constant with a definite value at a specific temperature for a specific reaction and is called Rate Constant.
- Rate law expression = $-d[R]/ dt = k [NO]^2 [O_2]$

Half life reactions : The time elapsed in reduction of the concentration of a reactant participating in a chemical reaction to one half of its original concentration is called half-life reaction and is represented by $t_{1/2}$.

Half-life for zero order reactions:

A --> B

At time t = 0 concentration of A (reactant) is a and B (product) is 0. At time t = t the concentration of A (reactant) is (a-x) and that of B (product) is x.

$x = k_0t$ à $a/2 = k_0t_{1/2} = a/2k_0$

$t_{1/2} =a/2k_0$

$a=(2k_0)(t_{1/2})$

y = mx

t = Independent variable. It is taken at x-axis.

$m = 2k_0$

Half-life for first order reactions:

$t = 2.303/k_1 \log a/(a-x)$

For half-life $x = a/2$; $t = t_{1/2}$

$t_{½} = 2.303/k_1 \log a/(a-a/2) \rightarrow t1/2 = 2.303/k_1 \log2$

$t_{½} = 2.303/k_1$ X 3.010

$t_{½} = 0.693/ k_1$

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Next →

Rate determining step

- The slowest step during a chemical reaction determines the overall speed of a reaction towards completion is called rate determining step.
- Let us consider the following reaction,

$NO_2(g)+CO(g)\rightarrow NO(g)+CO_2(g)$

- The elementary steps of the reaction are as follows:

Step 1: $NO_2+NO_2\rightarrow NO+NO_3$ (Rate constant = k_1, slow)

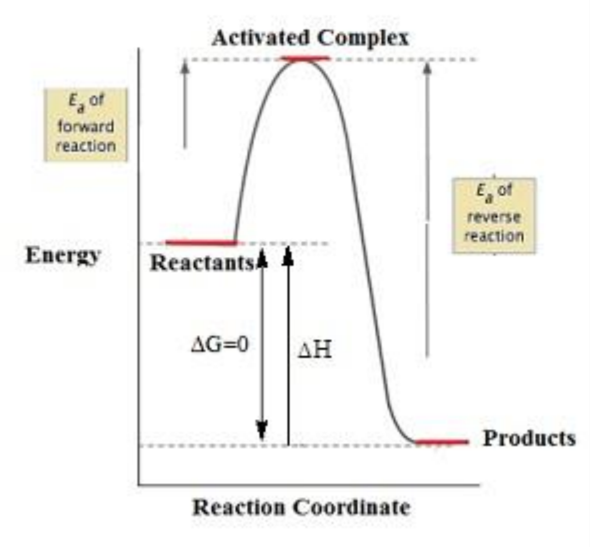
Step 2: $NO_3+CO\rightarrow NO_2+CO_2$ (Rate constant = k_2, fast)

- As the first step is the slowest step in the reaction it will determine the rate of the overall reaction. Therefore Step1 is the rate determining step of the given reaction and hence the rate expression for the given reaction is the product of rate constant and the reactants of this step.

Rate = $k1[NO_2][NO_2]=k1[NO_2]_2$

Activation energy

- The minimum quantitiy of external energy required for the conversion of reactant into product or to produce an unstable intermediate is called activation energy. It is E
- Rate of reaction is inversely proportional to the activation energy.
- Therefore, greater value of activation energy leads to lower rate of reaction and increased influence of temperature change on the rate constant.



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PROBLEM. The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate $E_{Solution}$.

SOLUTION. It is given that T_1 = 298 K

∴T2 = (298 + 10) K

= 308 K

We also know that the rate of the reaction doubles when temperature is increased by 10°.

Therefore, let us take the value of k_1 = k and that of k_2 = 2k

Also, R = 8.314 J K^{-1} mol^{-1}

Now, substituting these values in the equation:

Log $k_2/k_1 = E_a/2.303R\ [T_2-T_1/T_1T_2]$

Log $2k/k = E_a/2.303 \times 8.314\ [10/298 \times 308]$

$E_a = 2.303 \times 8.314 \times 298 \times 308 \times \log 2/10$

= 52897.78 J mol^{-1}

= 52.9 kJ mol^{-1}

Arrhenius equation

- The formula used to calculate the energy of activation and justify the effect of temperature on rate of reaction is called Arrhenius Equation.
- It is given by the formula,

$K = A\ e^{-Ea/RT}$

Where,

k = Rate constant

A= Frequency factor

e = mathematical quantity

E_a= activation energy

R = gas constant

T = kelvin temperature

ln K = ln A – Ea/(2.303RT)

Equation of a straight line with slope = $-E_a/R$.

- When $E_a = 0$, Temperature = Infinity

$K = Ae^0 = A$

$e^{-Ea/RT}$ =Boltzmann factor.

- For a chemical reaction the rate constant gets doubled for a rise of 10° temperature. This is because according to Arrhenius Equation,

$K = Ae^{-Ea/RT}$

Taking log on both sides of the equation

Ln k = ln A – E_a/RT

Comparing with the equation of a straight line

y= mx+c,

[m= slope of the line

c= y-intercept]

So we have:

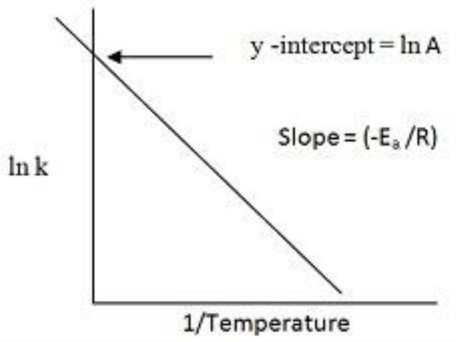
y = ln k

x = 1/T

m = $-E_a / R$

c = ln A

Plotting k Vs (1/*T*)



PROBLEM. Find the activation energy (in kJ/mol) of the reaction if the rate constant at 600K is 3.4 M^{-1} s^{-1} and 31.0 at 750K.

SOLUTION. Ln k = ln A – E_a/RT

To find E_a, subtract ln A from both sides and multiply by -RT.

E_a = (ln A - ln k)RT

Collision theory

- It states that:
- According to collision theory the molecules collides with great kinetic energy in order to bring about a chemical reaction.

The molecules of the reacting species collide through the space in a rectilinear motion.

Rate of a chemical reaction is proportional to the number of collisions between the molecules of the reacting species.

The molecules must be properly oriented.

- Rate of successful collisions ∝ Fraction of successful collisions X Overall collision frequency.
- The number of collisions per second per unit volume of the molecules in a chemical reaction is called collision frequency (Z).

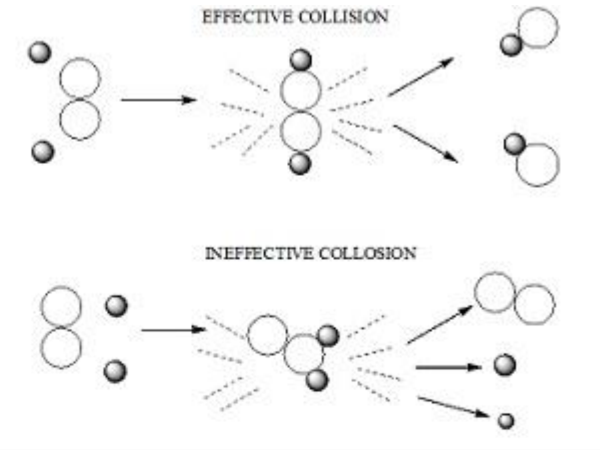
Let A+B --> C + D

Rate = $Z_{AB}e^{-Ea/RT}$

Here Z_{AB} = collision frequency of A and B.

- In many reactions Rate = P $Z_{AB}e^{-Ea/RT}$

Where p= steric factor which takes into account the proper orientation of the molecules participating in a chemical reaction.



PROBLEM. The activation energy for the reaction $2HI_{(g)} \rightarrow H_2 + I_{2(g)}$ is 209.5 kJ mol^{-1} at 581 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

SOLUTION. E_a = 209.5 kJ mol^{-1} = 209500 J mol^{-1}

T = 581 K

R = 8.314 JK^{-1} mol^{-1}

Fraction of molecules of reactants having energy equal to or greater than activation energy is as follows:

$x = e^{-Ea/RT}$

ln x = -Ea/RT

log x = Ea/2.303RT

log x = 209500 J mol^{-1}/2.303 X 8.314 J K^{-1}mol^{-1} X 581 = 18.8323

x = antilog (18.323)

= antilog 19.1977

= 1.471 X 10^{-19}

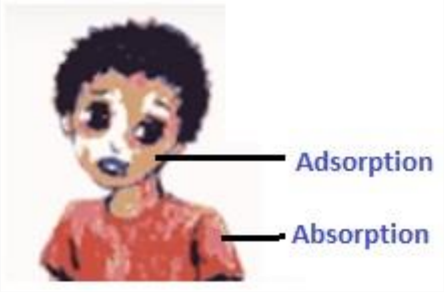
Introduction

Surface Chemistry deals with the study of physical and chemical phenomena occurring at the boundary (interface) separating two bulk phases.

- The bulk phase can be a pure compound or a solution.
- The bulk phases may be solid – liquid, solid – gas, solid – vacuum, liquid – gas etc.

Let us consider a simple example of a dirty shirt. The dirt stays in the surface of the fabric and the study of phenomena occurring at the interface between the fabric and the dirt is surface chemistry, in simple words.

Adsorption and Absorption



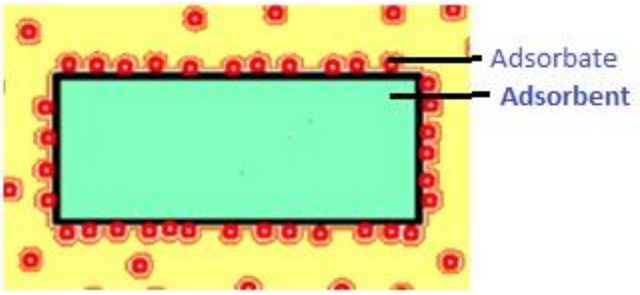
The dirt staying on the surface of the skin as a layer is termed as adsorbtion.

Now consider applying soap solution to the shirt containing dirt. The soap solution is absorbed by the fabric and does not stay on the fabric as a layer. This is called absorption.

Adsorption

Adsorption is the phenomenon of attracting and retaining molecules of a substance on the surface of a solid (or liquid) resulting as a higher concentration of molecules only on the surface.

- Adsorbent- the surface on which adsorption takes place
- Adsorbate- the substance which is adsorbed

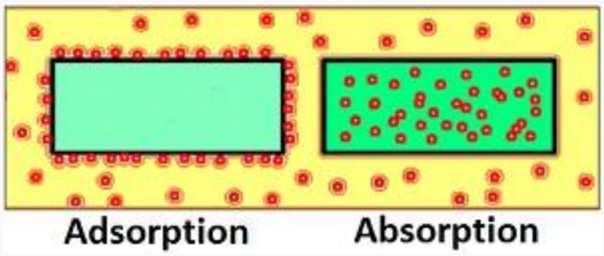


Example- Water vapour adsorbed by silica gel

- Adsorbent- Silica gel
- Adsorbate- Water vapour

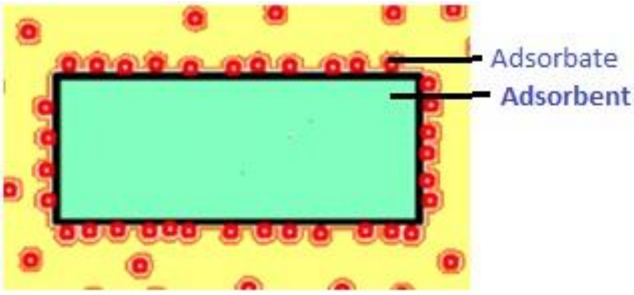
Differences between Adsorption and Absorption

ADSORPTION	ABSORPTION
Surface phenomenon- concentration of the adsorbate increases only on the surface	Bulk phenomenon- concentration is uniform throughout the solid
Exothermic process- heat is released	Endothermic process- heat is absorbed
It is favoured by low temperature	It is not affected by temperature
Eg- Chalk stick dipped in ink adsorbs the colour of the ink but when you break the piece of chalk, its core still remains white	Eg- When anhydrous $CaCl_2$ absorbs water vapour, it becomes wet and pasty



Mechanism of Adsorption

- Adsorption occurs because the particle on the surface and the particle in the bulk of the adsorbent are not in the same environment. That is, the net force acting on them is not the same.
- The particle on the surface has unbalanced forces acting on it which are also called residual attractive forces
- Due to these forces, the surface particles of the adsorbent attract the adsorbate particles



- During adsorption, there is always a decrease in the residual attractive forces of the surface. That is, the energy of the surface decreases and this appears as heat. This is called the heat of adsorption
- The amount of heat evolved when one mole of adsorbate is adsorbed on the adsorbent surface is called enthalpy of adsorption
- Adsorption is always exothermic and the enthalpy change, ΔH is always negative
- When the adsorbate molecules are adsorbed on the surface of the adsorbent, their freedom of movement becomes restricted and hence ΔS the entropy decreases
- We know that Gibbs free energy,**ΔG= ΔH –TΔS**.

For adsorption to be spontaneous, ΔG must be negative. This can happen if ΔH has a significantly high negative value as –TΔS is positive.

- As the adsorption continues, ΔH becomes less and less negative till it becomes equal to TΔS and ΔG becomes zero. At this point, equilibrium is attained.

Factors affecting adsorption of Gases by Solids

- Nature and Surface area of adsorbent:
    - The same gas is adsorbed by different solids at different extents even at the same temperature.
    - Greater the surface area, greater is the volume of gases adsorbed.
- Nature of the gas being adsorbed:
- Different gases are adsorbed are adsorbed to different extents even by the same solid.
- As the critical temperature of a gas increases, it is easier to liquefy and it is also more readily adsorbed.
- Reason- Higher the critical temperature, the easier it is to liquefy the gas as greater are the intermolecular forces to attraction between the molecules of the gas. For such a gas, the intermolecular forces of attraction are greater on the surface of the adsorbent and thus, the adsorption will be more.
- Temperature: As temperature increases, adsorption decreases

- Pressure: At constant temperature, the adsorption of a gas increases with increase in pressure.

- Activation of the solid adsorbent: It means increasing the adsorbing power of the adsorbent.

It can be done by-

1. Making the surface of the adsorbent rough- It can be done by rubbing the surface or chemical action or by depositing fine metal particles on the surface by electroplating
2. By dividing the adsorbent into small pieces or grains- It increases the surface area but this method has a practical limitation. If the particles are too fine like powder, the adsorption of the gas will become difficult.
3. By removing the already adsorbed gases
4. **Types of Adsorption**

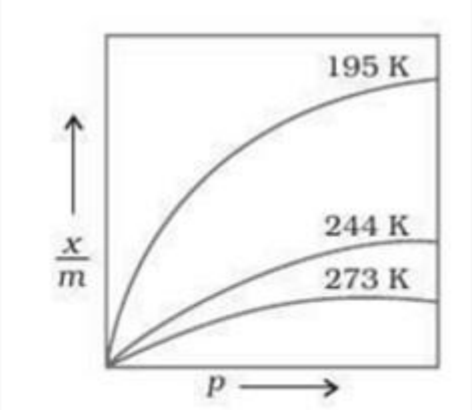
Physisorption	**Chemisorption**
Occurs due van der Waals forces	Caused by chemical bond formation

Not specific in nature that is all gases are adsorbed on the surface to an extent	Highly specific in nature
Reversible	Irreversible
More easily liquefiable gases are adsorbed more readily	Gases which can react with the adsorbent show chemisorption
Enthalpy of adsorption is low(20-40 kJ)	Enthalpy of adsorption is high (80-240 kJ)
It decreases with increase in temperature. Favours low temperature	It increases with increase in temperature. Favours high temperature
It does not need any activation energy	It does require activation energy.
It results into multimolecular layers on adsorbent surface under high pressure	It results into a unimolecular layer.

5. ← Prev
6. Next →

Adsorption isotherms

The variation in the amount of gas adsorbed by the adsorbent at constant temperature with change in pressure is shown by a curve called adsorption isotherm.



Freundlich adsorption Isotherm:

- Freundlich proposed this relation to show a relation between the extent of adsorption and pressure.

$$\frac{x}{m} = k(p)^{1/n} \quad ....1$$

$$\text{Log}\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log p \quad ...2$$

If there are solutions involved, the above equations become

$$\frac{x}{m} = k\,(C)^{1/n}$$

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log C$$

Where x -> amount of adsorbate

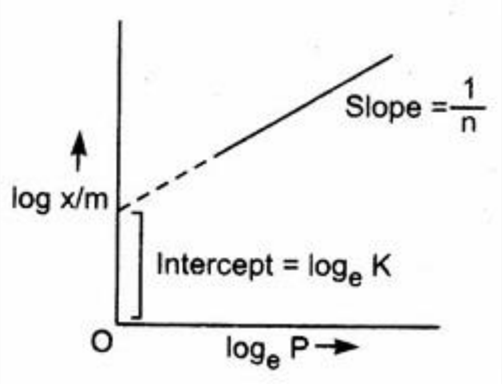
m-> mass of adsorbent

p-> pressure

C-> concentration of adsorbate

K and n->constants , n>1 always

Looking at equation 2, as we plot log x/m versus log p on a graph, we get a straight line with slope=1/n and y- intercept= log k.



Applications of adsorption

1. ***Production of high vacuum***- Remaining traces of air in a vessel already evacuated by vacuum pump can be adsorbed by charcoal to create high vacuum
2. ***Control humidity*** - Silica and aluminium gels can adsorb moisture and remove humidity
3. ***Gas masks***- Gas masks consist of activated charcoal or mixture of adsorbents and are used to breathe in coal mines
4. ***Removing coloured substances from solutions***- This is used in chromatographic analysis.
5. ***Separation of inert gases***- Different inert gases are adsorbed to different extents on coconut charcoal
6. ***Heterogeneous catalysis***- When gaseous reactants are adsorbed on the surface of a solid catalyst, the concentration of the reactants on the surface increases and thus, the rate of reaction also increases(adsorption theory). Eg- Using finely divided Nickel in the hydrogenation of vegetable oils

7. ***Adsorption indicators***- Many dyes have become useful due to adsorption. These dyes have been introduced as indicators especially in precipitation titrations. Eg- KBr is easily titrated with $AgNO_3$ using eosin as the indicator

8. ***Froth floatation process***- When sulphide ore is shaken with pine oil and water, the ore particles are adsorbed on the froth that floats and the gangue prticles (like silica, mud) settle down in the tank. This process is used in the concentration of sulphide ores
9. ***Chromatographic analysis***- The selective adsorption of some substances by a solution helps us separate components of a mixture. Example- All the dyes in ink

10. ***Curing Diseases-*** Some drugs can adsorb the germs on them and hence, kill them saving us from diseases

Catalysis

Substances which alter the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction are called catalysts.

- **Promoters**- Substances which enhance the activity of the catalyst
- **Poisons-** Substances which decreasethe activity of the catalyst

Example- In Haber's process for manufacturing ammonia, molybdenum acts as promoter for the catalyst-iron

N_2 (g) + $3H_2$ (g) --> $2NH_3$ (g)

Homogenous and Heterogeneous Catalysis

Catalysis can be classified into 2 types.

1. Homogenous catalysis:

The reactants and the catalyst are in the same phase (that is liquid or gas).

Example- In Oxidation of sulphur dioxide,

Sulphur dioxide, oxygen and the catalyst nitrogen oxide are all gases

$2SO_2$(g) + O_2(g) à $2SO_3$ (g)

2. Heterogeneous catalysis:

The reactants and the catalyst are in different phases

Example- In Oxidation of ammonia,

Ammonia and oxygen are gases but the catalyst Platinum is solid

$4NH_3$(g) +$5O_2$(g) --> 4NO(g) + $6H_2O$(g)

Adsorption theory of Heterogeneous catalysis:

- This theory explains the mechanism of heterogeneous catalysis.
- It is combination of the intermediate compound formation theory and the old adsorption theory. The Intermediate Compound Formation Theory is in the chapter of the Chemical Kinetics
- Old Adsorption theory- The reactants (gases or in solutions) are adsorbed on the surface of the solid catalyst. The increase in concentration of the reactant on the surface also increases the rate of reaction. The heat of adsorption(adsorption is exothermic) also increases the rate of reaction.

Mechanism of Catalytic Activity

1. Diffusion of reactants towards the surface of the catalyst
2. Adsorption of reactant molecules on the surface of the catalyst
3. Occurrence of a chemical reaction between the reactants and the catalyst which forms an intermediate
4. Desorption of product molecule from the surface because of the lack of its affinity to the catalyst's surface by which the surface is now available for the adsorption of new reactant molecules
5. Diffusion of product molecules away from the surface of the catalyst

Advantages of This Theory:

- Only a small quantity of the catalyst is required as it is regenerated again and again
- The catalyst does take part in the reaction but its mass and composition remain unchanged at the end of the reaction
- If catalytic poisons are present they preferentially get adsorbed onto the surface of the catalyst. This hinders the adsorption of the reactant molecules

Note- This theory does not satisfactorily explain the action of catalytic promoters

Important Features of Solid Catalysts

Activity

- Activity of a catalyst refers to the capacity of the catalyst to increase the speed of the chemical reaction. The activity depends upon the extent of chemisorption.
- The adsorption should be reasonably strong but not so strong that the adsorbed molecules become immobile and there is no place for other reactants to get adsorbed. Example- Combination of H_2 and O_2 in the presence of Platinum(catalyst) to form water is an explosive reaction.

- But in the absence of catalyst, H_2 and O_2 do not react and can be stored like that for a very long period of time.

$2H_2(g) + O_2(g) \dashrightarrow 2H_2O(l)$

Selectivity

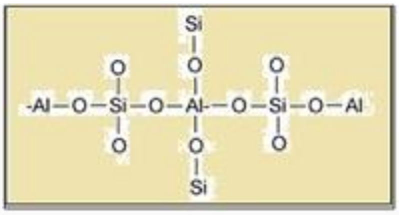
- Selectivity of a catalyst refers to its ability to direct the reaction to form particular products excluding others.
- Example- CO and H2 form different products in the presence of different catalysts

$$CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$$
$$CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO \cdot Cr2O7} CH_3OH(g)$$
$$CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$$

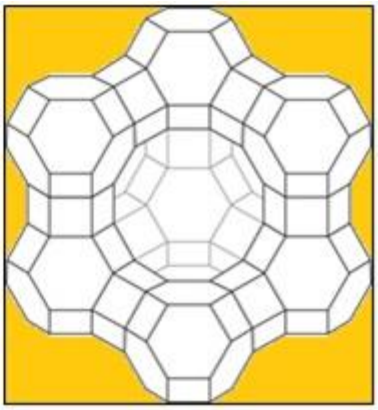
Note- Catalysts are very specific and selective in their action. So a substance which acts as a catalyst in one reaction may fail to catalyse another reaction

Shape selective catalysis-Zeolites

- The reactions taking place in zeolites depend on-
- They are good shape selective catalysts due to their honey-comb like structures
- They are three dimensional network of silicates where some silicon atoms are replaced by aluminium atoms forming a Al-O-Si network.
- Zeolites are microporousaluminosilicates.
- The catalytic reaction which depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis
    - The size and shape of the reactants and product molecules
    - The pores and cavities of the zeolites
- Widely used as catalysts in the petrochemical industry for cracking of hydrocarbons and isomerisation
- Eg: ZSM-5 is used in converting alcohols directly to gasoline(petrol) by dehydrating them



Zeolite structure



Honeycomb Structure

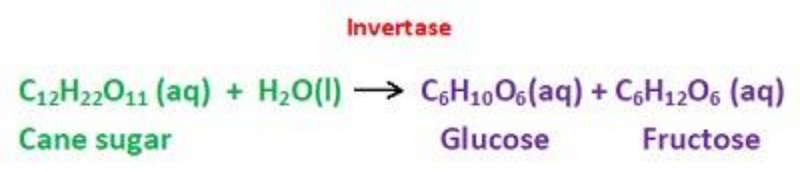
Enzymes

- Enzymes are complex nitrogenous compounds which are produced by plants and animals
- They are protein molecules of high molecular mass and form colloidal solutions with water
- They are very effective catalysts
- They catalyse many reactions which occur in the bodies of animals and plants to maintain life processes
- Thus, enzymes are called biochemical catalysts
- The phenomenon is called biochemical catalysis

Enzyme catalysed Reactions:

1. Inversion of cane sugar

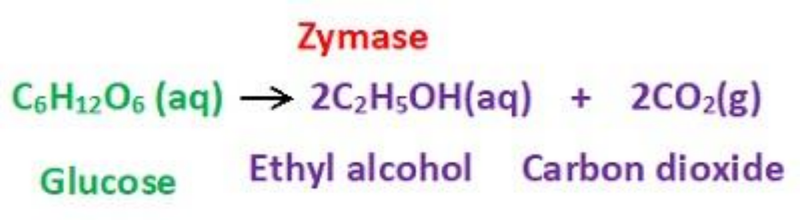
Invertase enzyme converts glucose into glucose and fructose



$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{10}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$$

2. Conversion of glucose into ethyl alcohol

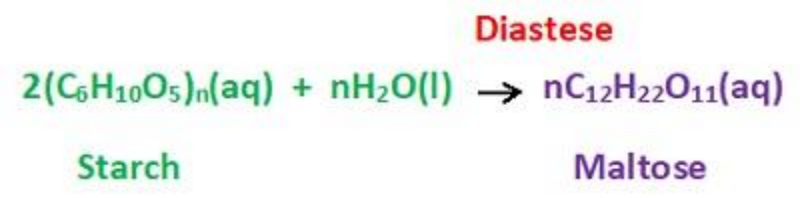
Zymase enzyme converts glucose into ethyl alcohol and carbon dioxide



$$\underset{\text{Glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH(aq)} + \underset{\text{Carbon dioxide}}{2CO_2(g)}$$

3. Conversion of starch into maltose

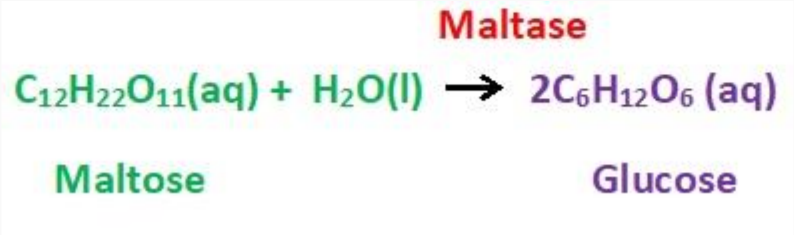
Diastese enzyme converts starch to maltose



$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n(aq)} + nH_2O(l) \xrightarrow{\text{Diastese}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}(aq)}$$

4. Conversion of maltose into glucose

Maltase enzyme converts maltose into glucose



$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6\,(aq)}$$

5. Decompostion of Urea into Ammonia and Carbon Dioxide

Urease enzyme helps decompose ammonia and carbon dioxide

$$\underset{\text{Urea}}{NH_2CONH_2(aq)} + H_2O(l) \xrightarrow{\text{Urease}} \underset{\text{Ammonia}}{2NH_3(g)} + \underset{\text{Carbon dioxide}}{CO_2(g)}$$

6. In stomach and intestine :

In **stomach- Pepsin** enzyme converts **Proteins to Peptides**

In the **intestine- Pancreatic Trypsin** converts **Proteins to Amino acids** by hydrolysis

7. Conversion of milk into curd : The **Lacto bacilli enzyme** present in **curd** helps convert **Milk to Curd**

Characteristics of Enzyme catalysis

Highly Efficient

- One molecule of an enzyme may transform one million reactant molecules per minute

Highly Specific in Nature

- Catalysts are highly specific

Example- Urease enzyme catalyses the hydrolysis of urea only and not the hydrolysis of any other amide

Highly active at Optimum temperature

- The temperature at which the rate of an enzyme catalysed reaction is maximum is called Optimum temperature. On either side this temperature, enzyme activity decreases

Example- Human body temperature(310K) is suitable for enzyme-catalysed reactions

Highly active at Optimum pH

- The rate of an enzyme-catalysed reaction is maximumat a particular pH called the Optimum pH

Activity Increases in presence of Activators and Co-enzymes-

- The enzymatic activity increases considerably in the presence of certain other substances called co-enzymes.

Example- When a certain non-protein(vitamin) is present along with the enzyme, catalytic activity is enhanced

Influence of inhibitors and Poisons-

- Like ordinary catalysts, enzymes are also inhibited by the presence of certain substances (inhibitors or poisons).
- These substances interact with the active functional groups on the surface of the enzyme and usually reduce or completely destroy the catalytic activity of the enzymes

Example- Many of the drugs we use is related to their action as enzyme inhibitors in our body

Mechanism of enzyme catalysis

Enzyme-catalysed reactions usually proceed in 2 steps-

1. Binding of the enzyme to the substrate to form an activated complex

E + S --> ES*

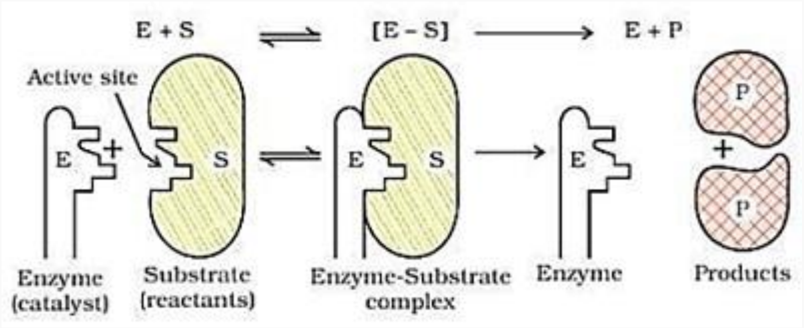
2. Decomposition of activated complex

ES* --> E +P

where E- Enzyme, S- Substrate , ES*- Activated complex , P- Product

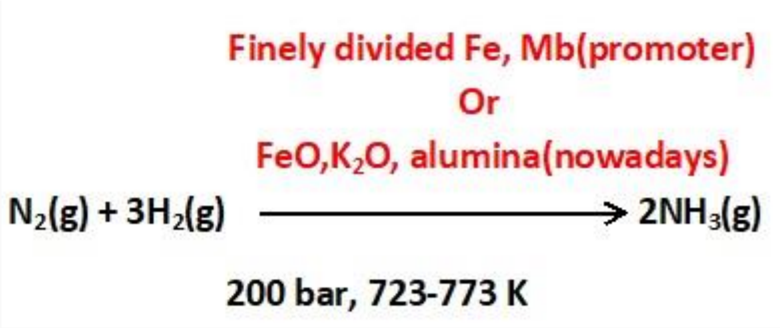
Lock and Key Mechanism- There are many cavities present on the surface of the enzyme. These cavities have a characteristic shape and active groups like –NH2, COOH, -SH, -OH etc. These are actually the active centres on the surface of the enzyme. The reactant molecules which have a complementary shape can fit into these cavities a lot like a key fitting into a lock. Due to the active centres (groups) present an activated complex also called enzyme-substrate complex is formed.

This complex decomposes to give products and the enzyme.



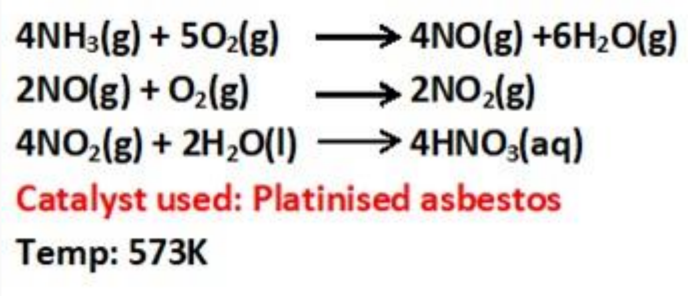
Catalysts in the industry-

1. Haber’s process to manufacture ammonia



$$N_2(g) + 3H_2(g) \xrightarrow[\text{200 bar, 723-773 K}]{\text{Finely divided Fe, Mb(promoter) Or } FeO, K_2O\text{, alumina(nowadays)}} 2NH_3(g)$$

2. Ostwald’s process to manufacture Nitric acid

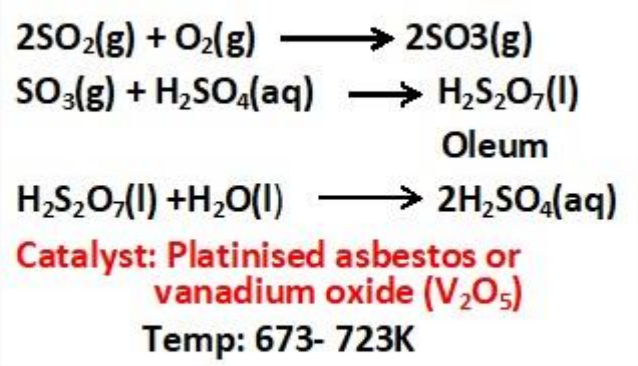


$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
$$4NO_2(g) + 2H_2O(l) \longrightarrow 4HNO_3(aq)$$

Catalyst used: Platinised asbestos

Temp: 573K

3. Contact process to manufacture Sulphuric acid



$$2SO_2(g) + O_2(g) \longrightarrow 2SO3(g)$$
$$SO_3(g) + H_2SO_4(aq) \longrightarrow \underset{\text{Oleum}}{H_2S_2O_7(l)}$$
$$H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(aq)$$

Catalyst: Platinised asbestos or vanadium oxide (V_2O_5)

Temp: 673- 723K

Colloids:

Colloidal solutions are mixtures in which the particle size is between 1-1000nm such that they can pass through filter paper but not animal or plant membranes. These particles also don’t settle upon standing for sometime.

They involve 2 substances called the dispersed phase and the dispersed medium

The dispersed phase- The substance that is dispersed in another medium to form a colloid. Usually lesser in quantity

Dispersed medium- The substance inside which the dispersed phase is dispersed

Classification of colloids

Colloids are classified in 2 different ways

Based on the physical state of the dispersed phase and dispersed medium:

S.No	Dispersed Phase	Dispersed Medium	Name of Colloid	Examples
1.	Solid	Solid	Solid sol	Gem stones
2.	Solid	Liquid	Sol	Muddy water, Paint, cell fluids
3.	Solid	Gas	Aerosol	Smoke,dust
4.	Liquid	Solid	Gel	Cheese, butter, jelly
5.	Liquid	Liquid	Emulsion	Milk, Hair cream
6.	Liquid	Gas	Aerosol	Fog, mist, cloud
7.	Gas	Solid	Solid Foam	Pumice Stone
8.	Gas	Liquid	Foam	Froth, soap lather

Based on nature of Interaction Between Dispersed Phase and Dispersed Medium

Lyophilic Colloids(liquid loving)-

- Some substances which can from colloids directly on mixing them with a suitable liquid(dispersion medium). These colloids are called lyophilic colloids. Examples of these substances are gum, geltine, starch, rubber.
- They are also called Reversible sols as in these sols(colloids) when the dispersion phase is separated from the dispersion medium (by say evaporation) , the sol can be formed again by just mixing the dispersion phase and medium again.
- They are also very stable and cannot be coagulated

Lyophobic colloids(liquid hating)

- Some substances cannot form colloid just by directly mixing them with a liquid. Their colloidal sols are prepared by special methods and are called lyophobic colloids. Examples of these substances are metals, metal sulphides.
- They are also called Irreversible colloids as on precipitation, they don't give back the colloid on simply mixing the dispersed phase and the dispersed medium.
- They are unstable and coagulate easily by heating shaking or adding electrolytes. Stabilising agents are used to preserve them

Based on the Types of Particles of the Dispersed Phase-

- Multimolecular Colloids: Many particles(atoms or small molecules) of the dispersed phase aggregate together to form species having the size of a colloidal particle(1-1000nm). These colloids are called multimolecular colloids. Example-gold sol, Sulphur sol

- Macromolecular colloids: Substances with large molecules (macromolecules) in suitable solvents form solutions but these macromolecules might be in the colloidal range. These solutions are called macromolecular colloids and resemble true solutions in many ways. Example- Starch, Cellulose, Proteins are natural macromolecules. Nylon, polythene, polystyrene are man-made macromolecules

- Associated Colloids: Some substances at high concentrations act as colloids due to the formation of aggregates. But at low concentrations they behave like normal strong electrolytes. These aggregates formed are called micelles. Such colloids are called associated colloids.

Kraft Temperature- The formation of micelles takes place only above a particular temperature called Kraft's temperature

Critical Micelle Concentration(CMC) – The concentration above which micelle formation takes place

Example- Soaps, synthetic detergents

Mechanism Of Micelle Formation-

- Soap is the sodium or potassium salt of fatty acid and may be represented as $RCOO^-Na$ (e.g. sodium stearate, ($CH_3(CH_2)16COO^-Na^+$]) . Whendissolved into water , it dissociates into $RCOO^-$ and Na^+ ions

- The $RCOO^-$ion consists of two parts – long hydrocarbon chain (also called non – polar tail) which is hydrophobic (water repelling) and a polar group COO^- (polar head) which is hydrophilic (water loving)

- At higher concentrations(CMC) RCOO- ions form an aggregate of spherical shape with the hydrocarbon chains pointing towards the centre and the COO- part facing outward on the surface of the sphere. This aggregate is called ionic micelle. It may have as many as 100 ions

Cleansing Action of Soaps

The cleansing action of soap is due to the formation of micelle by the soap molecules in such a way that the hydrophobic part is in the oil droplet(dirt) and the hydrolphilic part projects out. Since the polar groups interact with watersurrounded by soap ions is pulled from the surface and pulled into water.

Preparation of Colloids

A few ways to prepare colloids are given below

- Chemical method : Colloids can be prepared by chemical reactions leading to formation of molecules by double decomposition, oxidation, reduction or hydrolysis. These molecules then aggregate to form sols

- Electrical Disintegration/ Bredig's arc Method: This is applied to obtain colloidal sols of metals like gold, silver and platinum. An electric arc is stuck between the electrodes of the metal immersed in the dispersion medium. The intense heat produced vapourises the metal, which then condenses to form particles of colloidal size.

- Peptization- It is the process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte. The electrolyte used for this is called peptizing agent. During peptization the precipitate absorbs the one of the ions of the electrolyte on its surface. This causes +veor –vecharge to develop on the precipitate, which ultimately break up into small particles of the size of a colloid.

- **Purification of Colloids**
- The process used for reducing the amount of impurities to a required minimum is called purification of colloids.
- Some of processes used to do so are-
- Dialaysis- The process of sepeartaing the particles of a colloid by diffusion through a suitable membrane .
- Process – An apparatus called dialyser is used. A bag with a suitable membrane containing the colloid is suspended in a vessel through which fresh water flows continuously. The impurities diffuse through the membrane into the water leaving behind the colloid
-
- Here Crystalloid-Impurities
- Electro-dialysis- Dialysis is a slow method. It is made faster by this method. In this method, an electric filed is applied using metal electrodes. These ions present in the colloidal solution migrate out to the oppositely charge to electrodes. It is possible only if the dissolved substance in the impure colloid is an electrolyte.

- **Ultrafiltration-**

- This is the process of separating colloidal particles from the soluble solutes(impurities) using specially prepared filters, which are permeable to all substances except the colloid.

- Colloidal particles can usually pass through filter papers as the pores are too large. An ultrafilter paper can be made by soaking the filter paper in a colloidal solution, hardening by formaldehyde and then finally drying it. As this is slow process, pressure or suction is applied to speed it up. The colloidal particles left on the ultra-filter paper are stirred with fresh dispersion medium(solvent) to form a pure colloid.

Properties of Colloids

Colligative Properties-

The particles in colloids are bigger aggregates than those in a true solution. So, the number of particles in a colloid is lesser than a true solution of the same concentration. The values of colligative properties (osmotic pressure, lowering of vapour pressure, depression in freezing point, elevation in boiling point) are of small order as compared to values shown by true solution at same concentration.

Tyndall effect-

Tyndall effect is the scattering of the light by the particles present in the colloidal solution when viewed at right angles to the passage of light.

It is observed only when-

- The diameter of the dispersed particles is not much smaller than the wavelength of light used
- The refractive indices of the dispersed phase and dispersed medium have a large difference
- This effect was used to make an ultramicroscope and differentiate between true solution and colloids.

Colour-

The colour of the colloidal solution depends on the wavelength of the light scatter by the dispersed particles, size and nature of the dispersed particles and the manner in which it is viewed. Example- Finest gold sol is red in colour and as the size of the particle keeps increasing its colour changes to blue, then purple and finally gold.

Brownian Movement-

Brownian movement may be defined as continuous zigzag movement of the colloidal particles in a colloidal solution. It depends on the size of the particles and the viscosity of the colloid. Smaller the size of the particle and lesser its viscosity, faster is its motion. This movement is responsible for the stability of sols

Charge on Colloids-

Colloidal particles always have an electric charge. The nature of this charge is the same on all the particles in a given colloidal solution and maybe either +ve or –ve.

Positively charged sols-

- Haemoglobin
- Oxides-TiO_2 solution
- Hydrated Metal oxides like $Al_2O_3.xH_2O$, $Fe_2O_3.xH_2O$
- Dyes-methylene blue sols

Negatively charged sols-

- Metals- Cu, Ag, Au sols
- Metallic sulphides-As_2S_3, CdS
- Acid dye stuffs- Eosin
- Sols of starch, gelatin
- **Electrophoresis-**

- The movement of colloidal particles under the influence of an electric field is called electrophoresis. Negatively charged particles move towards the cathode and Positively charged particles moves towards anode.
- When the movement of particles is prevented, it is observed that the dispersion medium starts to move in the electric field. This is called electroosmosis.
- ← Prev
- Next →

Coagulation-

It is process of settling of colloidal particles. Also called precipitation of sol

Coagulation of Lyophobic Sols-

Coagulation of lyophobic sols can be done by the following methods:

- By electrophoresis - The colloidal particles move towards oppositely changed electrodes get discharged and precipitate.

- By mixing two oppositely charged sols - Oppositely charged sols when mixed together in almost equal proportion, neutralise their charges and get partially or completely precipitated.
- By Boiling- When a sol is boiled the adsorbed layer is disturbed due to increased number of collisions with the molecules of the dispersion medium. This reduces the charge on the particles and they ultimately settle down in the form of a precipitate.
- By Persistent dialysis - On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely. Colloids become unstable and coagulate.
- By addition of electrolyte - When excess of electrolyte is added, colloidal particles precipitate as colloids interact with ions carrying charge opposite to that present on themselves. This causes neutralisation leading to their coagulation.

Example- A negatively charged ion when added to a positively charged sol causescoagulation. The negatively charged ion is called coagulating ion/flocculative ion as it neutralises the colloid to cause coagulation.

Coagulation of Lyophillic Sols-

Lyophilic sols are stable because of charge and solvation of colloidal particles. So we remove these two factors to coagulate them. This is done by

- Addition of an electrolyte
- Addition of a suitable solvent

Protection of colloids -

- Lyophilic sols are more stable than lyophobic sols
- Lyophilic colloids have a unique ability to protect lyophobic colloids from electrolytes
- When a lyophilic sol is added to lyophobic sol, the lyophilic particles (colloids) form a layer around the particles of lyophobic sol
- Lyophilic colloids are also called protective colloids

Hardy-Schulze Rule-

- The greater the valency of the flocculating ion added, the greater is its precipitation.
- For negative sols, when positive ions are added

$Al^{3+} > Ba^{2+} > Na^{+}$ is the order in terms of flocculating power

- For positive sols, when negative ions are added

$[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$ is the order in terms of flocculating power

Emulsions

- Emulsions are colloids where both the dispersion phase and dispersion medium are liquids. These two liquids are immiscible or partially miscible. Generally one of the liquids is water.
- There are two types of emulsions

1. Oil dispersed in water (o/w type)- Water acts as dispersion medium

Example –Milk, vanishing cream

2. Water dispersed in oil (w/o type)- Oil acts as dispersion medium

Example- Butter, Cream

- Emulsions like water and oil separate into two layers and make the emulsion unstable. So emulsions are stabilised by stabilising agents.

- o/w emulsions are stabilised by proteins, gum, natural and synthetic soaps
- w/o emulsions are stabilised by metal salts of fatty acids, long chain alcohols

Applications of Colloids

1. Electro precipitation of smoke – The smoke is led through a chamber containing plates having a charged opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated. The particles settle down on the floor of the chamber. The precipitator is called Cottrell precipitator.

2. Purification drinking water – Alum is added to impure water to coagulate the suspended impuritiesand make water fit for drinking.

3. Medicines – Most of the medicines are colloidal in nature. Colloidal medicines are bmore effective because they have a larger surface area and are more easily absorbed by the body. Eg- Argyrol is a silver sol used as an eye lotion, milk of magnesia is used to cure stomach disorders

4. Tanning – Animal hides are colloidal in nature. When a hide that has positively charged particles is soaked in tannin/chromium salts, which contains negatively charged particles , mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning.

5. Cleansing action of soaps- already explained
6. Photographic plates and films – Photographic plates and films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.

7. Rubber industry- Latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of latex.

8. Industrial products- Paints inks, synthetic plastics, rubber, cement, graphite lubricants are all colloids

-

- The movement of colloidal particles under the influence of an electric field is called electrophoresis. Negatively charged particles move towards the cathode and Positively charged particles moves towards anode.

- When the movement of particles is prevented, it is observed that the dispersion medium starts to move in the electric field. This is called electroosmosis.

Introduction

- Metals have lot of importance in our day to day life.
- Uses of metals:-
    - The buildings around us are made up of steel, iron; wires that carry current are made up of metals.
    - The bridges, tall towers are all made up of metals.
    - The vessels which are made up of stainless steel; the body of ships made up of metals.
    - The batteries, vehicles, engines are made up of metals**.**

Pure metals can be extracted from ores by some chemical reactions.

Occurrence of Metals

- Earth crust is the source of many elements. Out of these elements, 70% are metals. Aluminium is the most abundant metal of earth crust and iron comes second.
- The percentage of different elements in earth crust is:-
- O-49%, Si-26%, Al-7.5%, Fe-4.2%, Ca-3.2%, Na-2.4%, K-2.3%, Mg-2.3%, H-l%
    - Metals occur in two forms in nature:-
- In native state
- In combined state, depending upon their chemical reactivities.

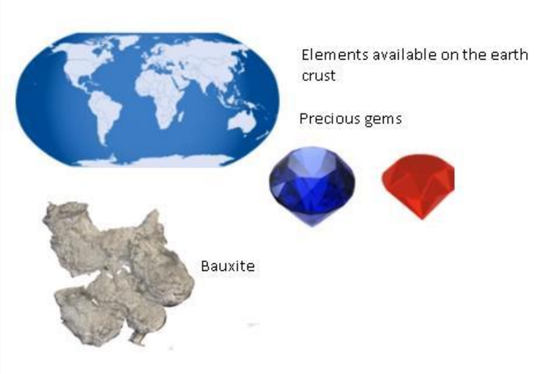
Native State

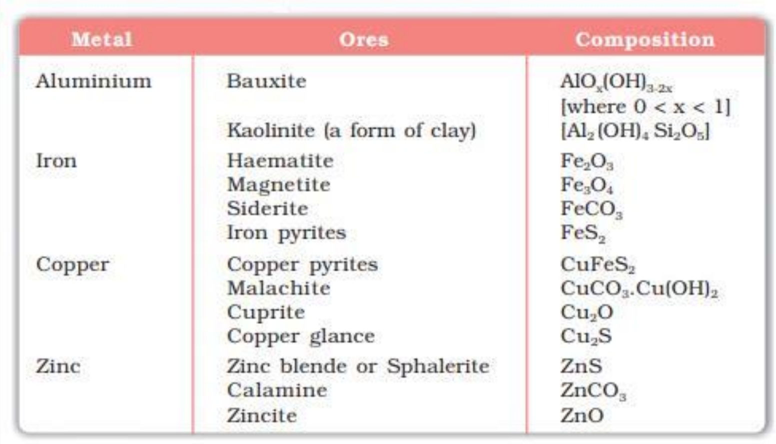
Elements which have low chemical reactivity or noble metals having least electropositive character are not attacked by oxygen, moisture and CO_2 of the air. These elements, therefore, occur in the Free State or in the native state, e.g., Au, Ag, Pt, S, O, N, noble gases, etc.

Combined State

Highly reactive elements such as F, CI, Na, K, etc., occur in nature combined form as their compounds such as oxides, carbonates sulphides, halides, etc.

Hydrogen is the only non-metal which exists in oxidised form only.

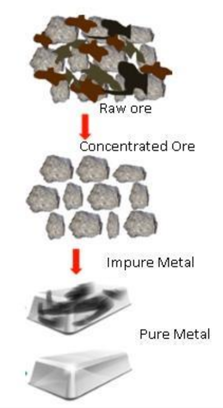




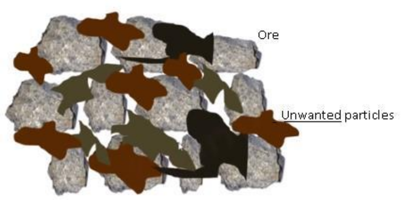
Metal	Ores	Composition
Aluminium	Bauxite	$AlO_x(OH)_{3-2x}$ [where $0 < x < 1$]
	Kaolinite (a form of clay)	$[Al_2(OH)_4Si_2O_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrites	FeS_2
Copper	Copper pyrites	$CuFeS_2$
	Malachite	$CuCO_3.Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

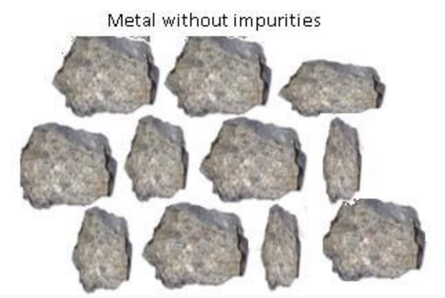
Extraction & Isolation of Metals

Following are the steps involved in extracting the metal, then isolating the impure metal from the ore and finally purify the metal.



- **Concentration of the Ore**: - The first step is to remove the impurities from the ore and it does not involve any chemical process. It is based on the difference between the physical properties of the metal and the unwanted particles.





Following are the physical processes involved:-

1. Hydraulic Washing
2. Magnetic separation
3. Froth Flotation Method
4. Leaching

- **Isolation of the metal from its concentrated ore**: - This process involves of getting impure metal from its concentrated ore. It is a chemical process.

Following are the processes involved:-

1. Conversion of oxide (Calcination & Roasting) & Reduction to form metal.
2. Electrochemical Process
3. Oxidation reduction

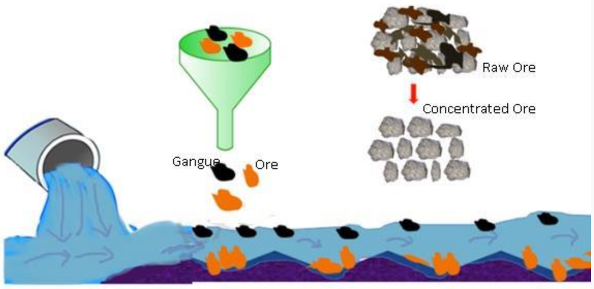
- **Purification of the metal**: - It involves the purification of the metal.

Following are the processes involved:-

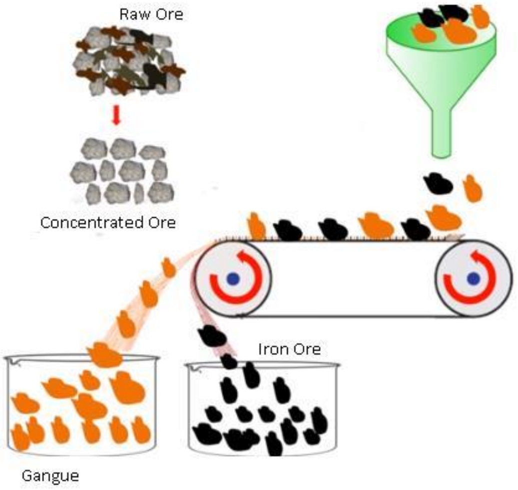
1. Distillation
2. Liquation
3. Electrolysis
4. Zone refining
5. Vapour phase refining
6. Chromatographic methods

Concentration of ores: -

1. Benefaction: - Removal of the unwanted materials (e.g., sand, clays, etc.) from the ore is known as **concentration**, **dressing** or **benefaction**. It involves several steps and selection of these steps depends upon the differences in physical properties of the compound of the metal present and that of the gangue.
2. Hydraulic Washing: - This method is based on the differences in gravities of the ore and the gangue particles. The process by which lighter earthy impurities are removed from the heavier ore particles by washing with water is called levigation. The lighter impurities are washed away. This method is commonly used for oxide ores such as haematite, tin stone and native ores of Au, Ag, etc.



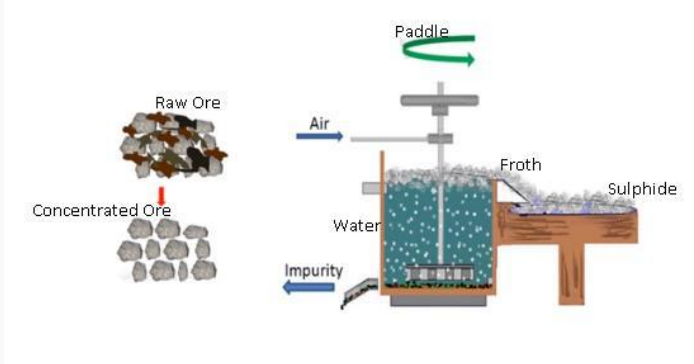
1. Magnetic Separation: - This method is based on differences in magnetic properties of the ore components. If either the ore or the gangue (one of these two) is capable of being attracted by a magnetic field, then such separations are carried out (e.g., in case of iron ores). The ground ore is carried on a conveyer belt which passes over a magnetic roller.



1. Froth Flotation Method: - In this method is use to remove gangue from sulphide ores. In this process, a suspension of the powdered ore is made with water. This method is based on the preferential wetting of ore particles by oil and that of gangue by water .As a result the ore particles become light and rise to the top in the form of froth while the gangue particles become heavy and settle down. Thus adsorption is involved in this method.

Working of Froth Flotation Method

1. It contains Collectors (e. g., pine oils, fatty acids, xanthates, etc.) which will enhance the non-wettability of the mineral particles and froth stabilisers (e. g., cresols, aniline) as a result it stabilises the froth.
2. The mineral particles become wet by oils while the gangue particles by water. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and is skimmed off. It is then dried for recovery of the ore particles.
3. Sometimes, it is possible to separate two sulphide ores by adjusting proportion of oil to water or by using '**depressants'**. For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.



1. Leaching: - Leaching is often used if the ore is soluble in some suitable solvent.

Following are the examples to explain the process of leaching.

(a) Leaching of alumina from bauxite :-

The principal ore of aluminium, bauxite, usually contains SiO_2, iron oxides and titanium oxide (TiO_2) as impurities.

Concentration is carried out by digesting the powdered ore with a concentrated solution of NaOH at (473 – 523) K and (35 – 36) bar pressure.

This way, Al_2O_3 is leached out as sodium aluminate (and SiO_2 too as sodium silicate) leaving the impurities behind:

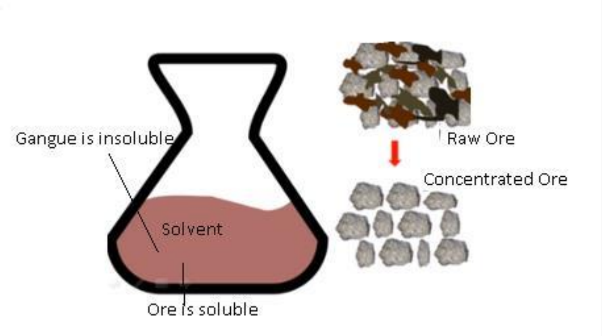
$Al_2O_{3(s)} + 2NaOH_{(aq)} + 3H_2O_{(l)} \rightarrow 2Na[Al(OH)_4]_{(aq)}$

The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces the precipitation

$2Na[Al(OH)_4]_{(aq)} + CO_{2(g)} \rightarrow Al_2O_3.xH_2O_{(s)} + 2NaHCO_{3(aq)}$

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure $A_{l2}O_3$:

$Al_2O_3.xH_2O(s)$ à $Al_2O_{3(s)} + xH_2O_{(g)}$ (Temp at 1470K)



(b) Other examples

In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained later by replacement:

$4M_{(s)} + 8CN^-_{(aq)} + 2H_2O_{(aq)} + O_{2\,(g)} \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-_{(aq)}$

(M= Ag or Au)

$2[M(CN)_2]^-_{(aq)}] + Zn_{(s)}$ à $[Zn(CN)_4]^{2-}_{(aq)} + 2M_{(s)}$

Extraction of Crude Metals from Concentrated Ore

The concentrated ore is usually converted to oxide before reduction, as oxides are easier to reduce.

Thus, isolation of crude metal from concentrated ore involves two major steps:

1. Conversion to oxide.
2. Reduction of the oxides to metal.

Conversion to oxide

- Calcination: - It is the process of converting an ore into its oxides by heating it strongly, below its melting point in a limited supply of air or in absence of air.

During calcination, volatile impurities as well as organic matter and moisture are removed.

- $Fe_2O_3 \, x H_2O$ (Δ)à $Fe_2O_{3\,(s)} + x\,H_2O_{(g)}$
- $ZnCO_{3\,(s)}$ (Δ)à $ZnO(s) + CO_{2\,(g)}$
- Roasting: - In roasting, the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal. This process is commonly used for sulphide ores and is carried out in blast furnace or reverberatory furnace. Roasting helps to remove the non-metallic impurities and moisture.

Some of the reactions involving sulphide ores are:

- $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$
- $2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$
- $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

If the ore contains iron, it is mixed with silica before heating.

Iron oxide 'slags of' as iron silicate and copper is produced in the form of copper matte which contains Cu_2S and FeS.

- $FeO + SiO_2 \rightarrow FeSiO_3$
    - (Slag)
- Meaning of slag: - During metallurgy, 'flux' is added which combines with 'gangue' to form 'slag'. Slag separates more easily from the ore than the gangue. This way, removal of gangue becomes easier.

Reduction of oxide to the metal

- The roasted or the calcined ore is then converted to the free metal by reduction. Reduction method depends upon the activity of metal.
- Metals which are low in the activity series (like Cu, Hg, and Au) are obtained by heating their compounds in air: metals which are in the middle of the activity "cries (like Fe. Zn, Ni, Sn) are obtained by heating their oxides with carbon while metals which are very high in the activity series (e.g., Na, K, Ca, Mg, Al) are obtained by electrolytic reduction method.

- Using the concepts of thermodynamics will help us to know the metallurgical transformations.
    - Gibb's Energy:- The change in Gibbs energy i.e. $\Delta G = \Delta H - T\Delta S$ equation(A)

Where, ΔH is the enthalpy change and ΔS is the entropy change for the process.

- This equation can also be written as:- $\Delta G^{(-)} = - RT\ln K$ equation(1)

Where, K is the equilibrium constant of the 'reactant – product' system at the temperature, T. A negative ΔG implies a +ve K in equation (1).

- Following conclusions can be made:-

- When the value of ΔG is negative in equation (A), only then the reaction will proceed.
- If reactants and products of two reactions are put together in a system and the net ΔG of the two possible reactions is –ve, the overall reaction will occur.
- During reduction, the oxide of metal decomposes:

$M_xO(s)$ à xM (solid or liquid) + (1/2) O_2 (g)   Equation (2)

The reducing agent takes away the oxygen. Equation (2) is the reverse of the oxidation of the metal. And then, the $\Delta_f G^{(-)}$ value is written in the usual way: xM(s or l) + (½) O_2 (g) → MxO(s) [$\Delta G^{(-)}_{(M,\ MxO)}$] equation (B)

- If reduction is being carried according to equation(2), the oxidation of the reducing agent(e.g. C or CO) will be:-
    - C(s) + (1/2) O_2(g) à CO (g) [$\Delta G^{(-)}_{(C,CO)}$]   equation (3)
    - CO(s) + (1/2) O_2(g) à CO_2 (g) [$\Delta G^{(-)}_{(C,CO)}$] equation(4)
- If carbon is taken, there may also be complete oxidation of the element to CO_2:
- (1/2) C(s) + (1/2) O_2(g) à (1/2) CO_2(g) [(1/2) $\Delta G_{(C,CO2)}$]   equation(5)
- On subtracting equation (B) from one of the three equations (3, 4 or 5).
- M_xO(s) + C(s) → xM(s or l) + CO(g)
- M_xO(s) + CO(g) → xM(s or l) + CO_2(g)
- M_xO(s) + (1/2) C(s) → xM(s or l) +(½) CO_2(g) equation(8)
- These reactions describe the actual reduction of the metal oxide, M_x

Extraction of Iron from oxide

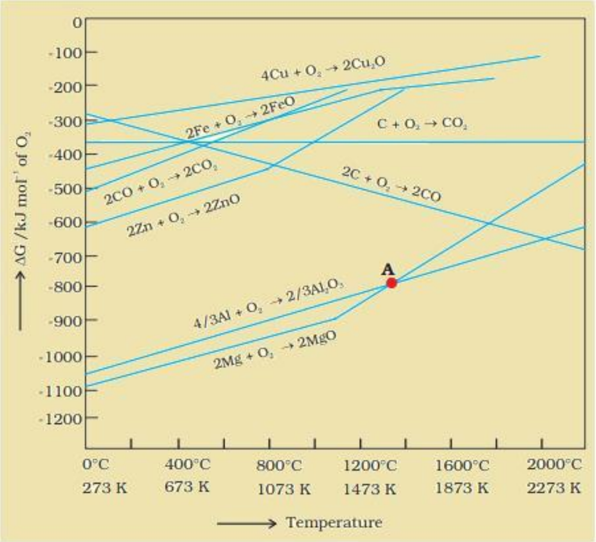
- Oxide ores of iron, after concentration through calcination/roasting (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with limestone and coke and fed into a Blast furnace from its top. In this case, the oxide is reduced to the metal.
- One of the main reduction steps in this process is:
- FeO(s) + C(s) → Fe(s/l) + CO (g)
- Consider the above reaction as 2 simpler reactions, in One reduction of FeO takes place and in another C is being oxidised to CO:
    - FeO(s) → Fe(s) +(½) O_2(g) [$\Delta G_{(FeO,\ Fe)}$] equation (C)
    - C(s) + (1/2) O_2 (g) → CO (g) [$\Delta G_{(C,\ CO)}$]
    - When both the reactions take place to yield the equation (8),

The net Gibbs energy change becomes:

$\Delta G_{(C,\ CO)} + \Delta G_{(FeO,\ Fe)} = \Delta_r G$ equation (9)

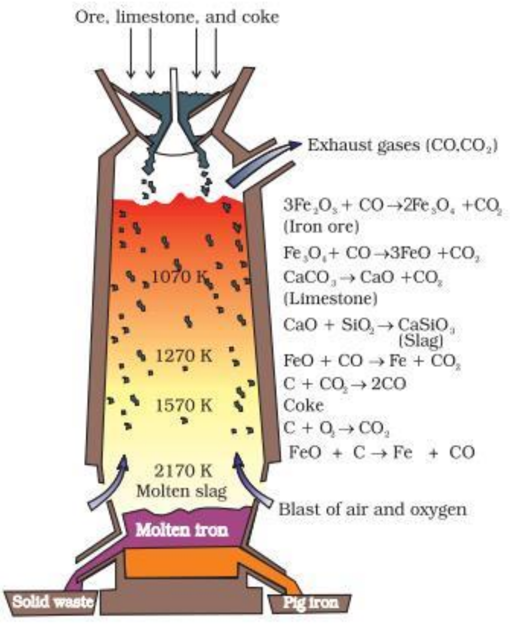
- The resultant reaction will take place if RHS of the equation (9) is negative.

- In $\Delta G^{\ominus}$ vs T plot representing reaction by equation (C), the plot goes upward and that representing the change C→CO (C, CO) goes downward.
- At temperatures above 1073K (approx.),
- The (C, CO) line comes below the Fe, FeO line [$\Delta G_{(C, CO)} < \Delta G_{(Fe, FeO)}$].
- So in this range, coke will be reducing the FeO and will itself be oxidised to CO.
- In a similar way the reduction of Fe_3O_4 and Fe_2O_3 at relatively lower temperatures by CO can be explained on the basis of lower lying points of intersection of their curves with the CO, CO_2



(Graph 1) Gibbs energy (ΔGV) vs T plots (schematic) for formation of some oxides (Ellingham diagram)

<u>Blast Furnace</u>



Blast Furance

- In the Blast furnace, reduction of iron oxides takes place in different temperature ranges.
- Hot air is blown from the bottom of the furnace and coke is burnt to give temperature upto about 2200K in the lower portion itself.
- The burning of coke therefore supplies most of the heat required in the process. The CO and heat moves to upper part of the furnace.

- In upper part, the temperature is lower and the iron oxides (Fe_2O_3 and Fe_3O_4) coming from the top are reduced in steps to FeO.
- Thus, the reduction reactions taking place in the lower temperature range and in the higher temperature range, depend on the points of corresponding intersections in the $\Delta_rG^{(-)}$ vs T plots.
- Following are the reactions which are taking place:-
    - At 500 – 800 K (lower temperature range in the blast furnace)–
        - $3Fe_2O_3 + CO$ à $2\ Fe_3O_4$
        - $Fe_3O_4 + 4\ CO$ à $3Fe + 4CO_2$
        - $Fe_2O_3 + CO$ à $2\ FeO + CO_2$

- At 900 – 1500 K (higher temperature range in the blast furnace):
- $C + CO_2$ à $2\ CO$
- $FeO + CO$ à $Fe + CO_2$

Products formed in Blast Furnace

- Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.
- The iron obtained from Blast furnace contains about 4% carbon and some other impurities. This iron is known as **pig iron**.
- **Cast iron** is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.
- **Wrought iron** or malleable iron is the purest form of commercial iron and is prepared from cast iron by oxidising impurities in a reverberatory furnace lined with haematite.
- This haematite oxidises carbon to carbon monoxide:
    - $Fe_2O_3 + 3\ C \rightarrow 2\ Fe + 3\ CO$
    - Limestone is added as a flux and sulphur, silicon and phosphorus are oxidised and passed into the slag. The metal is removed and freed from the slag by passing through rollers.

Extraction of copper from cuprous oxide [copper [I] oxide]

- Considering the Graph (1) the Cu_2O line is at the top.
- So to reduce oxide ores of copper directly to the metal by heating with coke (both the lines of C, CO and C, CO_2 are at much lower positions in the graph particularly after 500 – 600K).
- Most of the ores are sulphide and some may also contain iron. The sulphide ores
- are roasted/smelted to give oxides:
- $2Cu_2S + 3O2 \rightarrow 2Cu_2O + 2SO_2$
    - The oxide can then be easily reduced to metallic copper using coke:
    - $Cu_2O + C \rightarrow 2\ Cu + CO$
- In actual process, the ore is heated in a reverberatory furnace after mixing with silica. In the furnace, iron oxide 'slags of' as iron silicate and copper is produced in the form of copper matte. This contains Cu_2S and FeS.
    - $FeO + SiO_2 \rightarrow FeSiO_3$ (Slag)
- Copper matte is then charged into silica lined convertor.
- Some silica is also added and hot air blast is blown to convert the remaining
    - FeS_2, FeO and Cu_2S/Cu_2O to the metallic copper.
        - Following reactions take place:
            - $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$
            - $FeO + SiO_2 \rightarrow FeSiO_3$ (6.38)
            - $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$
            - $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

- The solidified copper obtained has blistered appearance due to the evolution of SO_2 and so it is called blister copper.

Extraction of Zinc from Zinc Oxide

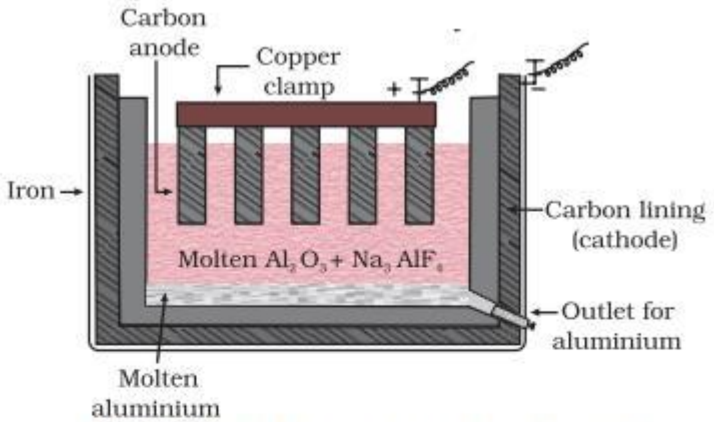
- The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper.
- For the purpose of heating, the oxide is made into brickettes with coke and clay.
    - ZnO + C àZn + CO (where coke is the catalyst, and temperature is 673 K)
- The metal is distilled off and collected by rapid chilling.

Electrochemical Principles of Metallurgy

- In the reduction of a molten metal salt, electrolysis is done.
- Consider the equation:-
    - $\Delta G^{(0)} = - nE^{(-)}F$ equation (1)
    - n= number of electrons and $E^{(-)}$ = electrode potential of redox couple formed in the system.
    - More reactive metals have large negative values of the electrode potential.
    - This implies their reduction is very difficult.
- If the difference of two $E^{(-)}$ values corresponds to a positive $E^{(-)}$ and consequently negative $\Delta G^{(0)}$ in equation (1) .
- As a result then the less reactive metal will come out of the solution and the more reactive metal will go to the solution.
    - For example:- Cu_2+ (aq) + Fe(s) → Cu(s) + Fe_2+ (aq)
    - In simple electrolysis, the M^{n+} ions are discharged at negative electrodes (cathodes) and deposited there. Sometimes a flux is added for making the molten mass more conducting.

Aluminium

- In the metallurgy of aluminium, purified Al_2O_3 is mixed with Na_3AlF_6 or CaF_2 which lowers the melting point of the mix and brings conductivity.
- The fused matrix is electrolysed.
- Steel cathode and graphite anode are used. The graphite anode is useful here for reduction to the metal.
- The overall reaction may be taken as:
    - $2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2$
- This process of electrolysis is widely known as Hall-Heroult process.
- The electrolysis of the molten mass is carried out in an electrolytic cell using carbon electrodes. The oxygen liberated at anode reacts with the carbon of anode producing CO and CO_2.
- This way for each kg of aluminium produced, about 0.5 kg of carbon anode is burnt away.
- The electrolytic reactions are:
- Cathode: Al_3+ (melt) + 3e– → Al(l)
- Anode: C(s) + O_2– (melt) → CO(g) + $2e^-$
- C(s) + $2O^{2-}$ (melt) → CO_2 (g) + $4e^-$



Electrolytic cell for the extraction of aluminium

Refining

- A metal extracted by any method is usually contaminated with some impurity.
- For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity.
- Following are the methods used to refine the metals:-
- Distillation
- Liquation
- Electrolysis
- Zone refining
- Vapour phase refining
- Chromatographic methods

Distillation

- This is very useful for low boiling metals like zinc and mercury. The impure metal is evaporated to obtain the pure metal as distillate.

(b) Liquation

- In this method a low melting metal like tin can be made to flow on a sloping surface. In this way it is separated from higher melting impurities.

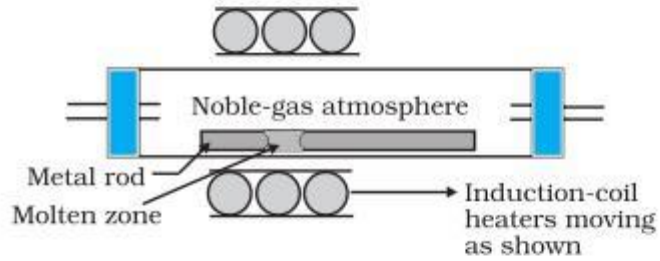
(c) Electrolytic Refining

- In this method the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode.
- They are put in a suitable electrolytic bath containing soluble salt of the same metal.
- The more basic metal remains in the solution and the less basic ones go to the anode mud.
- The reactions are:
    - Anode: $M \rightarrow M^{n+} + n^{e-}$
    - Cathode: $M^{n+} + n^{e-} \rightarrow M$
- This method is used to refine Copper, Zinc etc.
    - In case of copper refining-
    - Anodes are of impure copper and pure copper strips are taken as cathode.
    - The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode:
    - Anode: $Cu \rightarrow Cu^{2+} + 2$ e–
    - Cathode: $Cu_2+ + 2e- \rightarrow Cu$

  - Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum; recovery of these elements may meet the cost of refining.

(d) Zone refining

- This method is based on the principle that the impurities are more soluble in the molten form as compared to the solid state of the metal.
- A circular mobile heater is fixed at one end of a rod of the impure metal.
- The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone.
- The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated.
- This end is cut off. This method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.



- Vapour Phase Refining
- The metal is converted into its volatile compound and collected elsewhere. It is then decomposed to give pure metal.
- There are 2 requirements for this method:-
  - The metal should form a volatile compound with an available reagent,
  - The volatile compound should be easily decomposable, so that the recovery is easy.
  - For example: - Mond Process for Refining Nickel and van Arkel Method for Refining Zirconium or Titanium.
- Chromatographic method
- The principle of this method is that different components of a mixture are differently adsorbed on an adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent.
- Different components are adsorbed at different levels on the column.
- The adsorbed components are removed or eluted by using suitable solvents (eluant).
- Depending upon the physical state of the moving medium and the adsorbent material and also on the process of passage of the moving medium, the chromatographic method is given the name.
- The Al_2O_3 is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form. This is an example of column chromatography.
- There are several chromatographic techniques such as paper chromatography, column chromatography, gas chromatography, etc.

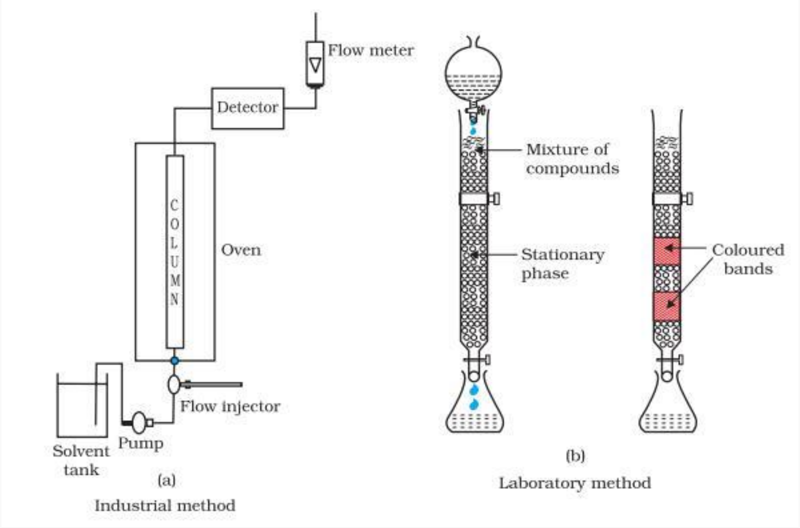


Diagram showing column chromatography

Group 15

The group 15 members are:

- Nitrogen (N)
- Phosphorous (P)
- Arsenic(As)
- Antimony (Sb)
- Bismuth (Bi)

Physical Properties of group 15:

1. **Electronic configuration of group 15 members**: general electronic configuration is ns^2np^3.

- Nitrogen (N) [He]$2s^2,2p^3$
- Phosphorous (P) [Ne]$3s^2,3p^3$
- Arsenic(As) [Ar]$3d^{10},4s^2,4p^3$
- Antimony (Sb) [Kr]$4d^{10},5s^2,5p^3$
- Bismuth (Bi) [Xe]$4f^{14},5d^{10},6s^2,6p^3$

2. **Atomic size**: As compared to group 14 they are smaller in size due to increased nuclear charge.

Along group, size increases as every time a new shell is being added due to which nuclear charge decreases.

3. **Ionization energy**: The group 15 has high ionization energy than group 14 because of smaller size.

Along group, ionization energy decreases as size increases

4. **Electro negativity**: Because of smaller size the group 15 members re more electronegative than group 14. Out of them the increasing order of electro negativity is:

N>P>As>Sb>Bi

5. **Metallic character**: They are less metallic than group 14 because of small size and increased nuclear charge.

Along group metallic character increases as size increases and ionization energy decreases. The order of their metallic character is: N<P<As<Sb<Bi

6. **Melting point and boiling point**: The melting point depends upon the type and number of bonds formed whereas boiling point depends upon Vander wall force which increases in magnitude with increase in size.

- Boiling points: It increases down the group as size increases. The order is – N<P<As<Sb<Bi
- Melting point: It first increases then decreases.

The order is: N<P<As>Sb>Bi

The reason for this decrease in case of antimony and bismuth is due to use of only three electrons out of 5 in bond formation because of inert pair effect.

7. **Catenation** : They show only up to small extent like P exist as P_4

Nitrogen as N_2.

8. **Oxidation states**: They have configuration ns^2np^3. Their common oxidation states are +5 and +3.

The oxidation states shown by them are:

- Nitrogen shows: -
- -3 (Ca_3N_2) Calcium Nitride
- -2 (NH_2NH_2) pyridine

Also show +3.

- Phosphorous shows:

-3 (Ca_3P_2) Calcium Phoshide

- Bismuth: as +3 due to inert pair effect. It has only one compound in +5 oxidation state that is BiF_5(Bismuth pentafluoride).

Please note**: Nitrogen do not form compounds in +5 oxidation states because:**

- It has no vacant d orbital therefore no excitation can occur. So, maximum covalence shown by it is 4.

Anomalous behavior of nitrogen:

- It has small size
- It has high ionization energy
- It is most electronegative

- It has no vacant d orbital
- In it no dπ-pπ bonding can occur.

Chemical properties of group 15:

1. **Reaction with hydrogen**: Whenever any substance reacts with hydrogen they form respective hydrides.

Like whenever 15 group elements react they form hydrides of order EH_3 that is:

NH_3	PH_3	AsH_3	SbH_3	BiH_3
Ammonia	Phosphine	Arsine	Stibine	Bismuthine

In this NH_3 is called ammonia and PH_3 is called phosphine.

All these hydrides are called Lewis bases.

These can be formed by reacting metal hydrides with water that is:

$Mg\ _3N_2 + H_2O \text{-->} Mg(OH)_2 + NH_3$

(Magnesium nitride) (magnesium hydroxide)(ammonia)

Likewise for preparing phosphine we take calcium phosphide:

$Ca_3P_2 + H_2O \text{-->} Ca\ (OH)_2 + PH_3$

(Calcium phosphide) (calcium hydroxide) (phosphine)

Ammonia can be industrially prepared by Haber's process:

In this nitrogen and hydrogen are taken in 1:3 ratios and catalyst Fe and MoO is used. This reaction can take place at conditions of low temperature and high pressure. The structure of these hydrides is pyramidal and hybridization sp^3.

The properties of hydrides are:

- **Bond angle**: The bond angle decreases down the group. The order of decrease of angle is:

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

The reason behind this is that when size of central atom increases, lone pair will push closer to bond pair-bond pair. Due to this bond angle decreases.

- **Basic character**: It refers to ability of molecule to donate its lone pair .the order of increase in basic character is :

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Most basic least basic

Due to large size of bismuth the lone pair density is less closer to bismuth therefore tendency to lose electron decreases.

- **Stability**: The stability of hydrides depends upon the comparability of size. The order of stability of hydrides is:

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Due to increase in size, bond length increase due to which bond dissociation energy decrease therefore stability decrease.

- **Reducing nature**: The order of reducing character of hydrides is:

$NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

Out of them in case of BiH_3, the bond strength is low therefore reducing character is lowest.

- **Boiling point**: The boiling point depends upon Vander wall force and this Vander wall force increases with increase in size.

The order of their boiling points for 15 group hydrides is:

$NH_3 > PH_3 < AsH_3 < SbH_3 < BiH_3$

In case of NH_3 and PH_3, ammonia has higher boiling point than phosphine because of hydrogen bonding.

- **Solubility**: The solubility of hydrides in water for group 15 is:

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

Ammonia has higher solubility due to formation of hydrogen bonds.

2. **Reaction with oxygen**: Whenever group 15 elements react with oxygen they form oxides of order E_2O_3 and E_2O_5.

E_2O_3- trioxides

E_2O_5. - Penta oxides

Nitrogen form maximum types of different oxides ranging from +1 to +5.

The oxides of nitrogen are:

- N_2O (laughing gas) oxidation state +1

- NO oxidation state +2
- N_2O_3 oxidation state +3
- N_2O_4 oxidation state +4
- N_2O_5 oxidation state +5(most acidic)

In all the oxides pπ-pπ bonding takes place.

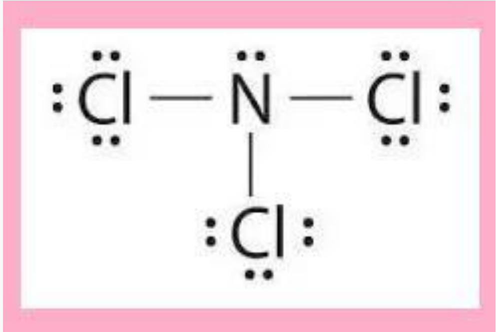
- P-forms oxide in oxidation state of +3 (P_4O_6), +4 (P_4O_8), +5 (P_4O_5)
- As forms oxide as As_2O_3, As_2O_5(Arsenic trioxide and Arsenic pentaoxide).
- Sb forms oxide as Sb_2O_3 and Sb_2O_5(Antimony trioxide and Antimony pentaoxide).
- Bi forms oxide as Bi_2O_5 and Bi_2O_3(Bismuth trioxide and Bismuth pentaoxide).

Nature of their oxides:

Nitrogen and phosphorous forms acidic oxides.
Arsenic and antimony forms amphoteric oxide.
Bismuth forms basic oxide.
"Higher is the oxidation state more acidic is the oxide"

3. **Reaction with halogens**

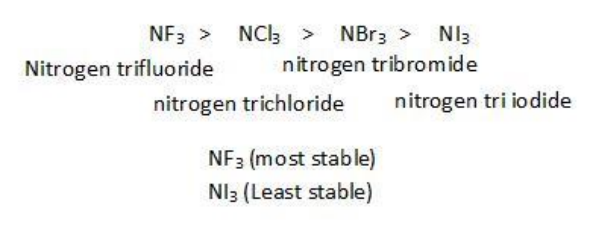
The group 15 elements combine with halogen to form their respective halides of general formula EX_3 and EX_5.
Nitrogen does not form pent halides due to non availability of d orbital but form trihalides.
The structure of trihalides is distorted tetrahedral of hybridization sp^3.
The geometry is given below:



Nitrogen trichloride

Characteristics of their trihalides:

- They are covalent and down the group ionization increase
- Trihalides of nitrogen are least stable
- Nitrogen triflourides are maximum stable
- The order of stability of nitrogen halides are :



NF_3 > NCl_3 > NBr_3 > NI_3

Nitrogen trifluoride
nitrogen tribromide
nitrogen trichloride
nitrogen tri iodide

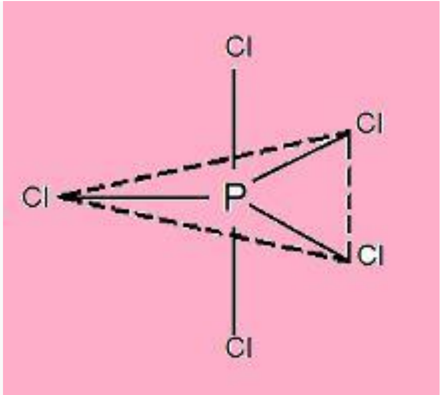
NF_3 (most stable)
NI_3 (Least stable)

The reason behind is incomparable sizes.

- Trihalides of phosphorous arsenic and antimony are good Lewis bases.
- Down the group trihalides of group 15 stability increases due to inert pair effect.

Characteristics of pentahalides:

- Their general formula is EX
- Their hybridization is sp^3
- The geometry of pentahalides is trigonal bipyramidal as shown below:



Phosphorous pentachloride

- Down the group stability of pent halides decreases due to inert pair effect.
- All pent halides are Lewis acids.

Please note that: The existence of PCl_5 (phosphorous pentachloride)is gas but in solid state it exist as dimer {$[PCl_4]^+[PCl_6]^-$}

Dinitrogen

Introduction

The molecular formula is N_2.

It was discovered by Daniel Rutherford in 1772.

- It is a diatomic gas.
- The triple bond that exists between nitrogen of molecule is quite strong therefore bond dissociation energy is high.
- It is an inert gas.
- Nitrogen is smallest in its group.
- Nitrogen is most electronegative.
- Nitrogen has highest ionization energy in its group.
- Nitrogen has no vacant d orbital.

Preparation of DiNitrogen

- It is prepared by reacting ammonium chloride with sodium hydroxide that is:

NH_4Cl + NaOH --> $NaCl + N_2 + H_2O$

Ammonium chloride soda lime sodium chloride

This nitrogen so formed has impurities nitric oxide and nitric acid. So, in order to remove them we have to bubble this nitrogen through concentrated sulphuric acid.

- Pure nitrogen can be prepared by heating Barium nitrate :

$Ba(NO_3)_2$ ---> $Ba + N_2 + O_2$

Barium nitrate Barium Nitrogen

(On heating)

Physical properties of nitrogen

- It is colorless, odorless and tasteless gas.
- It is slightly soluble in water.
- It exists as N
- It is non toxic gas.

Chemical properties of nitrogen

1. **Reaction with metal**: Nitrogen reacts with metal to form metal nitrides.

   $Ca + N_2$ --> Ca_3N_2 (Calcium Nitride)

1. **Reaction with non metal**: They react with non metal to form compounds like:

   $N_2 + O_2$ --> NO_2 (Nitrogen dioxide)

   $N_2 + H_2$ --> NH_3 (Ammonia)

Uses of nitrogen:

- Liquid nitrogen is used as preservative for specimens.

- It is used to manufacture compounds like nitric acid etc.
- It is used to create inert atmosphere.

Ammonia

The molecular formula of ammonia is NH_3.

Preparation:

Lab preparations:

1. **Hydrolysis of urea**: The reaction involved is given below that is

$$NH_2CONH_2 + H_2O \rightarrow NH_3 + CaCl_2 + H_2O \rightarrow (NH_4)_2CO_3$$

urea water ammonia calcium chloride ammonium carbonate

On dissociation

$$\updownarrow$$

$$NH_3 + CO_2 + H_2O$$

ammonia carbon dioxide water

2. **By reacting ammonium chloride with calcium hydroxide:**

$$NH_4Cl + Ca(OH)_2 \rightarrow NH_3 + CaCl_2 + H_2O$$

Ammonium chloride ammonia calcium chloride

2. **By reacting ammonium sulphate with sodium hydroxide:**

$$NH_4)_2SO_4 + NaOH \rightarrow Na_2SO_4 + NH_3 + H_2O$$

Ammonium sulphate sodium sulphate

Industrial preparation:

In this nitrogen and hydrogen are taken in 1:3 ratios and catalyst Fe and MoO is used. This reaction can take place at conditions of low temperature and high pressure. The structure of these hydrides is pyramidal and hybridization sp^3.

N_2 + H_2 (It is a irreversible reaction) <---> $2NH_3$

nitrogen hydrogen ammonia

The reaction takes place at low temperature, high pressure, catalyst Fe, catalytic promoter MoO (molybdenum oxide).

Physical properties of ammonia

- It is colorless gas with pungent smell.
- It is highly soluble in water forming ammonium hydroxide.
- It can be easily liquefied.
- It has high boiling point due to hydrogen bonding.

Chemical properties of ammonia

1. **Basic nature**: It behaves as a Lewis base because of lone pair of electrons. Also it has tendency to behave as bronsted base that is :

$$NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

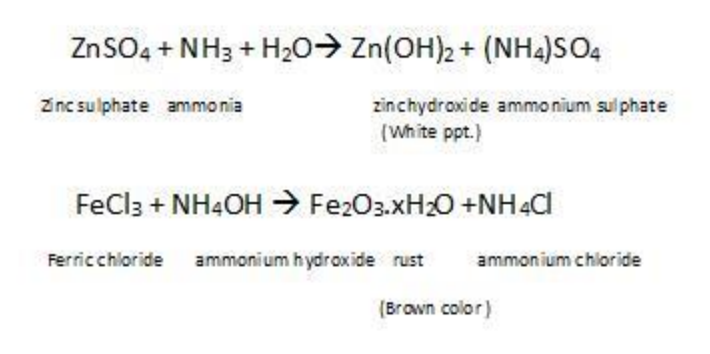
Ammonia sulphuric acid ammonium sulphate

$$NH_3 + HCl \rightarrow NH_4Cl$$

Ammonia hydrogen chloride ammonium chloride

Both the reactions above is neutralization reactions

2. **It behaves as weak base** that means it precipitates hydroxides.



$ZnSO_4 + NH_3 + H_2O \rightarrow Zn(OH)_2 + (NH_4)SO_4$

Zinc sulphate ammonia zinc hydroxide ammonium sulphate

(White ppt.)

$FeCl_3 + NH_4OH \rightarrow Fe_2O_3.xH_2O + NH_4Cl$

Ferric chloride ammonium hydroxide rust ammonium chloride

(Brown color)

2. The lone pair present helps in forming complexes so we can say it is a **complexion agent**.

$Cu^{2+} + NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$

Cuprous ion ammonia tetramainecopper(ii)ion

Blue color

Likewise:

$Ag + NH_3 \rightarrow [Ag(NH_3)_2]$

Silver ammonia diamine silver (i)ion

White color

This complexing nature of ammonia is due to the lone pair present in it so, it can act as electron donor.

Uses of ammonia

- Ammonia helps in making nitrogenous fertilizers like ammonium sulphate etc.
- It is used in manufacture of nitric acid.
- The liquid ammonia is used as refrigerant.

Oxides of nitrogen

The nitrogen forms variety of oxides that are given below:

- N_2O (laughing gas) oxidation state +1
- NO oxidation state +2
- N_2O_3 oxidation state +3
- N_2O_4 oxidation state +4
- N_2O_5 oxidation state +5(most acidic)

1. **N_2O: nitrous oxide or laughing gas**

- In it the oxidation sate of nitrogen is +1.

Preparation:

- It is prepared by heating ammonium nitrate that is:
- NH_4NO_3 (on heating) --> N_2O + H_2O
- (Ammonium Nitrate) Nitrous Oxide Water
- The laughing gas so formed is colourless, neutral and exist in gaseous state.
- It structure is :

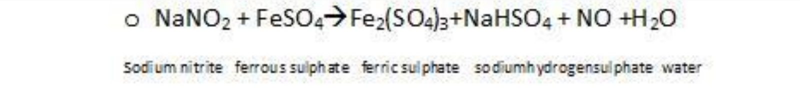
$N^- = N_+ = O$

Nitrous oxide

2. NO (nitric oxide)

- In it the oxidation state of nitrogen is +2.

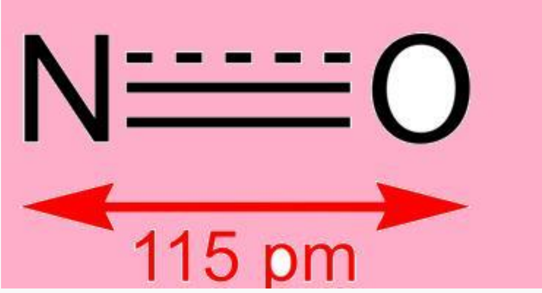
Preparation:



○ $NaNO_2 + FeSO_4 \rightarrow Fe_2(SO_4)_3 + NaHSO_4 + NO + H_2O$

Sodium nitrite ferrous sulphate ferric sulphate sodiumhydrogensulphate water

- The NO formed is colorless and neutral gas.
- The structure of nitric oxide is given below:



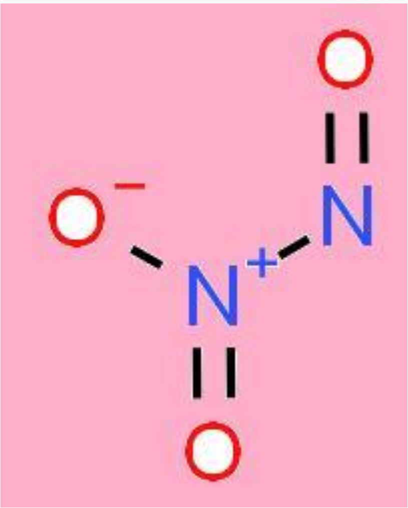
Nitric oxide

3. **N_2O_3 (nitrogen trioxide)**

- In it the oxidation state is +3.

Preparation:

- $NO + N_2O_4 \text{-->} N_2O_3$
- This nitrogen trioxide is blue solid and acidic in nature.
- The structure of it is:



Nitrogen trioxide

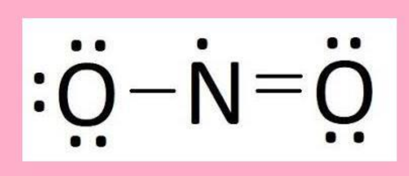
4. **NO_2 (Nitrogen dioxide)**

- In it the oxidation state of N is +4.

Preparation:

$Pb(NO_3)_2$ (ON heating)---> PbO + NO_2 + O_2
Lead Nitrate LeadOxide Nitrogen dioxide

- The nitrogen dioxide so formed is brown gas with acidic nature.
- The structure of it is:



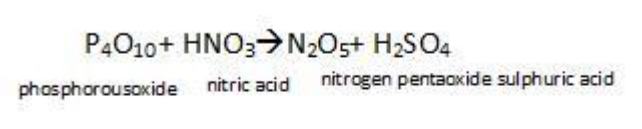
Nitrogen dioxide

This single electron system in it helps it in existing as dimer (N_2O_4).
$2NO_2$ <---> N_2O_4
Nitrogen dioxide Dimer of Nitrogen dioxide
On cooling we get dimer and on heating dimer we get nitrogen dioxide.

5. **N_2O_5 (nitrogen pent oxide)**

- In it the oxidation state is +5.
- This is most acidic among all oxides of nitrogen.

Preparation:

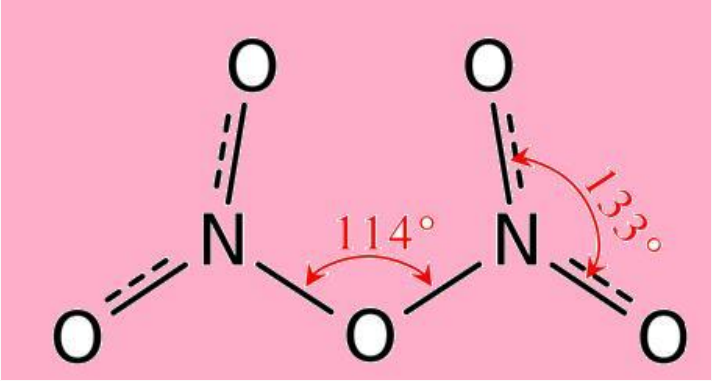


P_4O_{10}+ HNO_3→N_2O_5+ H_2SO_4

phosphorousoxide nitric acid nitrogen pentaoxide sulphuric acid

This nitrogen pent oxide is colorless gas with acidic nature.

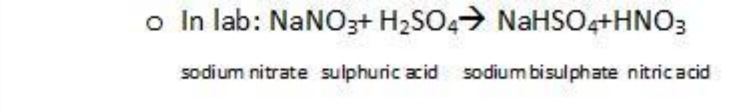
- The structure of this nitrogen pent oxide is given below:



Nitrogen pentaoxide

Nitric acid (HNO_3)

Preparation:

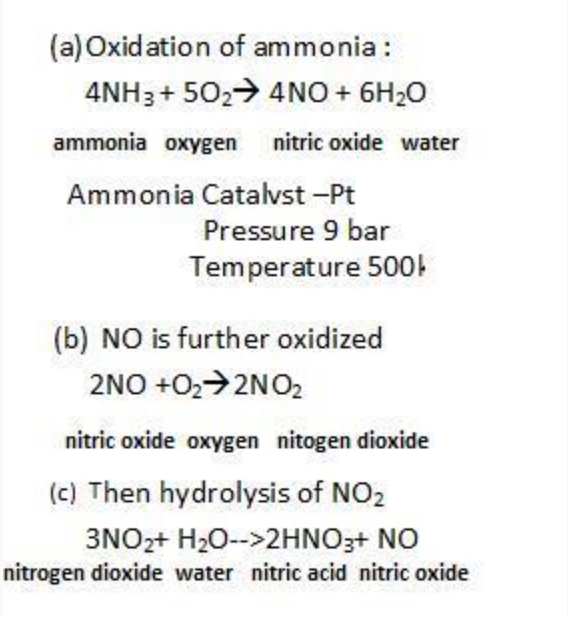


- In lab: $NaNO_3$+ H_2SO_4→ $NaHSO_4$+HNO_3

  sodium nitrate sulphuric acid sodium bisulphate nitric acid

- Industrially : It is prepared from Ostwald's process

The reaction involves various steps:



(a) Oxidation of ammonia :

$4NH_3 + 5O_2$→ $4NO + 6H_2O$

ammonia oxygen nitric oxide water

Ammonia Catalvst –Pt

Pressure 9 bar

Temperature 500l

(b) NO is further oxidized

$2NO + O_2$→$2NO_2$

nitric oxide oxygen nitogen dioxide

(c) Then hydrolysis of NO_2

$3NO_2$+ H_2O-->$2HNO_3$+ NO

nitrogen dioxide water nitric acid nitric oxide

The nitric acid so prepared is 98% pure rest 2% can be purified by concentrated sulphuric acid.

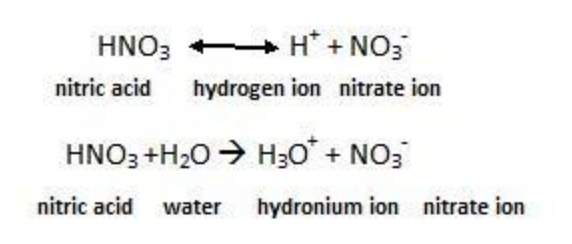
Physical properties of nitric acid

- It is colorless liquid.
- The impure nitric acid is yellow because of nitrogen dioxide in it as impurity therefore nitric acid is called as fuming nitric acid also.
- It is corrosive in nature.

Chemical properties of nitric acid

It keeps on oxidizing and forms nitrogen dioxide that is why we see brown color fumes coming out from the bottle.

1. **Acidic nature**: Nitric acid is acidic in nature because it dissociates to give hydrogen ion when dissolved in water:



$$HNO_3 \longleftrightarrow H^+ + NO_3^-$$

nitric acid hydrogen ion nitrate ion

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$

nitric acid water hydronium ion nitrate ion

Because this is acidic therefore, it reacts with base showing neutralization reaction:

HNO_3 + NaOH ---> $NaNO_3$ + H_2O

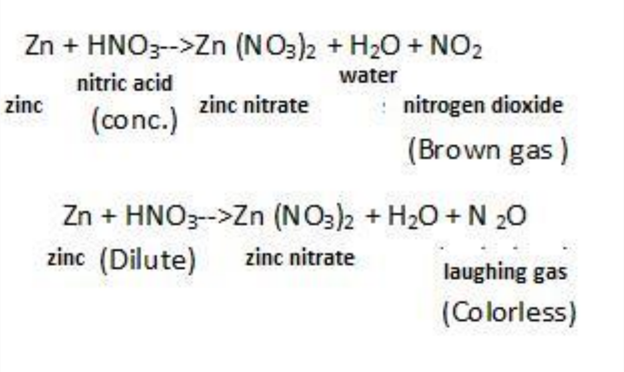
Nitric Acid Sodium Hydroxide Sodium Nitrate Water

2. **Reaction with metals**: To give nitrates and nascent hydrogen:

M + HNO_3 ---> metal nitrates + $[H]^+$

This nascent hydrogen can bring about reduction of substance:

Example:



$$Zn + HNO_3 \dashrightarrow Zn(NO_3)_2 + H_2O + NO_2$$

zinc nitric acid (conc.) zinc nitrate water nitrogen dioxide (Brown gas)

$$Zn + HNO_3 \dashrightarrow Zn(NO_3)_2 + H_2O + N_2O$$

zinc (Dilute) zinc nitrate laughing gas (Colorless)

Please note certain metals like chromium, aluminium do not dissolve in nitric acid due to formation of passive layer of oxide film on it which prevents further reaction.

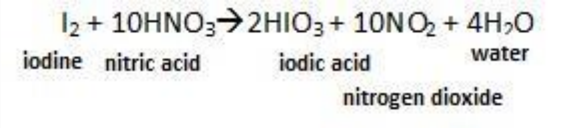
Aqua regia: It is a mixture of nitric acid and hydrochloric acid in ratio 1:3 and it is used in dissolving noble metals.

1. **Oxidizing nature of nitric acid**: It helps in oxidation of non metals like for example:

- Converting I_2 --> IO_3^-

I_2--- >IO_3^-

In this oxidation state of iodine is changed from 0 to +5 that is increase in oxidation number:



$$I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

iodine nitric acid iodic acid nitrogen dioxide water

Test for nitrates

It is also called as brown ring test.

In this we take test tube and sample (salt containing nitrate) to it.

- Then slowly pour concentrated sulphuric acid to it.
- Then we put solution of ferrous sulphate and allow it to stand.
- Then on interface a brown ring is formed that shows the presence of nitrates.
- The ring that is formed is chemically $[Fe(H_2O)_5(NO)]^{2+}$(Nitroso ferrous sulphate).

Uses of nitric acid:

- In manufacturing of ammonium nitrate and other fertilizers.
- In manufacturing of explosives like TNT (trinitrotoluene).
- In purification of gold and silver by using aqua regia.
- It is used as oxidizer in rocket fuels.

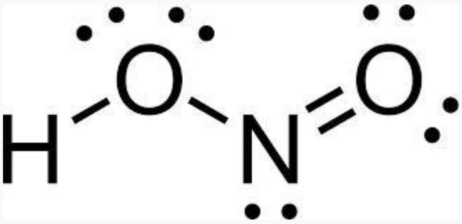
Formation of oxy-acids

(a)Oxy-acids of nitrogen: nitrogen forms four types of oxy-acids that is:

- Nitric acid (HNO_3)

- Nitrous acid (HNO_2)
- Hypo nitrous acid ($H_2N_2O_2$)
- Per nitric acid (HNO_4).

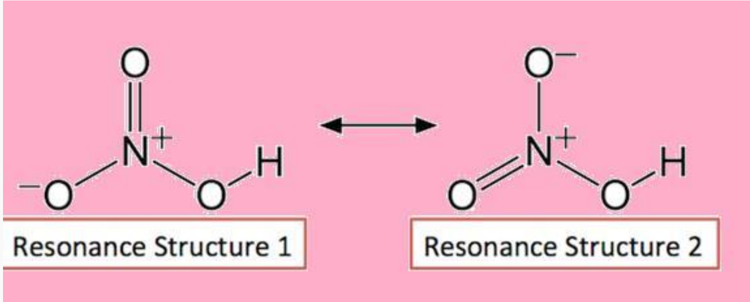
Nitrous acid: Nitrous acid oxidizes H_2S to S ,KI to I_2 and act as an oxidizing agent. In the presence of strong oxidizing agent it also acts as reducing agent like it reduces potassium dichromate etc to form complex.
It structure is:



Nitrous acid

Nitric acid:

- It stains skin yellow due to formation of nitro compound xanthoprotein. It is also called as aqua Fortis meaning strong water because it attacks almost all metals.
- It also forms a constant boiling mixture with water which has 68% of acid.
- Concentrated nitric acid attains a yellow color on standing. This is due to the presence of nitrogen dioxide which is formed due to decomposition of nitric acid in sunlight. This yellow color may be removed by warming it or bubbling air through it.
- Fuming nitric acid contains nitrogen dioxide in concentrated nitric acid. It is obtained by distilling concentrated nitric acid with little amount of starch.
- It structure is:



Nitric acid

Hypo nitrous acid:

- It is a weak dibasic acid
- Its structure is:

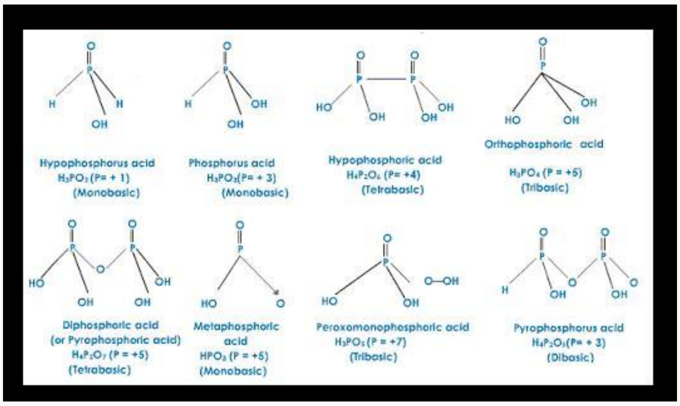
Hypo nitrous acid

Oxy-acids of phosphorous: Its oxy acids are:

- Hypo phosphorous acid (H_3PO_2)
- Phosphorous acid (H_3PO_3)
- Orthophosphoric acid (H_3PO_4)
- Metaphosphoric acid (HPO_3)
- Hypo phosphoric acid ($H_4P_2O_6$)
- Pyro phosphoric acid ($H_4P_2O_7$)

- Pyro phosphorus acid ($H_4P_2O_5$)
- Isohyphosphoric acid ($H_4P_2O_6$)

Their structures are given below:



Hypo phosphoric acid

- It is also called as phosphinic acid.
- It is powerful reducing agent because of the presence of two P-H bonds.
- The oxidation state of P is +1(monobasic).

Phosphorous acid

- It is also called as phosphonic acid.
- It is dibasic acid.
- In it the oxidation state of P is +3.
- It is strong reducing agent but weaker than hypo phosphorous acid due to only one P-H bond.
- It undergoes disproportionate reaction giving orthophosphoric acid and phosphine.

Orthophosphoric acid

- It is a weak tri basic acid.
- In it the P is in +5 oxidation state.
- It has no oxidizing or reducing properties.
- On heating it gives pyro phosphoric acid at 525K and meta phosphoric at 875K.

H_3PO_4à$H_4P_2O_7$ àHPO_3
(At 525K) (At 875K)

Metaphosphoric acid

- It is also called as glacial phosphoric acid.
- It is monobasic having P in +5 oxidation state.
- It has no reducing property.
- It exists as polymer and thus contains P-O-P bonds which can further form calgon.

Hypo phosphoric acid

- It is tetra basic in nature.
- Due to absence of P-H bond it has no reducing properties.
- In the P is in +4 oxidation state.

Pyro phosphoric acid

- It is also called as di phosphoric acid.
- In it the oxidation state is +5.
- It is also tetra basic.
- It has no reducing property.

Pyrophosphorous acid

- It is also called as di phosphorous acid.
- In it the oxidation state of P is +3.
- It contains P-O-P bond and is dibasic.
- It is strong reducing agent due to presence of P-H bonds.

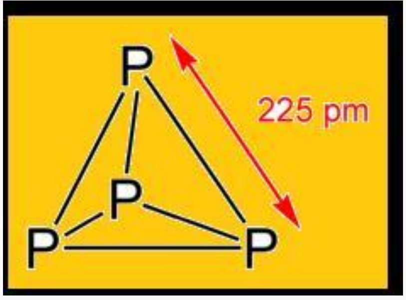
Isohyphosphoric acid

- It contains one P-O-P bond and one P-H bond.
- It is also called as diphosphoric acid.

- It is tri basic in nature in it the oxidation state of P is +3 which are attached to hydrogen and rests have +5 oxidation state.
- It has reducing properties also.

Phosphorous

It exists as P_4 with tetrahedral geometry as shown below:



Phosphorous

It has three forms:

- White P
- Black P
- Red P

White phosphorous

- It has a normal tetrahedral structure. They are soft waxy solids.
- They can be cut with knife.
- They are poisonous.
- They are chemiluminescent.
- It is most reactive form of phosphorous.
- It undergoes disproportionate reaction as shown :
- P_4 + NaOH ---> PH_3 + NaH_2PO_2
- Phosphorous Sodiumhydroxide Phosphine Sodiumhypo Phosphite
- In this oxidation sate of phosphorous changer from 0 to +1 and -3.

Black phosphorous

It exists in two forms:

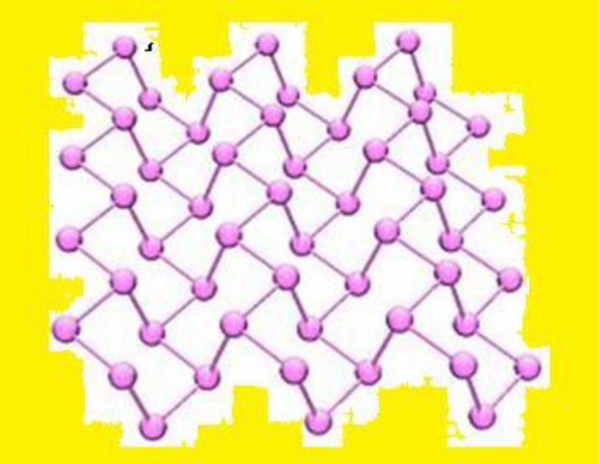
Alpha phosphorous

Beta phosphorous

Alpha phosphorous: is formed by heating red phosphorous at 803 K

Beta phosphorous: is formed by heating white phosphorous at 473K

It has most stable due to three dimensional structure as shown:

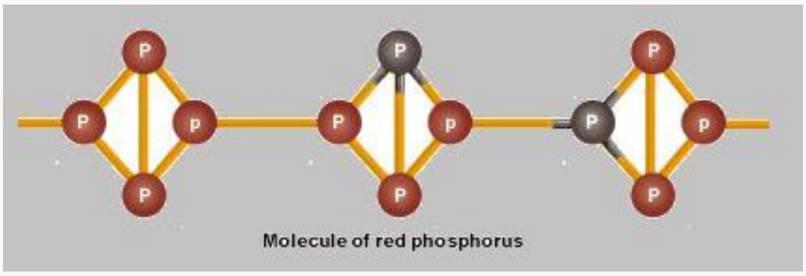


Alpha phosphorous

Red phosphorous

- It is obtained by heating white phosphorous at 573 K in inert atmosphere.

- It has polymeric structure as shown:



Red phosphorous

- It is crystalline solid.
- It shines grey.

It is non poisonous. **Phosphine**

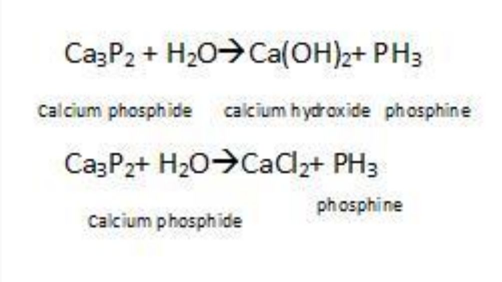
Its molecular formula is PH_3

Its structure is:

Phosphine

Preparation

It is prepared by dropping water on calcium phosphide.



$Ca_3P_2 + H_2O \rightarrow Ca(OH)_2 + PH_3$

Calcium phosphide calcium hydroxide phosphine

$Ca_3P_2 + H_2O \rightarrow CaCl_2 + PH_3$

Calcium phosphide phosphine

Lab preparation: By disproportionate reaction

$$\underset{\text{phosphorous}}{P_4}+\underset{\text{sodium hydroxide}}{NaOH}\rightarrow\underset{\text{phosphine}}{PH_3}+\underset{\text{sodium hypo phosphite}}{NaH_2PO_2}$$

This phosphine produced can be purified by reacting it with HI to get PH_4I and then this PH_4I react with KOH to form pure PH_3 ,KI and water.

Physical properties:

- It is colorless gas with smell of rotten fish.
- It is poisonous.
- It is slightly soluble in water.
- The solution of phosphine is unstable and decomposes in presence of light.

Chemical properties

1. It is weakly basic due to lone pair of electrons.
2. It undergoes precipitation reaction that is:

$$\underset{\text{Copper sulphate}}{CuSO_4}+PH_3\rightarrow\underset{\substack{\text{copper phosphide}\\\text{(Black ppt.)}}}{Cu_3P_2}+H_2SO_4$$

$$\underset{\text{silver nitrate}}{AgNO_3}+PH_3\rightarrow\underset{\substack{\text{silver phosphide}\\\text{(Black ppt.)}}}{Ag_3P}+HNO_3$$

Uses of phosphine:

(a) Combustion of $PH_3$is used in Holmes's signals for ships.

(b)It is also used as smoke screens in warfare.

-
- It is more stable.
- It is also chemiluminescent.
- Stability of different forms of phosphorous:

White P< red P <black P

Introduction of group 16

The members of this family are:

- Oxygen (O)
- Sulphur (S)
- Selenium (Se)
- Tellurium(Te)
- Polonium (Po)

Physical properties of group 16

1. **The electronic configuration for them are : $ns^2\ np^4$**

- Oxygen (O) $[He]2s^2,2p^4$
- Sulphur (S) $[Ne]3s^2,3p^4$
- Selenium (Se) $[Ar]3d^{10}4s^24p^4$
- Tellurium(Te) $[Kr]4d^{10,}5s^2,5p^4$
- Polonium (Po) $[Xe]4f^{14},5d^{10},6s^2,6p^4$

2. **Atomic size**: It increases down the group as every time a new shell is added as we move down. If we compare size of group 16 elements with group 15 then we see that group 16 is smaller due to increased nuclear charge.
3. **Ionization energy**: If we compare ionization energy of group 16 and group 15 we see, that group 16 has lower energy than group 15 because of half filled stable electronic configuration of group 15 i.e. ns^2np^3.

As we move down the group, the ionization energy decreases because the size increases down the group.

4. **Electro negativity**: The group 16 elements are more electro negative than group 15 because of small size of group 16 elements. This group has second highest electro negativity in whole periodic table.

- Oxygen is second most electronegative in periodic table.
- Down the group electro negativity decreases as size increases.

5. **Oxidation states:** They generally show -2 oxidation state.

- For oxygen: Common oxidation state is -2 but oxygen also show +2 oxidation state like in case of OF_2 and in O_2F_2 the oxidation state is +1. The oxidation state of oxygen is in +ve because oxygen is less electronegative than fluorine.
- For sulphur: The oxidation state shown is +2, +4, +6 (because of vacant d orbital). Like in SO_2 the oxidation state of sulphur is +4 and in sulphuric acid the oxidation state is +6 and in H_2S it is -2.
- Down the group the vacant d orbital are present therefore they all can show +2, +4, +6 oxidation states.

Anomalous behavior of oxygen:

- It has smallest size in its family.
- It has highest ionization energy.
- No vacant d orbital is present in it.
- It is highly electronegative in its family.

5. **Electron gain enthalpy**

Along period it is more negative because of attraction towards electron because of increased nuclear charge.

Down the group electron gain enthalpy keeps on becoming less negative because nuclear charge decreases and size increases.

The trend that was expected

- O>S>Se>Te (wrong trend)
- O<S>Se>Te (right trend)
- Please note that oxygen has less electron gain enthalpy than sulphur because due to small size of oxygen the incoming electron suffers repulsion therefore electron gain enthalpy is less negative as compared to sulphur.

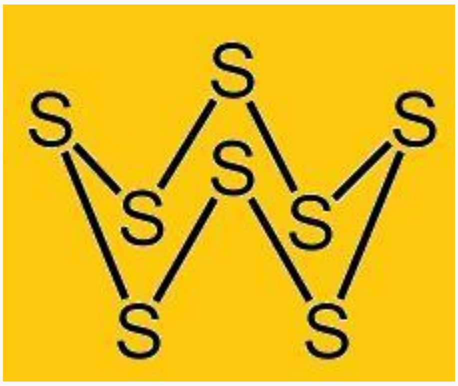
This whole group is called chalcogens as they are ore forming.

For example:

- Al –bauxite ore
- Pb-galena
- Hg-cinnabar ore
- Zn-zinc blende and many more.

Elemental state of oxygen and sulphur

Oxygen exists as diatomic gas, whereas sulphur exists as S_8 in solid form in a puckered ring like structure as shown below:



Sulphur (crown-like structure)

- In case of oxygen pπ-pπ bonding takes place but in sulphur no such bonding takes place .That is the reason oxygen exist as gas and sulphur exist as solid.

Chemical properties of group 16

Trends in chemical reactions:

- The order of reactivity of group 16 elements is:
  O>S>Se>Te

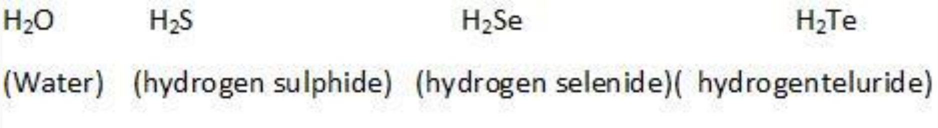
That is oxygen is quite reactive and as we move down reactivity decreases.

- Oxygen in this group is quite reactive as the bond between oxygen atoms is quite strong and the energy required to break it is 493.3kJ/mol.
- Almost all the reactions of oxygen are exothermic, therefore, the reactions are called combustion reaction.

The most stable compounds of this group are: **selenides and tellurides.**

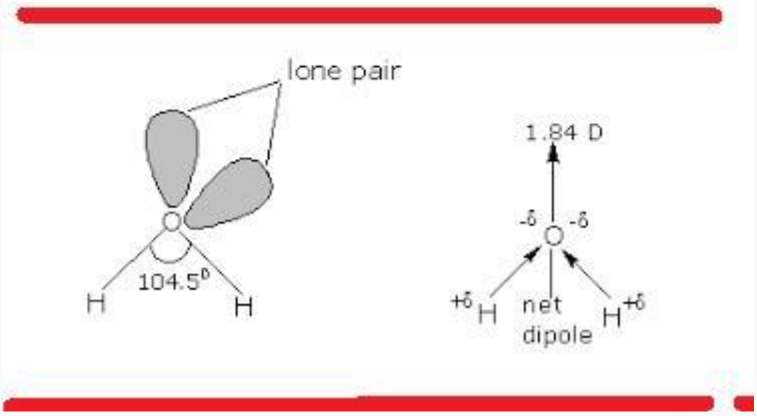
1. **Reaction with hydrogen**: When group 16 elements combine with hydrogen they form hydrides with general formula H_2

The hydrides formed are:



H_2O	H_2S	H_2Se	H_2Te
(Water)	(hydrogen sulphide)	(hydrogen selenide)(	hydrogenteluride)

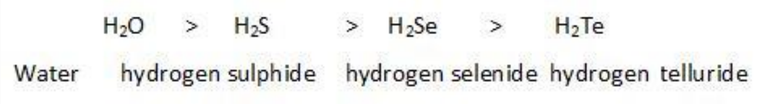
All of them have bent geometry with sp^3 hybridization. The geometry shown by them is:



Structure of water

The properties of hydrides are:

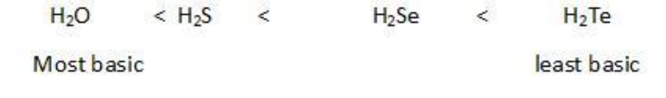
- **Bond angle**: The bond angle decreases down the group. The order of decrease of angle is:



H_2O >	H_2S >	H_2Se >	H_2Te
Water	hydrogen sulphide	hydrogen selenide	hydrogen telluride

The reason behind this is that when size of central atom increases, lone pair will push closer to bond pair-bond pair. Due to this bond angle decreases.

- **Basic character**: It refers to ability of molecule to donate its lone pair. The order of increase in basic character is:



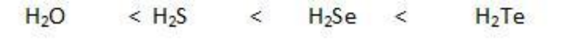
H_2O	< H_2S <	H_2Se <	H_2Te
Most basic			least basic

- **Stability**: The stability of hydrides depends upon the comparability of size. The order of stability of hydrides is:

Due to increase in size, bond length increase due to which bond dissociation energy decrease therefore stability decrease.

- **Reducing nature**: The order of reducing character of hydrides are:

Out of them in case of H_2Te the bond strength is low therefore reducing character is lowest.



$H_2O < H_2S < H_2Se < H_2Te$

- **Boiling point**: The boiling point depends upon Vander wall force and this Vander wall force increases with increase in size.

The order of their boiling points for 15 group hydrides is:

$H_2O > H_2S < H_2Se < H_2Te$

In case of H_2O and H_2S, water has higher boiling point than hydrogen sulphide because of hydrogen bonding.

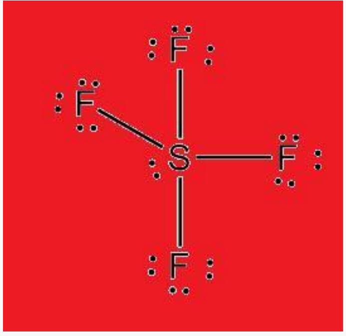
2. **Reaction with halogen**: They react with halogen to form halides of formula EX_4, EX_6 and EX_2.

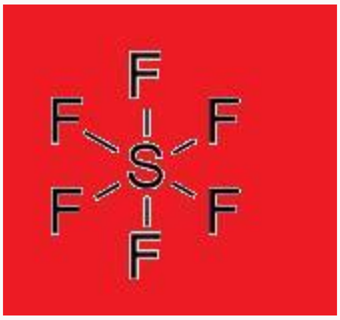
The order of stability oh halides are:

F>Cl>Br>I

The group 16 elements react with iodine to form tetra iodides.

- Oxygen only forms halides OF_2 and O_2F Out of them oxy difluoride is most stable halide.
- Sulphur forms SCl_2 (sulphur dichloride), SF_6 (sulphur hexafluoride) and SF_4 (sulphur tetra fluoride).
- The geometry of SF_4 is tetrahedral with hybridization sp^3d and geometry of SF_6 is trigonal bipyramidal with hybridization sp^3d^2 as shown:





Sulphur tetrafluoride Sulphur hexafluoride

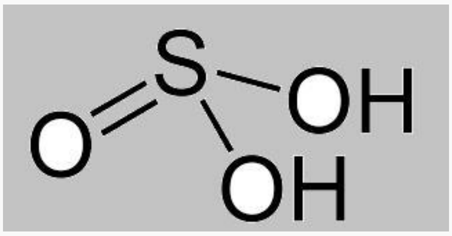
Hexa halides are only formed by fluorine because as size increases, coordination number decreases, therefore others they will not form halides .

- Out of all halides sulphur hexahalide is most non reactive halide in this group because it has excess octet .So, no vacant d orbital is present moreover it is protected from all sides by fluorine .

3. OxO acids of sulphur

Some important oxo acids of sulphur are:

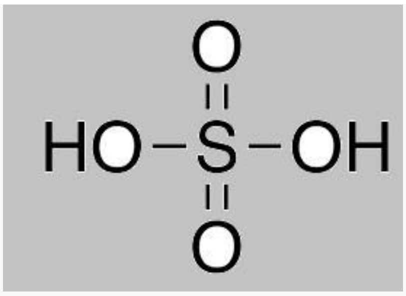
- **Sulphurous acid**: it is reducing in nature.
- It acts as oxidizing and reducing action.
- It bleaches the articles due to reduction.
- Its structure is given :



Sulphurous acid

(b)Sulphuric acid:

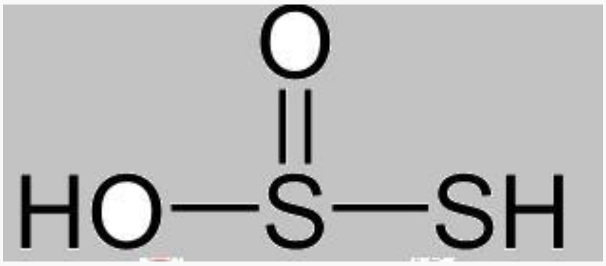
- It is called king of chemicals.
- It is used as an acid, oxidizing agent, dehydrating agent etc.
- It is highly viscous due to hydrogen bonding.
- It is also called as brown oil of vitrol.
- It is further concentrated and form rectified oil.
- It is prepared by contact process.
- Its structure is given below:



Sulphuric acid

(c)Thiosulphurous acid

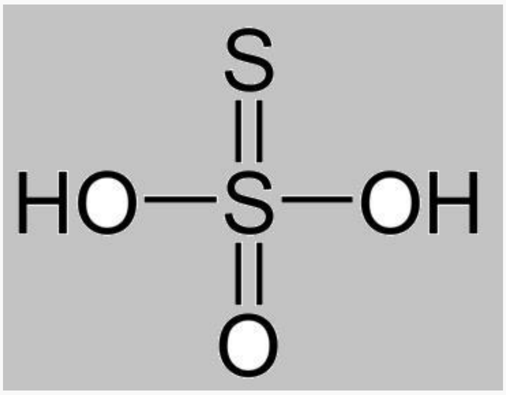
- It contains double bond between S atoms.
- Its structure is given below:



Thiosulphurous acid

(d)Thiosulphuric acid:

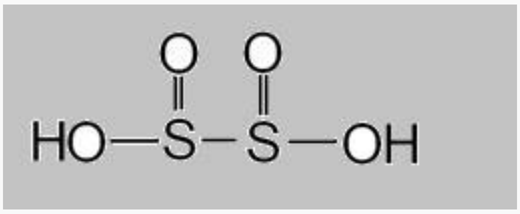
- It contains one double bond S linkage between S atoms.
- Its structure is given below:



Thiosulphuric acid

(e)Dithionous acid

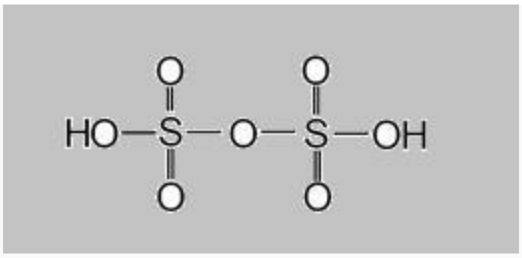
- It contains one S-S bond.
- Its structure is given:



Dithionous acid

(f)Pyrosulphuric acid

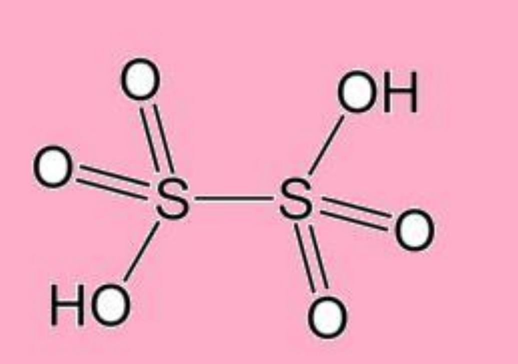
- It is known as oleum.
- It contains one S-S linkage.
- Sulphur dissolves in oleum to give clear brightly colored solution which contains polyatomic sulphur cations of general formula S_4^{2-}.
- The color of solution depends upon the time of reaction and strength of oleum.
- The bright yellow color solution has $S^{2-}{}_4$ ions, deep blue solution S_8^{2+} and bright red solution has totally unexpected $S^{2+}{}_{19}$
- Its structure is given below:



Pyrosulphuric acid

(g)Dithionic acid:

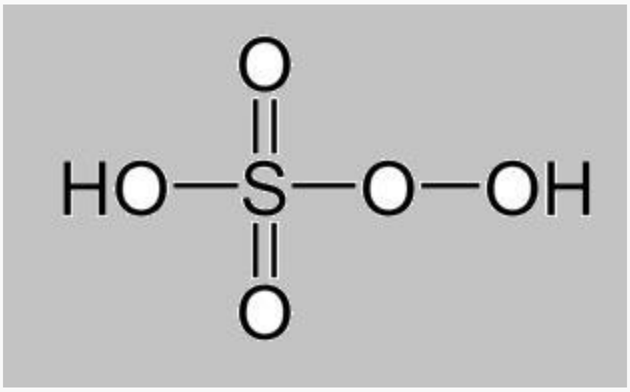
- It contains one S-S bond.
- Its structure is given below:



Dithionic acid

(h)Peroxymonosulphuric acid:

- It contains one peroxo group, it is also known as Caro's acid.
- It contains one peroxo group.
- In it the oxidation state of S is +6.
- Its structure is given below.



Peroxymonosulphuric acid

Di oxygen

Oxygen is 21% by volume of air.

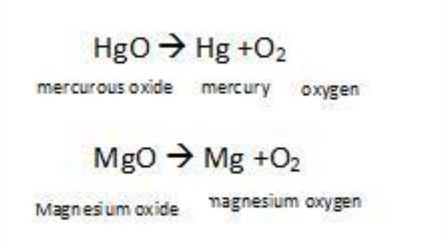
It is prepared by Karl Wilhelm Scheele and the other reactions were done by Priestly.

Isotopes of oxygen: O^{16}, O^{17}, O^{18}

Preparation of dioxygen

General method of preparation:

We get oxygen whenever we heat any metal oxide like:



$HgO \rightarrow Hg + O_2$

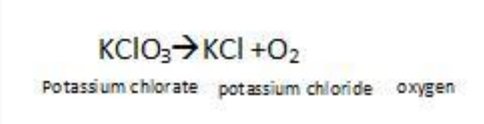
mercurous oxide mercury oxygen

$MgO \rightarrow Mg + O_2$

Magnesium oxide nagnesium oxygen

In laboratory we prepare oxygen by:

By heating potassium chlorate



$KClO_3 \rightarrow KCl + O_2$

Potassium chlorate potassium chloride oxygen

This reaction occurs on heating, in presence of MnO_2 at 420k.

Industrial preparation: By electrolysis of water.

The silent electric discharge is passed so that the reaction do not becomes reversible.

$H_2 + O_2$ ---> H_2O

Properties of di oxygen

- It is colorless, odorless and tasteless gas.
- It is soluble in water.
- It is highly inflammable.
- Chemical properties.
- It is neutral to litmus solution.
- It is supporter of combustion.
- It oxidizes food and produce energy.
- Reaction with metals :
- $Mg + O_2$ ---> MgO
- Magnesium Oxide
- Al + O2 ---> Al_2O_3
- Aluminium Oxide

It also reacts with some compounds:

$SO_2 + O_2$ ---> SO_3

$NH_3 + O_2$ ---> $NO + H_2O$

Uses of di oxygen

- It is supporter of life.
- It is used in oxy acetylene flame.
- Liquid oxygen is used as rocket fuel.
- The radioactive isotope of it is used as tracer for many chemical reactions.
- It is used to prepare synthesis gas.

Classification of oxides

We have different types of oxides

- Normal oxides
- Poly oxides

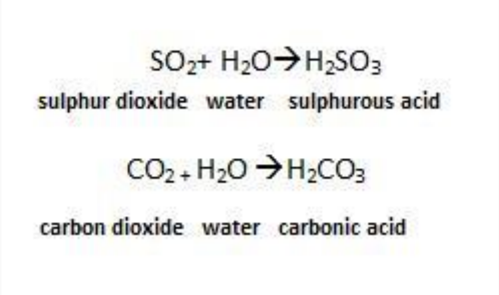
The poly oxides are of further different types:

- Peroxides: In this the O_2^{2-} ion is present like H_2O_2
- Super oxides: In this the O_2^- ion is present like KO_2
- Sub oxides: In this oxygen has valence less than -2 like N_2
- Mixed oxides: In this oxygen has oxidation number in fraction like Fe_3O_4

On the basis of nature they are classified as:

- Acidic
- Basic
- Neutral

1. **Acidic oxides**: That dissolve in water to give acids:



$SO_2 + H_2O \rightarrow H_2SO_3$

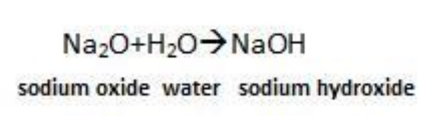
sulphur dioxide water sulphurous acid

$CO_2 + H_2O \rightarrow H_2CO_3$

carbon dioxide water carbonic acid

All non metallic are acidic in nature.

2. **Basic oxides**: That dissolves in water to give bases.

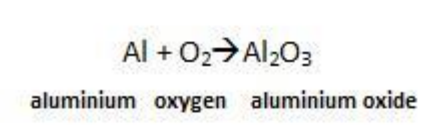


$Na_2O + H_2O \rightarrow NaOH$

sodium oxide water sodium hydroxide

The metal oxides are basic in nature.

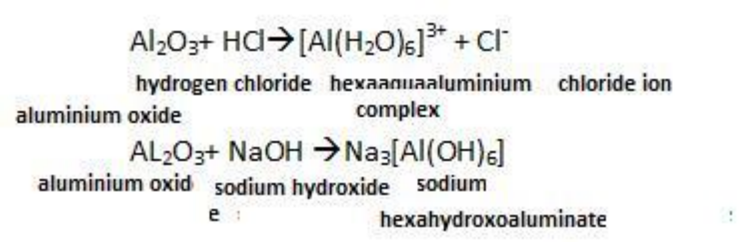
3. **Amphoteric oxides**: Metalloids give amphoteric oxides.



$Al + O_2 \rightarrow Al_2O_3$

aluminium oxygen aluminium oxide

It behave as acid as well as base.



$Al_2O_3 + HCl \rightarrow [Al(H_2O)_6]^{3+} + Cl^-$

aluminium oxide hydrogen chloride hexaaquaaluminium complex chloride ion

$AL_2O_3 + NaOH \rightarrow Na_3[Al(OH)_6]$

aluminium oxide sodium hydroxide sodium hexahydroxoaluminate

4. **Neutral oxides**

They are very less in number. They are neither acidic nor basic

Example: laughing gas.

Ozone

It is represented as O_3. It is found in upper atmosphere.

Preparation:

- It is prepared when ultraviolet rays. They react with oxygen of upper atmosphere and splits oxygen molecule in oxygen atoms. Then this oxygen atom combines with oxygen molecule to form ozone:
- $3O_2$ ---> $2O_3$
- Oxygen Ozone
- The reaction is endothermic approx. 142.7kJ of heat is needed.
- For preparing pure ozone we use ozoniser, in which the electric spark is passed through oxygen gas and we get ozone.

Properties of ozone

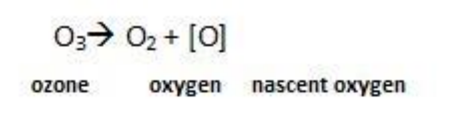
Physical properties

- It is blue gas with pungent odour.
- It is heavier than air.
- It is slightly soluble in water.
- It is diamagnetic.
- The depletion of ozone is harmful for us.

Chemical properties

1. Effect of heat: If we heat ozone t decompose to give oxygen molecule that is $2O_3$ ---> 3O
2. Oxidizing agent: It is stronger oxidizing agent than oxygen gas

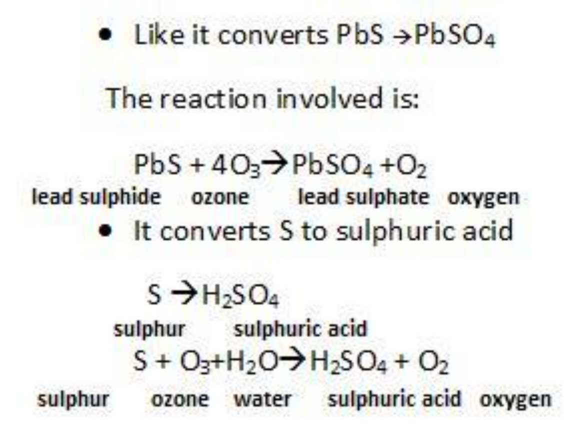
Because it decomposes to form:



$O_3 \rightarrow O_2 + [O]$

ozone oxygen nascent oxygen

So both the oxygen form oxidizes the other.



- Like it converts PbS →PbSO₄

The reaction involved is:

$PbS + 4O_3 \rightarrow PbSO_4 + O_2$
lead sulphide ozone lead sulphate oxygen

- It converts S to sulphuric acid

$S \rightarrow H_2SO_4$
sulphur sulphuric acid
$S + O_3 + H_2O \rightarrow H_2SO_4 + O_2$
sulphur ozone water sulphuric acid oxygen

ulphuric acid

Its molecular formula is H_2SO_4.

Preparation of sulphuric acid

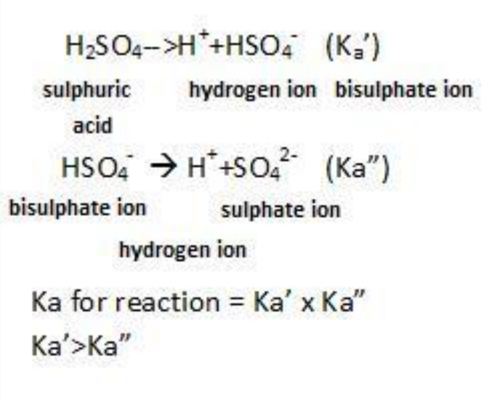
It is prepared from Contact's process that is:

1st step: Preparation of sulphur dioxide:
$S + O_2 \rightarrow SO_2$
Sulphur Oxygen Sulphur dioxide
2nd step: Preparation of sulphur trioxide:
$SO_2 + O_2 \rightarrow SO_3$
Sulphur dioxide Oxygen Sulphur trioxide
3rd step: Reaction of sulphur trioxide with concentrated Sulphuric acid:
$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$
Sulphur Trioxide Sulphuric Acid Olleum
4TH step: Diluting this oleum:
$H_2S_2O_7 + H_2O \rightarrow H_2SO_4$(dilute)
Olleum Water Sulphuric Acid
This sulphuric acid formed is 99% pure.

It is highly reactive due to:

- Low volatility
- Strong acidic character
- Strong affinity for water
- Its ability to act as oxidizing agent

1. **Dissociation**: Sulphuric acid is dibasic in nature



$H_2SO_4 \rightarrow H^+ + HSO_4^-$ (Ka')
sulphuric acid hydrogen ion bisulphate ion
$HSO_4^- \rightarrow H^+ + SO_4^{2-}$ (Ka")
bisulphate ion hydrogen ion sulphate ion

Ka for reaction = Ka' x Ka"
Ka'>Ka"

Because of formation of this bisulphate and sulphate ions it forms two types of salts bisulphate's and bisulphites that is $NaHSO_4$ and Na_2SO_4.

- Because of low volatility, it can be used for preparing volatile acids that is halogen acids.

$$\underset{\text{metal halide}}{MX} + \underset{\text{sulphuric acid}}{H_2SO_4} \rightarrow \underset{\text{metal sulphate}}{MSO_4} + \underset{\text{hydrogen halide}}{HX} \text{ (halogen acid more volatile).}$$

- It behaves as dehydrating agent, that is, if it falls on skin it causes burning sensation.

In a same way it can convert sugar solution to black mass.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{(conc. } H_2SO_4\text{)}} \text{black mass 12 C}$$

- It behaves as oxidizing agent.

$$\underset{\text{sulphuric acid}}{H_2SO_4} \rightarrow \underset{\text{sulphur dioxide}}{SO_2} + H_2O + \underset{\text{nascent oxygen}}{[O]}$$

It oxidizes many like Cu to Cu^{2+}.

$$\underset{\text{copper}}{Cu} + \underset{\text{sulphuric acid}}{H_2SO_4} \rightarrow \underset{\text{sulhur dioxide}}{SO_2} + \underset{\text{water}}{H_2O} + \underset{\text{copper sulphate}}{CuSO_4}$$

Uses of sulphuric acid

- It is used in making fertilizers.
- It is king of chemicals so have wide use in industries.
- It is dehydrating agent.
- It acts as an oxidizing agent.

Introduction

The members of group 17 are:

- Fluorine(F)
- Chlorine(Cl)
- Bromine(Br)
- Iodine (I)
- Astatine (At)

Physical properties of group 17

1. 1**. Electronic configuration**-The general electronic configuration for this group is ns^2np^5
- Fluorine (F) $[He]2s^2,2p^5$
- Chlorine (Cl) $[Ne]3s^2,3p^5$
- Bromine(Br)$[Ar]3d^{10}4s^24p^5$
- Iodine (I)$[Kr]4d^{10},5s^2,5p^4$
- Astatine (At) $[Xe]4f^{14},5d^{10},6s^2,6p^4$
2. **Atomic size**: It increases down the group as every time a new shell is added as we move down. If we compare size of group 17 elements with group 16 then we see that group 17 is smaller due to increased nuclear charge.
3. **Ionization energy**: If we compare ionization energy of group 17 and group 16 we see that group 17 has higher energy than group 16 because of smaller size of group 17 elements.

4. **Electron gain enthalpy:**
- Along period it is more negative because of attraction towards electron as of increased nuclear charge.
- Down the group electron gain enthalpy keeps on becoming less negative because nuclear charge decreases and size.
- So, the group 17 has highest electron gain enthalpy due to smallest size in periodic table.
- Please note that: Fluorine has less electron gain enthalpy than chlorine because due to small size of oxygen the incoming electron suffers repulsion therefore, electron gain enthalpy is less negative as compared to chlorine.
5. **Electro negativity**: Group 17 elements are more electro negative than group 16 because of small size of group 17 elements. This group has highest electro negativity in whole periodic table.

Fluorine is most electronegative in periodic table. Down the group electronegativity decreases as the size increases.

6. **Melting point and boiling points**: It increases down the group as size and mass increases the Vander wall force also increases therefore melting and boiling point increases.
7. 7**. Color**: All halogens are colored like:

Fluorine: Dull yellow in color.
Chlorine: Greenish yellow.
Bromine: Reddish brown.
Iodine: Violet.

8. **Oxidation states**: They show variable oxidation states like:

Fluorine: -1
Chlorine: -1, +1, +3, +7
Bromine : -1, +1, +3, +5, +7
Iodine: -1, +1, +3, +5, +7

- Higher oxidation states of halogens are used when they are combining with small size highly electronegative ions.
- All halogens are very reactive and reactivity decreases down the group.
- All act as Lewis acids as they accept electron.
- Fluorine is the strong oxidizing agent among all.

Anomalous behavior of Fluorine:

- Smallest size.
- Highest electronegativity.
- No vacant d orbital.

Low F-F bond dissociation energy.

Trends in chemical reactions

1. **Reaction with hydrogen**: They form their respective halogen acids of formula HX that is :

HF (Hydrogen Fluroide) HCl (Hydrogen Chloride) HBr(Hydrogen Bromide)
HI (Hydrogen Iodide)

The properties of halogen acids are:

(a) All have linear structure with bond angle 180 degree.

(b) Out of all only HF is liquid otherwise all are gases.

HF is liquid due to hydrogen bonding they occur as associated molecules.

(c) Stability: The stability of hydrides depends upon the comparability of size. The order of stability of hydrides is:

HF > HCl > HBr > HI

Due to increase in size, bond length increase due to which bond dissociation energy decrease therefore stability decrease.

(d) Reducing nature: The order of reducing character of hydrides is:

HF < HCl < HBr < HI

All are Arrhenius acids. The HI has weakest bond therefore release of H is much easier.

(e) Boiling point: The boiling point depends upon Vander wall force and this Vander wall force increases with increase in size.

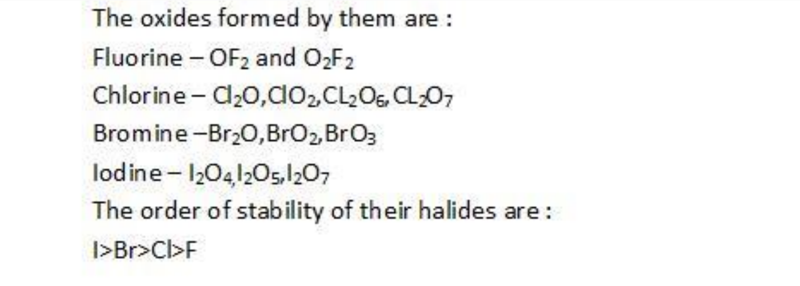
HF > HCl < HBr < HI

Due to hydrogen bonding HF has highest boiling point.

(f)Polarity: All halogen acids are polar in nature. Greater the size of anion more is the polarizibility more is the covalent character. Out of all, HF is highly polar.

2. **Reaction with oxygen**: They react with oxygen to form their respective oxides.

Due to less electro negativity difference the oxides are un-stable.



The oxides formed by them are :

Fluorine – OF_2 and O_2F_2

Chlorine – $Cl_2O, ClO_2, CL_2O_6, CL_2O_7$

Bromine –Br_2O, BrO_2, BrO_3

Iodine – I_2O_4, I_2O_5, I_2O_7

The order of stability of their halides are :

I>Br>Cl>F

The reason behind this trend is due to some thermodynamic reasons.

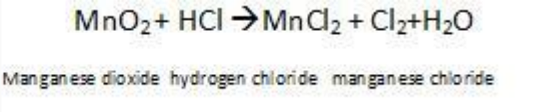
Chlorine gas (Cl_2)

It was discovered by Scheele .The name of chlorine was given by Davy.

Preparation

Lab. Preparation:

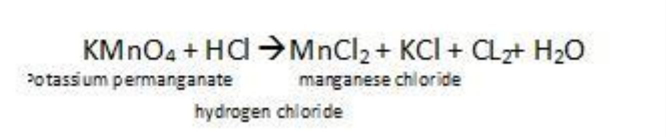
- By heating pyrolusite ore that is MnO_2 with HCl



$MnO_2 + HCl \rightarrow MnCl_2 + Cl_2 + H_2O$

Manganese dioxide hydrogen chloride manganese chloride

(b)By heating potassium permanganate with KCl:

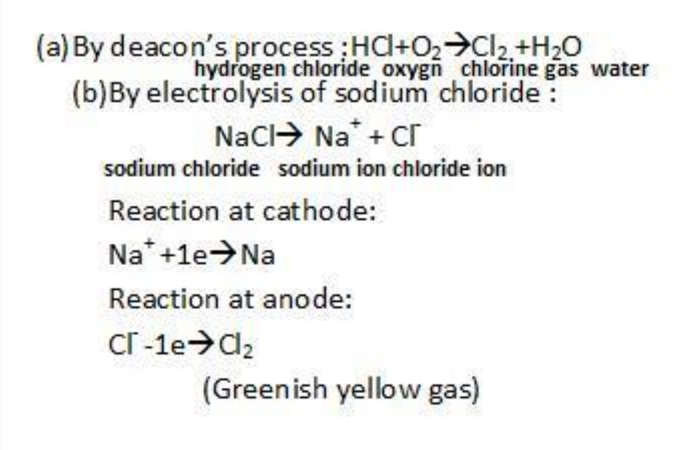


$KMnO_4 + HCl \rightarrow MnCl_2 + KCl + CL_2 + H_2O$

otassium permanganate manganese chloride

hydrogen chloride

Industrial preparation:



(a) By deacon's process : $HCl+O_2 \rightarrow Cl_2 + H_2O$

hydrogen chloride oxygn chlorine gas water

(b) By electrolysis of sodium chloride :

$NaCl \rightarrow Na^+ + Cl^-$

sodium chloride sodium ion chloride ion

Reaction at cathode:

$Na^+ + 1e \rightarrow Na$

Reaction at anode:

$Cl^- - 1e \rightarrow Cl_2$

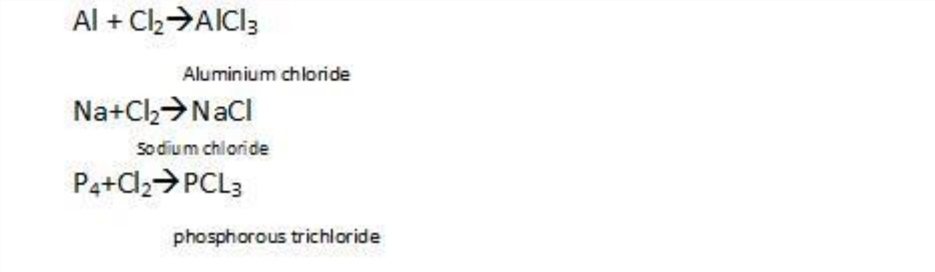
(Greenish yellow gas)

Physical properties of chlorine gas:

- It is greenish yellow gas.
- It has strong pungent suffocating odor.
- It is poisonous gas.
- It is soluble in water and the solution so formed is chlorine water.

Chemical properties of chlorine gas

1. **Effect on litmus:** Dry chlorine gas has no effect on litmus but the moist chlorine do have the effect, as it turns blue litmus red due to formation of HCl.
2. **Reaction with metals and non metals**: It reacts with metals and non metals to form respective chlorides that is given below:



$Al + Cl_2 \rightarrow AlCl_3$

Aluminium chloride

$Na+Cl_2 \rightarrow NaCl$

Sodium chloride

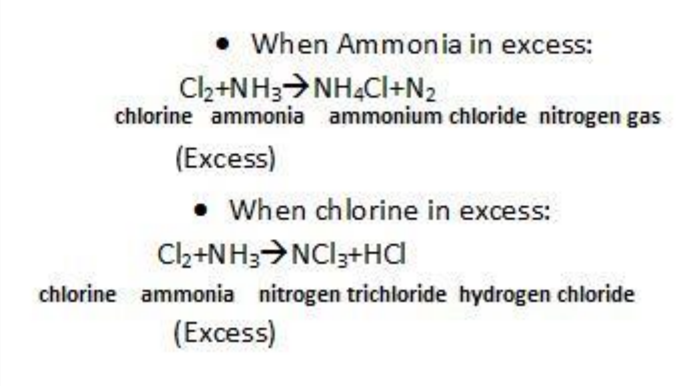
$P_4+Cl_2 \rightarrow PCL_3$

phosphorous trichloride

1. **It has great affinity for hydrogen to form HCl**

$H_2 + Cl_2$ ---> 2HCl

4. **Reaction with ammonia**



- When Ammonia in excess:

$Cl_2+NH_3 \rightarrow NH_4Cl+N_2$

chlorine ammonia ammonium chloride nitrogen gas

(Excess)

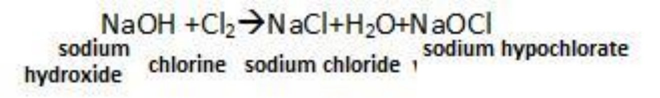
- When chlorine in excess:

$Cl_2+NH_3 \rightarrow NCl_3+HCl$

chlorine ammonia nitrogen trichloride hydrogen chloride

(Excess)

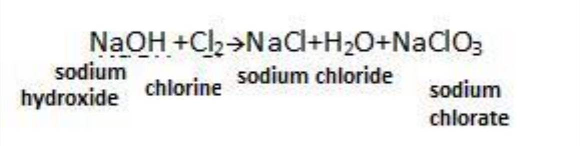
- **Reaction with alkalis**
- With dilute and cold sodium hydroxide



$NaOH + Cl_2 \rightarrow NaCl+H_2O+NaOCl$

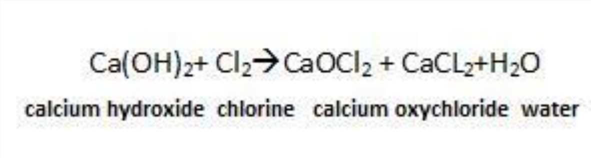
sodium hydroxide chlorine sodium chloride sodium hypochlorate

- With hot and concentrated NaOH:



$NaOH+Cl_2 \rightarrow NaCl+H_2O+NaClO_3$

With calcium hydroxide it forms bleaching powder:



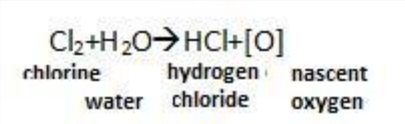
$Ca(OH)_2+Cl_2 \rightarrow CaOCl_2+CaCL_2+H_2O$

5. **Reaction with hydrocarbons: It occurs in presence of light.**

$CH_4+Cl_2 \rightarrow CCL_4+HCl$

6. **Bleaching action of chlorine gas**

It is due to nascent oxygen produced by moist chlorine:



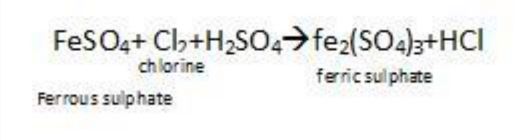
$Cl_2+H_2O \rightarrow HCl+[O]$

Colored matter + [O] --> colorless matter

7. **Chlorine act as oxidizing agent**: It is due to nascent oxygen.

For example:

- It oxidizes Fe^{2+} ---> Fe^{3+}



$FeSO_4+Cl_2+H_2SO_4 \rightarrow fe_2(SO_4)_3+HCl$

-

Uses of chlorine gas

- It is used for bleaching purpose.
- It is used in extraction of gold and silver.
- It is used in manufacture of dyes etc.
- It is used in preparation of poisonous gases like phosgene $CoCl_2$, tear gas CCl_3NO_2

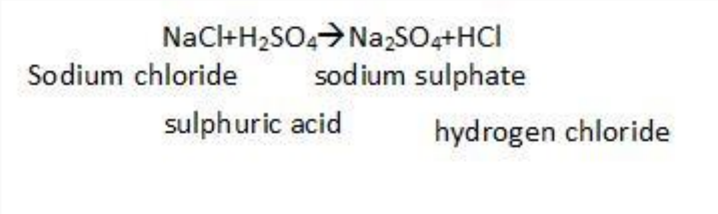
Hydrogen chloride

It was discovered by Glauber and the Davy was the one who said that it consist of H and Cl.

Preparation of hydrogen chloride

Preparation:

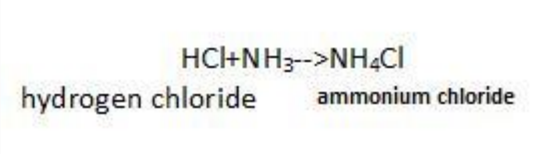
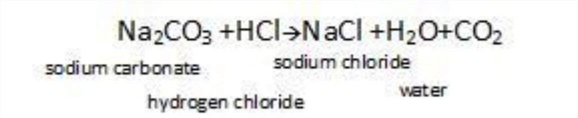
It is prepared by reacting sodium chloride with sulphuric acid and the following reaction occurs:



$NaCl+H_2SO_4 \rightarrow Na_2SO_4+HCl$

Properties of hydrogen chloride

- It is colorless gas with pungent smell.
- It can be easily liquefied.
- It freezes to white crystalline solid.
- It is highly soluble in water.
- It readily reacts with ammonia forming ammonium chloride:

- 
  $HCl+NH_3 \dashrightarrow NH_4Cl$
  hydrogen chloride ammonium chloride
- It forms aqua regia that is a mixture of HNO_3 with HCl in ratio of 1:3 that helps in dissolving noble metals.
- It can decompose salts of weaker acids:
- 
  $Na_2CO_3 + HCl \rightarrow NaCl + H_2O + CO_2$
  sodium carbonate hydrogen chloride sodium chloride water

Uses of hydrogen chloride

- It is used in manufacturing of chlorine gas, ammonium chloride, etc.
- It is used for extracting glue from bones.
- It is used in making medicines.
- It is used in making aqua regia.

Oxy acids of halogens

The oxy acids of halogens are:

Fluorine

- HFO(+1) Hypofluorous acid

Chlorine

- HClO (+1) Hypochlorous acid
- $HClO_2$ (+2) Chlorous acid
- $HClO_3$(+3) Chloric acid
- $HClO_4$(+4) Perchloric acid

Bromine

- HBrO(+1) Hypobromous acid
- $HBrO_3$(+3) Bromic acid
- $HBrO_4$(+4) Perbromic acid

Iodine

- HIO (+1) Hypoiodous acid
- HIO_3 (+3) Iodic acid
- HIO_4(+4) Periodic acid

Properties of oxy acids of halogens

Acidic strength :

- The acidic strength of these oxy acids having same oxidation number decreases with increase in size because the electro negativity decreases as we go down the group from chlorine to iodine.
- This is the reason that to withdraw electrons from oxygen atom towards itself decreases from chlorine to iodine.
- As a result the tendency to pull the electrons from hydrogen decreases and the release of hydrogen ion becomes difficult.
- The order of acidic strength is :

$HClO < HClO_2 < HClO_3 < HClO_4$

1. **Oxidizing power and thermal stability :**

- As the oxidation number increase the oxidation power decreases in order :

$HClO > HClO_2 > HClO_3 > HClO_4$

- This is because the halogen oxygen bond becomes more covalent. As a result the thermal stability increases. Thus the hypohalites are stronger oxidizing agents than perhalates.
- With increase in oxidation number of halogen the thermal stability of both the acids and salts increases thus the stability of oxy acids are in order:

$HClO < HClO_2 < HClO_3 < HClO_4$

- As the number of oxygen atoms increases in an ion, there is greater dispersal of negative charge therefore, greater is the stability of ion formed.

- The acidity of oxo- acids of different halogens which have same oxidation number decreases from chlorine to iodine. This is due to decrease in electro negativity with increase in size.

Inter-halogen compounds

The compound of on halogen with the other halogen is called inter halogen compounds.

They are formed due to large electro negativity and size difference between halogens.

Let's take an example: Let's assume two halogens A and B.

B is more electronegative than A then they will form four types of compounds:

- AB example: ClF (Chlorine monofluoride),BrF(Bromine monofluoride).
- AB_3 example: ClF_3 (Chlorine trifluoride), BrF_3 (Bromine trifluoride).
- AB_5 example: BrF_5 (Bromine pentafluoride).
- AB_7 example: IF_7 (iodine heptafluoride).

The inter-halogen compounds are unstable and very reactive.

Properties:

- The larger halogen always serves as a central atom.
- The bonds formed are covalent.
- As the size difference decreases stability decreases and the polarity increases.
- Hydrolysis of these compounds always produces halide ion from smaller halogen and oxy halide from bigger halogen.
- They are strong oxidizing agents.

Structure of inter-halogen compounds:

1. AB type – linear
2. AB_3 type - trigonal bi pyramidal
3. AB_5 type - square pyramidal
4. AB_7 type - pentagonal bipyramidal
5. **Introduction**
6. This group has noble gases or inert gases
7. The members of this group are:
8. Helium (He)
9. Neon (Ne)
10. Argon (Ar)
11. Krypton (Kr)
12. Xenon (Xe)
13. Radon (Rn)

Physical properties of group 18

1. The electronic configuration for them are ns^2np^6

- Helium $1s\ ^2 2s^2$
- Neon $1s^2,2s^2,2p^6$
- Argon $1s^2,2s^2,2p^6,3s^2,3p^6$
- krypton$1s^2,2s^2,2p^6,3s^2,3p64s^2 3d^{10}4p6$
- xenon $1s^2,2s^2,2p^6,3s^2,3p64s^2 3d^{10}4p^6 4d^{10}5s^2 5p^6$
- radon $1s^2,2s^2,2p^6,3s^2,3p64s^2 3d^{10}4p^6 4d^{10}5s^2 5p^6 4f^{14}5d^{10}6s^2 6p^6$

2.Atomic size : : It increases down the group as every time a new shell is added as we move down. They actually have Vander wall radii.

3. **Ionization energy**: They have highest ionization energy due to complete octet.
4. 4. **Electron gain Enthalpy**: It is positive as they have complete octet so they have no attraction for incoming electron.
5. **Melting and boiling point**: It is low due to weak force that exists that is Vander wall force.

Down the group size increases therefore Vander wall force also increases so as melting and boiling point increase.

6. All noble gases are **odorless and colorless and tasteless.**
7. All noble gases are **sparingly soluble in water.**
8. All are inert gases as they have **complete octet.**
9. All of them **are monatomic.**

Chemical properties of group 18

- According to the stable electronic configuration fact they have no compounds but the scientist Neil Bart let found that oxygen and xenon are very much similar.

Like both have almost same masses. Atomic radius of both is same.

- So, like oxygen combines with platinum fluoride in the same way xenon also combines:

$$O_2 + PtF_6 \rightarrow {}^{+}O_2[PtF_6]$$

oxygen platinium hexafluoride dioxygenyl hexafluoroplatinate

$$Xe + PtF_6 \rightarrow Xe^{+}[PtF_6]$$

Xenon

Xenon hexafluoroplatinate

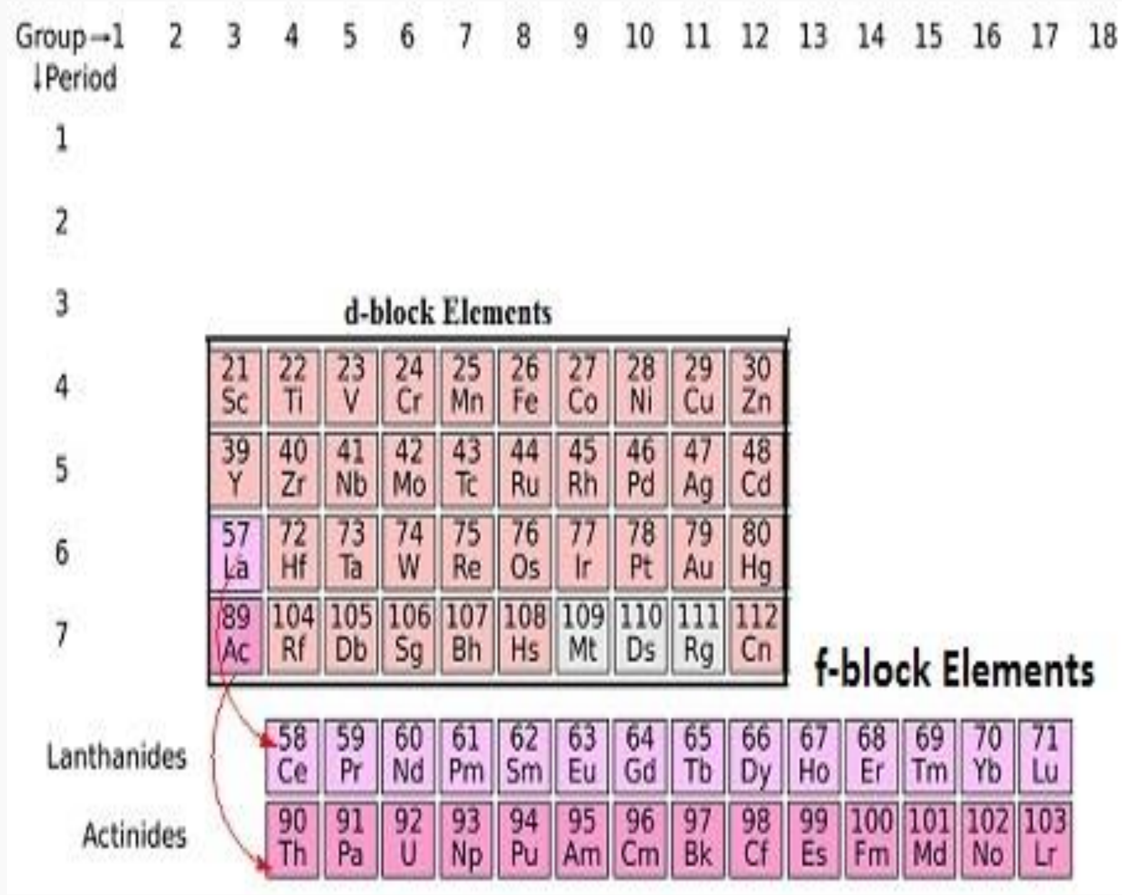
platinium hexafluoride

Uses of noble gases

- Helium is used in weather balloons.
- A mixture of helium and oxygen is used in cylinders by divers etc.
- Liquid helium is used maintain low temperature or we can say it is cryogenic liquid.
- Neon is used in sign board signals.
- Neon is used in filling up sodium vapor lamp.
- Neon is used in protecting electrical instruments like voltmeter.
- Argon is used in filling electric bulbs.
- Argon helps in providing inert atmosphere.
- Krypton is used in flash bulbs of high speed photography.
- Radon is used in treatment of cancer.
- Radon is used to treat metals.

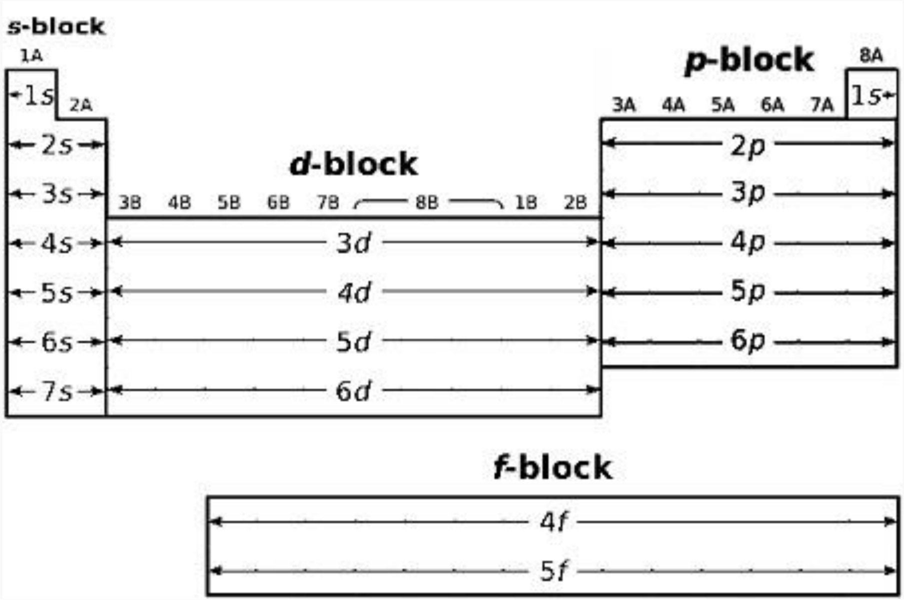
8.The d and f block elements

Introduction to d-block elements



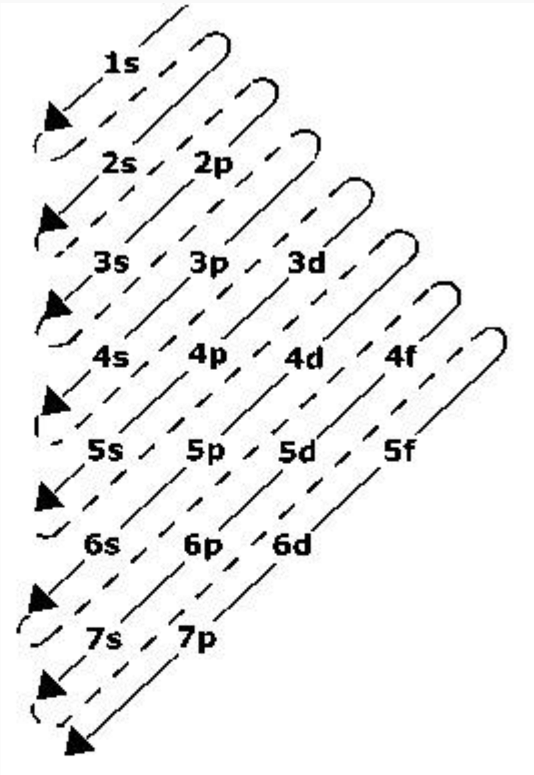
- In the periodic table the d block consist of the elements of group 3 to 12.
- The d orbital of the d-block elements in four periods are filled.
- The three series of the transitionmetals are 3d series from Sc to Zn, 4d series from Y to Cd and 5dseries from La to Hg.
- The fourth 6dseries begins from Ac and is incomplete till now.

Position of d-block in periodic table

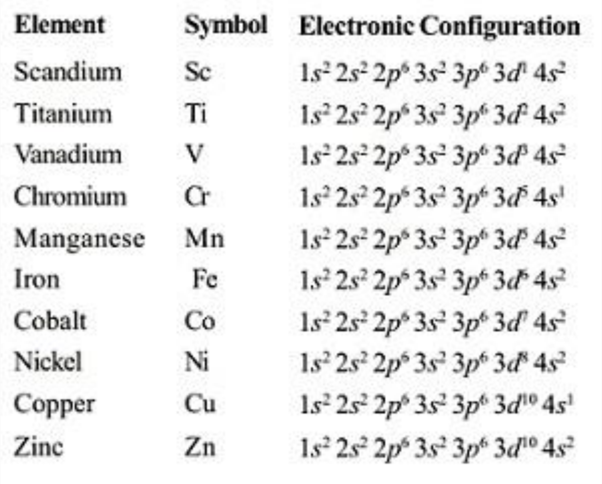


- The d-block elements are found in the middle section of s- and p- block elements in the periodic elements.
- This lead to its name ‘transition’ due to its position between s- and p- block elements.

Electronic Configurations of the d-Block Elements



- The electronic configuration of d-block elements is$(n-1)\ d^{1–10}\ ns^{1–2}$. They have two incomplete outershells.
- Where (n–1) = Inner d orbitals having electrons from 1-10.
- ns = Outermost orbital may have one or two
- $(n-1)\ d^{10}\ n\ s^2$ represents the electronic configurations of Zn, Cd and Hg.
- They exhibit variable valency that differ by units of one.



Element	Symbol	Electronic Configuration
Scandium	Sc	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$
Titanium	Ti	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
Vanadium	V	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$
Chromium	Cr	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
Manganese	Mn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
Iron	Fe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
Cobalt	Co	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ 4s^2$
Nickel	Ni	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
Copper	Cu	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
Zinc	Zn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$

Physical Properties

- The transition metals are hard and tough. They have low volatility butZn, Cd and Hg are an exception.

- They have high melting and boilingpoints due to the greaterquantity of electrons from (n-1) d along with the ns electrons metallic

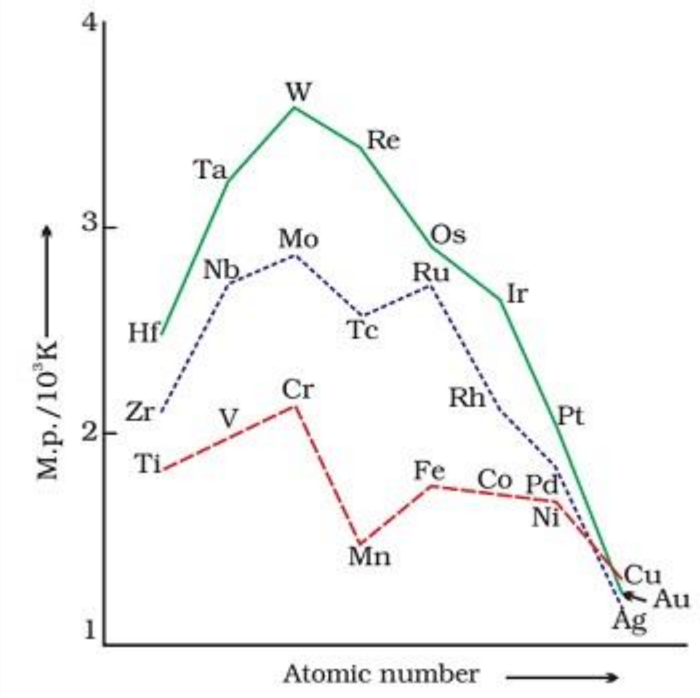


Fig. The trends in melting point of d-block elements.

- Metals possessing high boiling point are noble in their
- The metals belonging to second and third series have greater enthalpies ofatomisation than the elements belonging to first series.

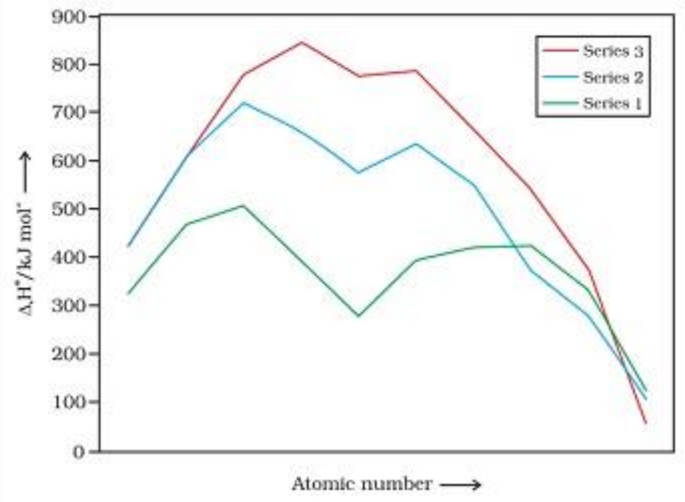


Fig. Enthalpies of atomisation

Metallic characteristics:

- All transition metals exhibit metallic character.

- They are good conductors of heat and electricity.

Fig. Metal is used at the tip of the plug that is inserted into the socket

- They are hard and tough.
- Being metal they exhibit the property of malleability, ductility and sonorousity.

Fig. Aluminium is beaten into thin sheets to make aluminium foil used to pack food (Malleability)

Fig. bells in temples are made of metal that when struck against hard surface produces sound (Sonorousity)

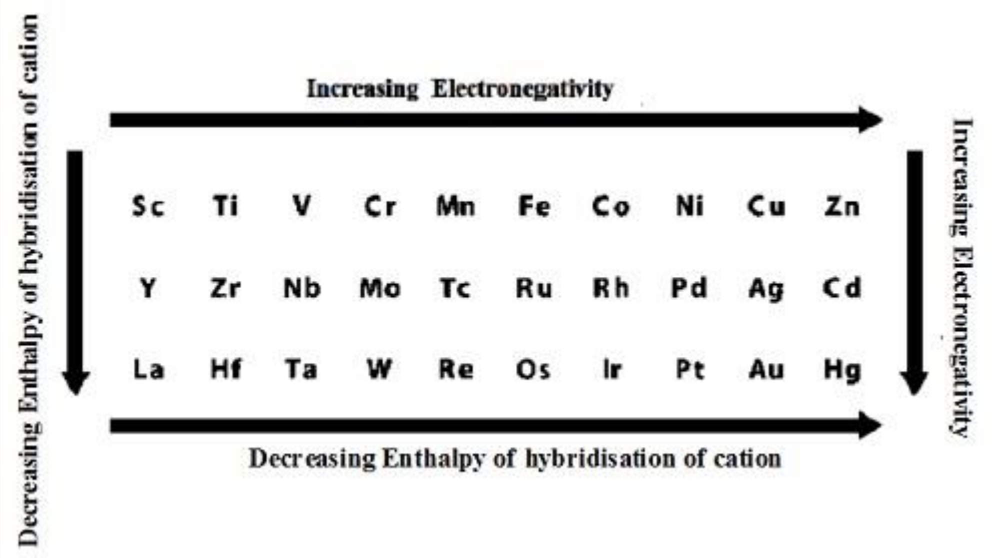
Fig. Metals are drawn into wires (Ductility)

- They form alloys by combining with some other metals.
- They are found to exist in face- centered cubic (fcc) structure, hexagonal close-packed (hcp) structure and body-centered cubic (bcc) structure.
- The transition elements exhibit covalent as well as metallic bonding within the atoms.

Atomic radii

- The atomic radii of the elements of 3d-series decreases as the atomic number increases.

- The atomic radii increase from 3d to 4d, the atomic radii of the 4d and 5d transition series are very close due to lanthanoid contraction. For example, Zirconium and Hafnium.
- This decrease in the metallic radius due to increase in the atomic mass leads to an increase in the density of elements. Consequently the density increases from titanium to copper.

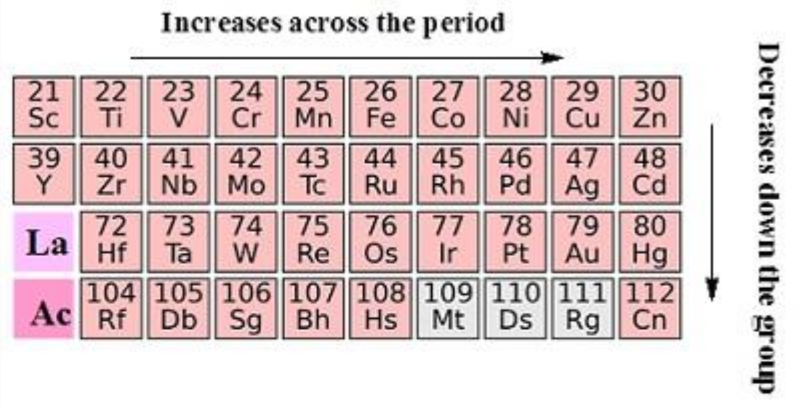


Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Ionisation Enthalpies

- Transition elements have small size which results in high ionization energy.
- They exhibit less electro positivity than the s-block elements due to their ionization potentials lying between S and P block elements.
- They form covalent compounds.
- The d-block elements exhibit an increase in the ionization potentials from left to right due to the screening effect of the new electrons added into the (n-1) d subshell.
- The first transition series exhibit an increase in the second ionisation energies with the increase in atomic number due to stable electronic configuration.

- Ionization energy decreases down the group.
- Ionization energy increases across the period.



21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

Oxidation States

- The number allotted to an element in a compound representing the number of electrons lost or gained by an atom of the element of the compound is called oxidation state.

For example, the electron configuration of copper is [Ar] $3d^{10}$ $4s^1$. It attains noble gas configuration by losing one electron. The energy required to lose one more electron is very less and hence copper loses 2 electrons and forms Cu^{2+} ion. Therefore copper exhibits +1 and +2 oxidation state. But +2 oxidation states are more common.

It forms compounds like $CuCl_2$ and also with oxygen like CuO. In both the cases the oxidation state of Cu is +2.

- Transition elements exhibit varying oxidation states due to the minor energy difference between ns and (n -1) d orbitals.
- Along with ns electrons, (n -1) d electrons takes part in bonding. But due to the availability of few electrons for bonding Scandium does not show variable oxidation states.
- Due to presence of more d electrons, zinc has less orbital available for bonding and hence does not exhibit varying oxidation state.
- Among d-block elements the elements belonging to 8th group exhibit maximum oxidation state.
- Among the elements of 3d –series Manganese belonging to 7th group exhibits maximum oxidation state.
- Among the elements of 4d-Series Ruthenium belonging to 8th group exhibits maximum oxidation state.
- Among the elements of 5d-Series Osmium belonging to 8th group exhibits maximum oxidation state.
- The oxidation number of a free element is always 0.
- Oxidation number of (group I) elements like Li, Na, K, Rb, Cs is +1.
- Oxidation number of (group II) elements like Be, Mg, Ca, Sr, Ba is +2.
- Oxidation number of oxygen is -2.
- For example, oxidation state of Phosphorous in the compound HPO_3^{2-} can be calculated by the following method:

Oxidation state of H = +1

Oxidation state of O = -2

Oxidation state of O_3 = 3(-2) [Since it has 3 atoms of oxygen.]

Overall oxidation state of the compound = -2

Let P represent the oxidation state of Phosphorous.

Therefore,

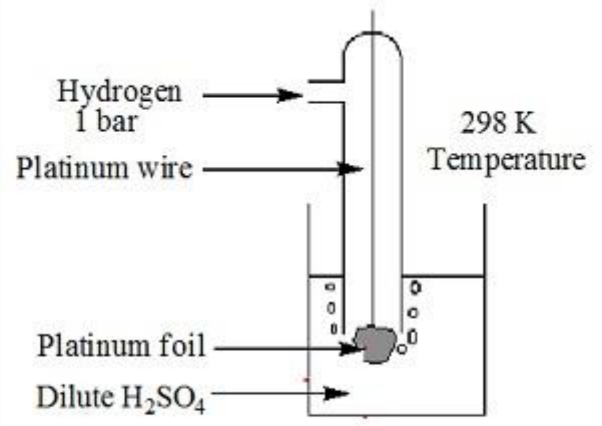
$HPO_3^{2-} = +1+P+3(-2) = -2$

- P = +3

Standard hydrogen electrode

- The electrode is connected to a **standard hydrogen electrode (SHE)** to constitute a cell
- It consists of a platinum electrodecoated with a layer of platinum black.

$$H^+\ (aq) + e^- \rightarrow \frac{1}{2} H_2(g)$$



- The electrode is immersed in an acidicsolution and the pure hydrogen gas is bubbled through it.
- Theconcentration of the reduced form and the oxidized form of hydrogen issustained at unity with following conditions:
- Pressure of hydrogen gas = 1 bar
- Concentration of hydrogen ion in the solution = 1 molar

$E_{cell} = E_{cathode} - E_{anode}$

$E_{cell} = E_{cathode} - 0 = E_{cathode}$

- The measured Emf of the cell:

Pt| H_2 (1 bar)| H^+ (1M) || Cu^{2+} (1M)| Cu is 0.34 V.

The positive value of the standard electrode potential signifies the easy reduction of Cu^{2+} ions than H^+ ions.

- The measured Emf of the cell

Pt| H_2 (1 bar)| H^+ (1M) || Zn^{2+} (1M)| Zn is -0.76 V.

The negative value of the standard electrode potential signifies that the hydrogen ions oxidizes the zinc (or it can be said that zinc can reduce hydrogen ions).

- An electrode with standard electrode potential greater than zero is stable in its reduced form compared tohydrogen gas.
- Whereas an electrode with negative standard electrode potential is less stable in its reduced form compared to hydrogen gas.
- This decreases the standard electrodepotential which in turn decreases the oxidizing power ofthe specific electrode on the left and increases the reducing power of the electrodeto the right of the reaction.

Magnetic Properties

Substances, depending on their behaviour in an external magnetic field, are classified into 2 types:

Paramagnetic

- They are weakly attracted on application of magnetic field due to presence of one or more unpaired electrons that gets attracted by the magnetic field.
- Application of a magnetic field magnetizes the paramagnetic substances in the same direction but lose their magnetism in the absence of magnetic field.
- O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} are some examples of such substances.

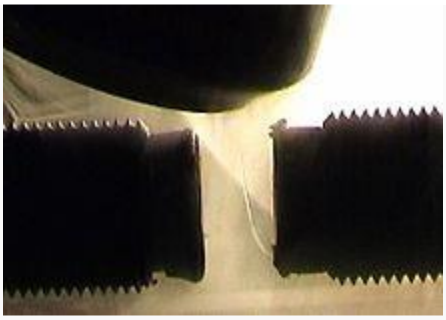
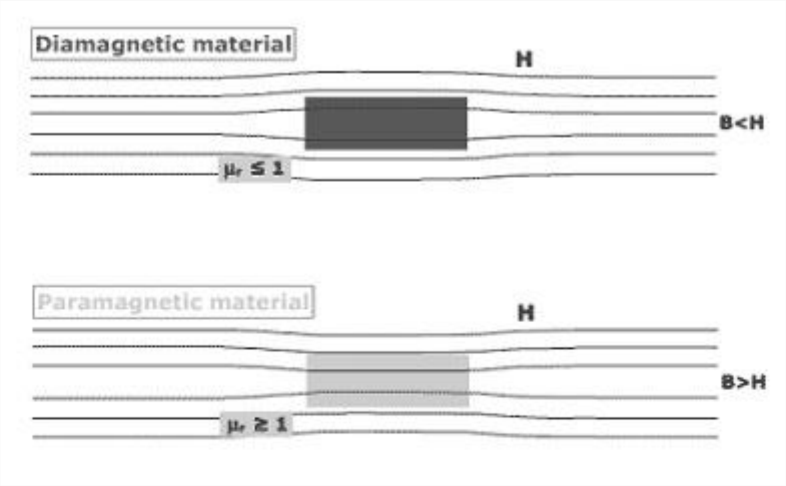


Fig. A trickle of liquid oxygen is deflected by a magnetic field, illustrating its paramagnetism.

Diamagnetic

- They are weakly repelled by a magnetic field due to the absence of unpaired electrons.
- They are weakly magnetized on application of magnetic field in opposite direction.
- Pairing of electrons cancels out their magnetic moments and they lose their magnetic character.
- For example, H_2O, NaCl and C_6H_6 are some examples of such substances.

In 3d series the orbital angular momentum of the electrons of the elements is less due to which they exhibit less contribution.



The magnetic moment for these elements is calculated using the spin only formula

μ = √(n(n+2))

Where n = number of unpaired electrons

μ = magnetic moment in units of Bohr Magneton (BM).

PROBLEM: Calculate the 'spin only' magnetic moment of M2+(aq) ion (Z = 27).

SOLUTION: Z = 27 = [Ar] $3d^7$ $4s^2$

M^{2+} = [Ar] $3d^7$

This means that it has 3 unpaired electrons.

n = 3

$$\Rightarrow \sqrt{n(n+2)} = \mu$$

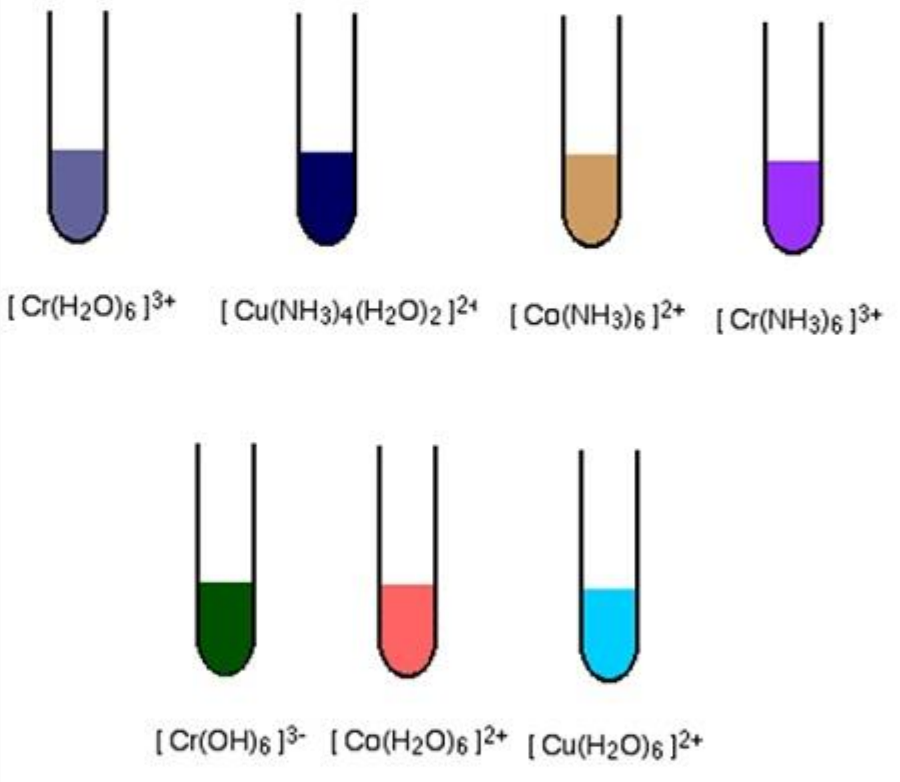
$$\Rightarrow \sqrt{3(3+2)} = \mu$$

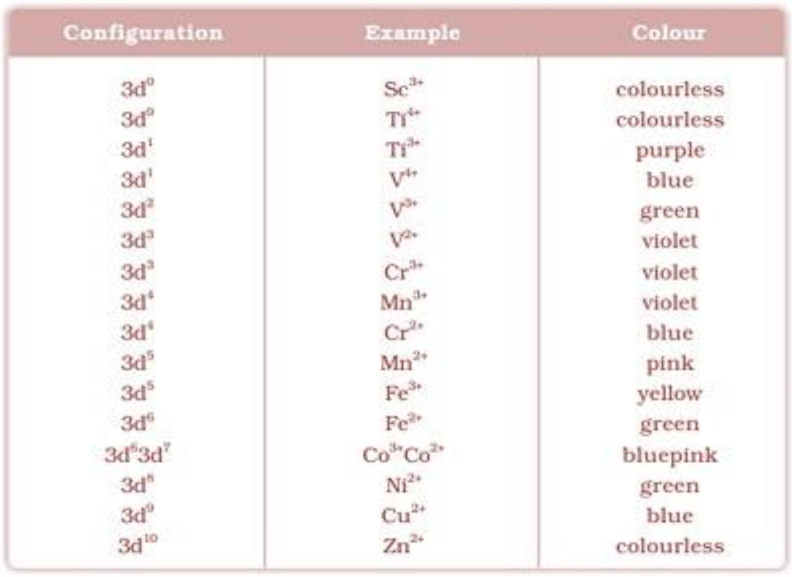
$$\Rightarrow \sqrt{15} = \mu$$

μ ≈ 4 BM

Formation of Coloured Ions

- An electron from a lower energy d orbital is excited to a higherenergy d orbital, the energy of excitation corresponds to the frequencyof light absorbed.
- This frequency generally lies in the visible
- The colour of the transition metal ions is due to the presence of unpaired or incomplete d-orbitals.
- The absorption of visible light and hence coloured nature of the transition metal cations is due to the promotion of one or more unpaired d-electron from a lower to a higher level within the same d-subshell. This promotion requires small amount of energy available in the visible light.
- Sc^{3+}, Ti^{4+}, Cu^{+} and Zn^{2+} have either entirely empty or entirely filled 3d-orbital, i.e. they do not have any unpaired d-electron, and hence appear colourless.

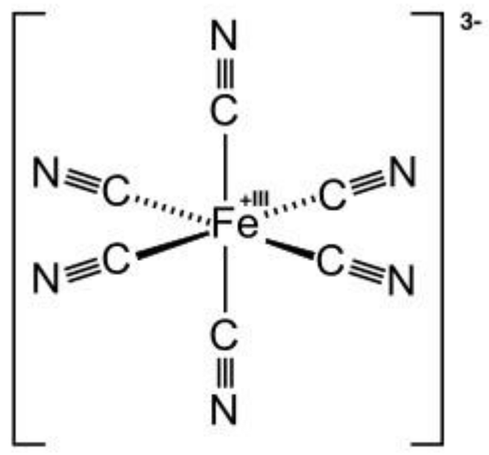




Configuration	Example	Colour
$3d^0$	Sc^{3+}	colourless
$3d^0$	Ti^{4+}	colourless
$3d^1$	Ti^{3+}	purple
$3d^1$	V^{4+}	blue
$3d^2$	V^{3+}	green
$3d^3$	V^{2+}	violet
$3d^3$	Cr^{3+}	violet
$3d^4$	Mn^{3+}	violet
$3d^4$	Cr^{2+}	blue
$3d^5$	Mn^{2+}	pink
$3d^5$	Fe^{3+}	yellow
$3d^6$	Fe^{2+}	green
$3d^6 3d^7$	$Co^{3+}Co^{2+}$	bluepink
$3d^8$	Ni^{2+}	green
$3d^9$	Cu^{2+}	blue
$3d^{10}$	Zn^{2+}	colourless

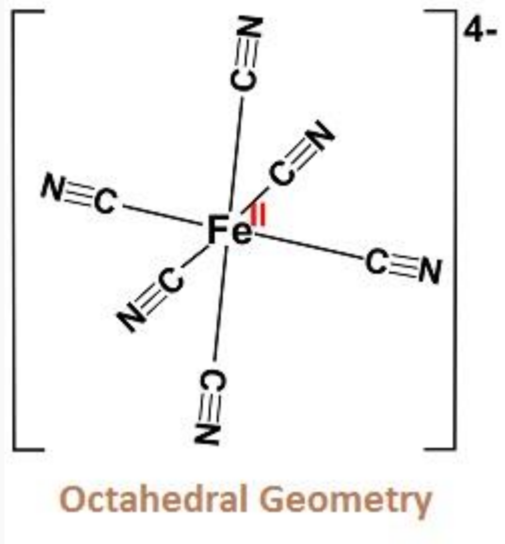
Formation of Complex Compounds

- The cations of transition metals have great tendency to form complexes with several molecules or ions called ligands.
- The bonds involved in the formation of complexes are coordinate and hence the complexes are called coordinate complexes.
- The structure of these complex ions is linear, square, planar, tetrahedral, octahedral depending upon nature of hybridization of metal ions.
- The weak ligand like CO, NO forms complexes only when transition metals are in zero due to the availability of vacant orbitals in the donor atom of the ligand in addition to lone pair.
- The highly electronegative and basic ligand like F-, Cl- can form complexes with transition metals even though there are in high oxidation states due to the presence of small, highly charged or neutral ligands with lone pair of electrons that can form strong sigma bond by donating a lone pair of electrons.
- In a transition series the stability of complexes increases with the rise in atomic number.
- The transition metal atom reveals multiple oxidation state; the higher valent ion forms more stable complexes.
- A few examples are: [Fe (CN)6]$^{3-}$

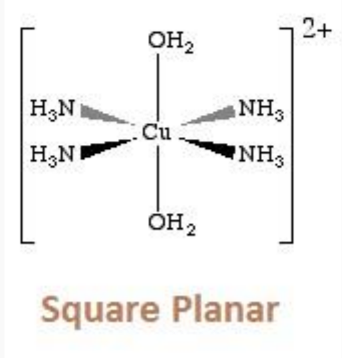


Octahedral Geometry

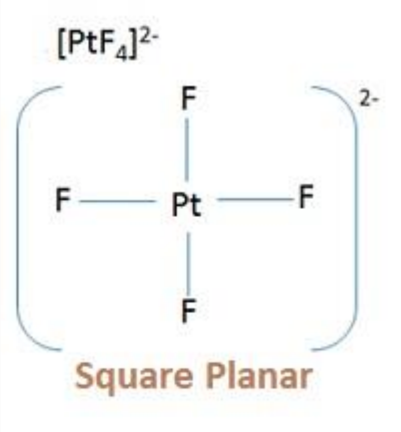
- [Fe(CN)6]$^{4-}$



- [Cu(NH3)4]$^{2+}$



- [PtCl4]$^{2-}$

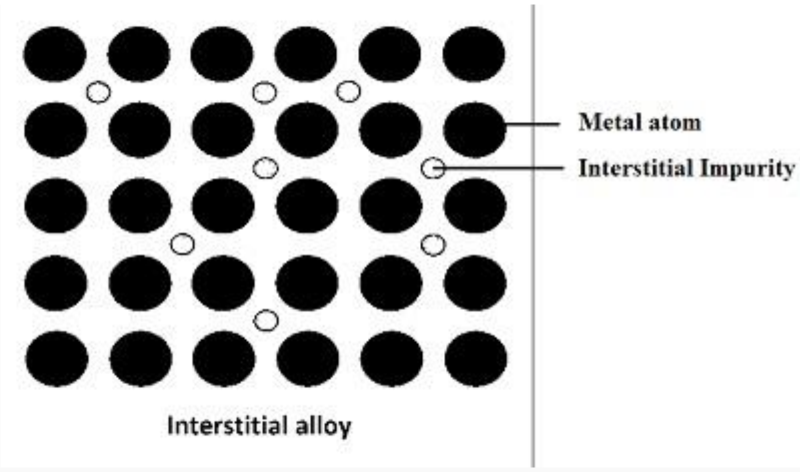


Formation of Interstitial Compounds

- Transition elements in combination with small atoms like H, B, C, N etc. leads to the formation of interstitial compounds that are non-stoichiometric in composition.

E.g.: $TiH_{1.3}$, $VH_{0.54}$

- The interstitial compounds so formed are chemically inert having higher melting points as compared to pure metals. These componds are hard and tough and keeps metallic conductivity.



Alloy Formation

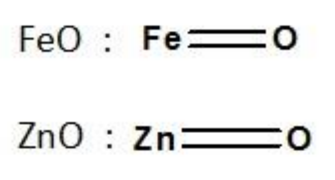
- Alloys are homogeneous mixtures of more than one metal that can displace another metal from the crystal lattice due to their comparable sizes. This leads to the formation of alloys.
- The alloys so formed are hard with high melting points. For example, chromium, vanadium, tungsten, manganese, molybdenum are the ferrous alloys.
- Some other examples are brass (alloy of copper + zinc), stainless steel, bronze (alloy of copper + tin), etc.

Medal made of Brass

Hinges made of bronze

Non-stoichiometric Compounds

- The compounds in which the there is no conformity in chemical composition with the ideal chemical formula are called non-stoichiometric compounds.
- These compounds are formed due to variable valency in transition metals and also due to the defects arising in solid state.
- The compounds formed with O, S, Se, Te, Fe, Zn etc. are the examples of such compounds.



FeO : Fe$\equiv$O

ZnO : Zn$\equiv$O

Preparation of $K_2Cr_2O_7$

Potassium dichromate, ($K_2Cr_2O_7$) is an orange-ish inorganic chemical reagent. In different laboratory or industry it is basically used as an oxidizing agent usually for alcohols.

It can be prepared through the following process:

- At first the fusion of chromite ore $FeCr_2O_4$ with sodium or potassium carbonate in the presence of access of air.

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2$ --> $8Na_2CrO_4 + 2FeO_3 + 8CO_2$

- Solution of sodium chromate is first filtered and then acidified with a solution of sulfuric acid which results in an orange sodium dichromate solution $Na_2Cr_2O_7\ 2H_2O$ can be crystallized.

$2Na_2CrO_4 + 2H^+ \dashrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

- Sodium dichromate is more soluble than potassium dichromate and therefore it is fused with KCl that leads to the formation of orange crystals of potassium dichromate.

$Na_2Cr_2O_7 + 2KCl \dashrightarrow K_2Cr_2O_7 + 2NaCl$

- At pH equal to 4 the dichromates and chromates exists in equilibrium and can be inter convertible.

$2CrO_4{}^{2-} + 2H^{2+} \dashrightarrow Cr_2O_7^{2-} + H_2O$

$Cr_2O_7{}^{2-} + 2OH- \dashrightarrow 2CrO_4^{2-} + H_2O$

- The yellow colour of chromate changes to orange coloured dichromate in the presence of acidic medium whereas the dichromate changes into chromate in the presence of basic medium.

$2CrO_4^{2-} + 2H^+ \dashrightarrow 2HCrO_4^-$ (Hydrogen chromate)

$2HCrO^{4-} \dashrightarrow Cr_2O_7^{2-} + H_2O$ Dichromate (orange)

- The chromate ion is tetrahedral and the dichromate ion consists of two tetrahedral sharing at one corner, with Cr-O-Cr bond angle 126 degree.
- **Properties of Potassium dichromate ($K_2Cr_2O_7$)**
- **Oxidizing properties**

  Potassium dichromate is a powerful oxidizing-agent in an acidic medium.
- $Cr_2O_7{}^{2-} + 14H^+ + 6$ electron $\dashrightarrow 2Cr^{3+} + 7H_2O$
- It oxidizes iodides to iodine.
- $Cr_2O7{}^{2-} + 14H^+ + 6I^- \dashrightarrow 2Cr{}^{3+} + 7H_2O + 3I_2$
- It oxidizes ferrous salts to ferric salts.
- $Cr_2O_7{}^{2-} + 14H^+ + 6\ Fe2+ \dashrightarrow 2Cr{}^{3+} + 7H_2O + 6Fe^{3+}$
- It oxidizes stannous salts to stannic salts.

- $Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \text{-->} 2Cr^{3+} + 7H_2O + 3Sn^{4+}$
- It oxidizes H2S to sulphur.
- $Cr_2O_7^{2-} + 8H^+ + 3H_2S \text{-->} 2Cr^{3+} + 7H_2O + 3S$
-
- **Action of heat**

  Application of heat leads to the decomposition of Potassium dichromate leading to the formation of potassium chromate, chromic oxide and oxygen.
- $4K_2Cr_2O_7 \text{ -Heat-> } 4K_2CrO_4 + 2CrO_3 + 3O_2$

Preparation of Pottassium Permanganate ($KMnO_4$)

Pottassium Permanganate ($KMnO_4$) is a dark purple solid consisting of two ions: a potassium ion (K^+) and a permanganate ion ($MnO^-{}_4$). It is a strong oxidizing agent and also possess medication properties due to which it is extensively used to clean wounds and in dermatitis.

- Fusion of powdered **Pyrolusite ore** (**MnO_2)** with an alkali metal hydroxide like KOH in the presence of air or an oxidizing agent like KNO_3 leads to the formation of dark green **potassium Manganate** (**K_2MnO_4**) which disproportionate either in a neutral or acidic medium and results in the formation of **potassium permanganate**.

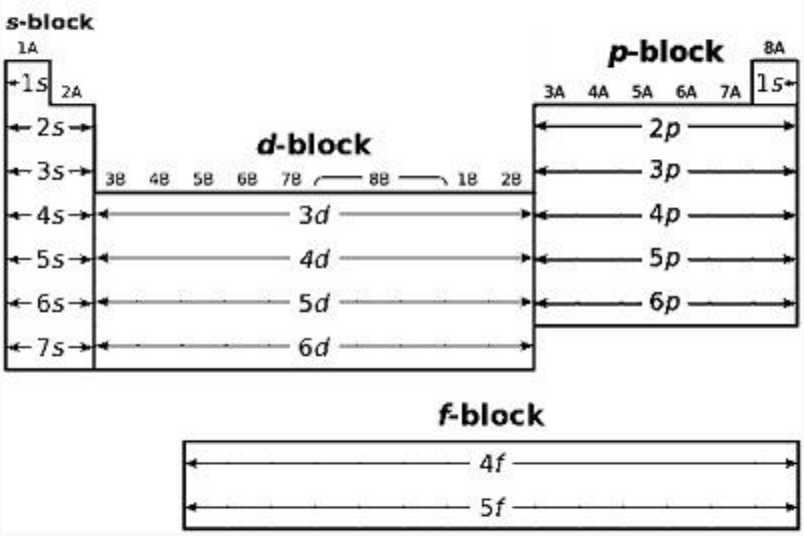
$2 MnO_2 + 4 KOH + O_2 \text{-->} 2K_2MnO_4 + 2H_2O$
$3 MnO_4^{2-} + 4H^+ \text{-->} 2MnO_4^- + MnO_2 + 2H_2O$

- Potassium permanganate is commercially prepared by an alkaline oxidative fusion of Pyrolusite ore (MnO_2) and again by the electrolytic oxidation of manganate (4) ion.

$2 MnO_2 + 4KOH + O_2 \text{-->} 2K_2MnO_4 + 2H_2O$
MnO_4^{2-} + (electrolytic oxidation) $\text{-->} MnO_4^- + e^-$

Introduction to F-block elements

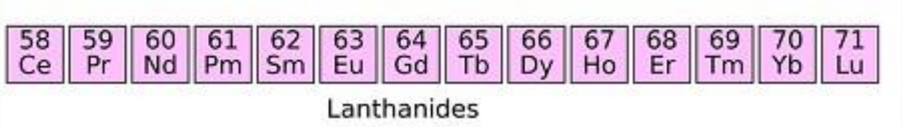
- The elements with gradually filled f orbitals are called f-block elements.
- The elements of 4f series of the inner transition metals are called lanthanoids whereas the elements of 5f series are called actinoids.



Problem: Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Solution: In actinoids, 5f orbitals are filled having poorer shielding effect than 4f orbitals (in lanthanoids) due to which the effective nuclear charge experienced by the electrons in valence shells of actinoids is more than what is experienced by lanthanoids. Therefore, the size of contraction in actinoids is greater as compared to that in lanthanoids. They are termed as inner transition elements due to their occurence inside the series of transition elements.

Lanthanoid:



58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

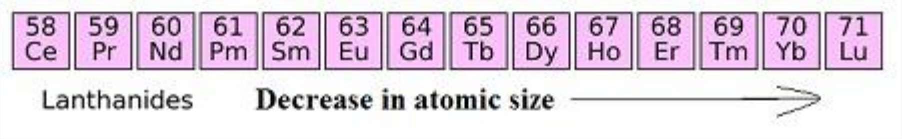
Lanthanides

- The electronic Configuration of lanthanoid is [Xe] $4f^{n+1}$ 5d° $6s^2$ or [Xe] 4fn $5d^1$ $6s^2$ with their valence shell electronic configuration as $4f^{1-14}$ $6s^2$.
- They exhibit the oxidation state of +3, +2 and +4.
- The initial members of this series are somewhat reactive towards calcium which resembles their behaviour to that of aluminum with the gradual increasing atomic number.
- On application of gentle heat Lanthanides combine with hydrogen.
- Heating them with carbon leads to the formation of carbides and halides (in presence of halogens while burning).
- Reaction of Lanthanides with dilute acids releases hydrogen gas.
- They form basic alkaline earth metal oxides and hydroxides like N_2O_3 and $M(OH)_3$.

Lanthanoid contraction:

- As we move along the lanthanoid series, the atomic number gradually increases by one or we can say number of electrons and protons increases by one.
- Addition of electrons to the same shell increases the effective nuclear charge.

- Increase in atomic number also increases the number of electrons in the 4*f* orbital having poor shielding effect due to which the effective nuclear charge upon the outer electrons also increases.
- Therefore the size of lanthanoids steadily decreases with the increase in the atomic number and phenomenon is called lanthanoid
- As a result of lanthanoid contraction there is a similarity in the properties of second and third transition series.

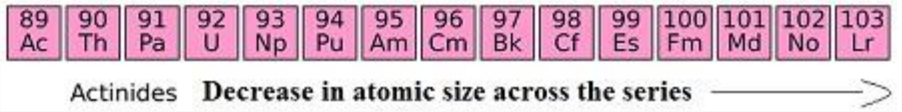


Oxidation States of lanthanoids

- The elements belonging to lanthanide series exhibit an oxidation state of +3. For example, Praseodymium (Pr) shows +3 oxidation state.
- Some elements exhibit +2 oxidation states in their complexes in solutions. For example, Samarium (Sm), Europium (Eu), Thulium (Tm) and Ytterbium (Yb) show +2 oxidation state.
- Some elements exhibit +4 oxidation states due to high stability of empty, half-filled or fully filled f-subshells.
- Praseodymium (Pr), Neodymium (Nd), Terbium (Tb) and Dysprosium (Dy) exhibits +4 oxidation state in their oxides.
- Cerium (Ce) shows both +3 as well as +4 state.

Actinoids

- The elements from Th to Lr belong to the series of Actinoids i.e. Actinoids contain 14 elements.
- They are radioactive elements.
- The former elements have long half-lives whereas the latter elements have a half-life value ranging from1 day to 3 minutes for lawrencium with atomic number 103.
- Actinoids have the electronic configuration of $7s^2$ and inconstant occupancy of the 5f and 6d subshells.
- Electronic configuration of Thorium is $5f^1\ 6d^1\ 7s^2$, Am is [Rn] $5f^7 7s^2$ and Cm is [Rn] $5f^7 6d^1 7s^2$
- The ionic radii gradually decrease across the series due to the poor screening effect of nuclear charge exerted by the *f* electrons. This is called Actinoid contraction.



Oxidation state in Actinoids

- In general the oxidation state of these elements is +3 (similar to lanthanides).
- They also exhibit +4 oxidation states.
- Some of the elements also exhibit higher oxidation states.
- The oxidation state initially rises to the middle of the series (+4 for Th to +5, +6 and +7 for Pa, V and Np) and then descends in the succeeding elements.

General Characteristics and Comparison of Actinoids with Lanthanoids

(i) Electronic configuration

- The general electronic configuration for actinoids is $[Rn]^{86}\ 5f^{1\text{-}14}\ 6d^{0\text{-}1}\ 7s^2$ and for lanthanoids is $[Xe]^{54}\ 4f^{0\text{-}14}\ 5d^{0\text{-}1}\ 6s^2$.

(ii) Atomic and Ionic sizes

- Like lanthanoids the ionic radii of actinoids gradually decrease across the series due to the poor screening effect of nuclear charge exerted by the *f* electrons.

(iii) Oxidation states

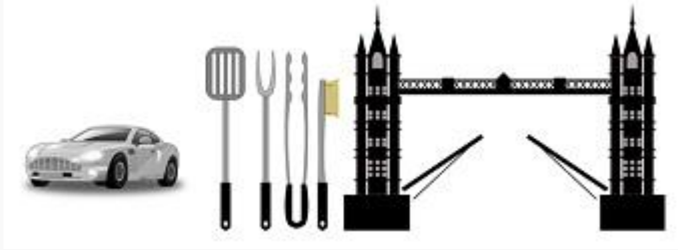
- The lanthanoids exhibit +3 oxidation states. Some elements may exhibit + 2 and + 4 oxidation states due to extra stability of fully-filled and half-filled orbitals.
- On the other hand Actinoids also exhibit + 3 oxidation state. They also exhibit varying oxidation states due to the comparable energies of 5*f*, 6*d*, and 7*s*.

(iv) Chemical reactivity

- Earlier members of the lanthanide series are more reactive and are comparable to CSolution: They resemble Al with increasing atomic number.
- Finely divided Actinoids are highly reactive metals and when added to boiling water gives a mixture of oxide and hydride.
- At moderate temperatures Actinoids combine with most of the non-metallic elements.
- Actinoids remain unaffected by the action of alkalies but gets slightly affected by nitric acid due to the formation of a protective oxide layer.

Applications of d- and f-Block elements

- Iron and steels are used for making tools, utensils, vehicles, bridges and much more.



- TiO for the pigment industry and MnO_2 for use in dry battery cells.

- Zn and Ni/Cd is also used for battery industry.
- Elements of Group 11 called the coinage metals.

- V_2O_5 catalyses the oxidation of SO_2 in the manufacture ofsulphuric acid.
- $TiCl_4$ with $A1(CH_3)_3$ forms the basis of the Ziegler catalystsused to manufacture polyethylene (polythene).
- Iron catalysts are used inthe Haber process for the production of ammonia from N_2/H_2 mixtures.
- Nickel catalysts enable the hydrogenation of fats
- Wackerprocess the oxidation of ethyne to ethanal is catalysed by $PdCl_2$.
- Nickel useful in the polymerisation of alkynes and other organiccompounds such as benzene.
- The photographic industry relies on thespecial light-sensitive properties of AgBr.

Problem: Write down the electronic configuration of:

(i) Cr^{3+} (iii) Cu^{+} (v) Co^{2+} (vii) Mn^{2+}

(ii) Pm^{3+} (iv) Ce^{4+} (vi) Lu^{2+} (viii) Th^{4+}

Solution:

(i) Cr^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$

Or, $[Ar]^{18}3d^3$

(ii) Pm^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}5s^2\ 5p^6\ 4f^4$

Or, $[Xe]^{54}\ 3d^3$

(iii) Cu^{+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

Or, $[Ar]^{18}\ 3d^{10}$

(iv) Ce^{4+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$

Or, $[Xe]^{54}$

(v) Co^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7$

Or, $[Ar]^{18}3d^7$

(vi) Lu^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^1$

Or, $[Xe]^{54}2f^{14}3d^3$

(vii) Mn^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Or, $[Ar]^{18} 3d^5$

Introduction

The Coordination compounds are very important in day to day life, many compounds exist as coordination compounds as they have special type of linkage that is coordinate bond .It is formed between electron rich and electron deficient species.

Coordinate bond: It is a bond in which sharing of electrons occurs but not mutual sharing. In this the shared pair is donated by only one atom and the one that **donates** is donor and the other which accepts is **acceptor.**

For example:

NH_3: + BF_3--à{H_3N :-> BF3}

In this NH_3 is donor atom as it has lone pair and BF_3 is acceptor as it is electron deficient compound.

The branch of chemistry that deals with the study of coordination compounds are called as" **coordinate chemistry "**

Examples of some coordinate compounds like:

- Hemoglobin – coordination compound of iron (Fe)
- Chlorophyll – coordination compound of magnesium (Mg)
- Vitamin B12- coordination compound of cobalt (Co)

Most of time coordination compounds are confused with double salts but there exists a lot difference between the two.

Double salts

Double salt is the association of many substances or we can say they mainly contain two salts in equimolar concentration.

1. like Mohr's salt $FeSO_4.(NH_4)_2SO6H_2O$
2. Potash alum $K_2SOAl_2 (SO_4)_3.24H_2O$ etc.

In coordination compound once the compound is formed its ions than the compound as a whole do not lose its identity but when dissolved in water they show different properties whereas in case of double salts they don't show different properties but looses their identity in water

{$Co(NH_3)_6$}Cl_3à $Co(NH_3)_6$ + 3Cl (coordination compound in water)

$FeSO_4.(NH_4)_2SO_4.6H_2O$à$Fe^{2+}$,NH_4^+,SO_4^{2-},H^+,OH^- ions (double salt in water)

- Coordination compounds exist in solid as well as aqueous state whereas the double salts exist in solid state and in aqueous state they dissociate into ions .
- The coordination compounds exist in extended octet whereas in double salts they exist in their own valances.

Terminology involved

central metal atom:

- it is the acceptor metal atom present in the coordination compound
- It is mostly d block element
- It act as an acceptor as it has vacant d orbital
- Due to accepting nature they act as Lewis acids

For example in complex: {Co$(NH_3)_6$}Cl_3 in this Co is central metal atom

Ligands:

- They are donor atom may be single atom or group of atoms
- They are negatively charged or neutral species with lone pair Br^-,Cl^- etc or neutral like NH_3,NO,CO etc
- They act as Lewis bases
- We can also call ligands as nucleophile as they are nucleus loving

For example in complex: {Co$(NH_3)_6$}Cl_3 in this NH_3 is ligand

coordination sphere:

- It is the combination of atom and ligands.

Example: in [Co $(NH_3)_6$ Cl_3]

[Co $(NH_3)_6$] is coordination entity or complex

- They are written in square brackets [coordination entity]
- This coordination sphere may be positively changed, negatively charged
- If it is positively charged than it is called as **cationic entity** and in case of negative charge it is **anionic entity or complex.**

Example: $[Co(NH_3)_6]^{3+}$ cationic entity $[Ag\ (CN)_6]^-$ anionic entity

counter ion:

- The atom or group of atoms written outside bracket is called counter ion.

Example: in $[Co(NH_3)_6].Cl_3$

Cl_3 is a counter ion or the ionizable part when dissolved in water

- If coordination sphere is with positive charge than counter ion is with negative charge or vice versa.

Coordination entity

- The central metal atom and ligands attached to it forms coordination entity and is written within square brackets

Example :in $[Co(NH_3)_6].Cl_3$

In this in $[Co(NH_3)_6]$ is coordination entity

Nature of ligands: Their nature is determined by the property denticity

Denticity

it determines the total number of donor atoms in a molecule.

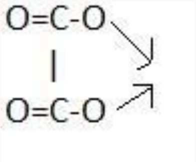
On the basis of the property denticity ligands are :

- **Monodentate /unidentate**: is that which has one donor atom

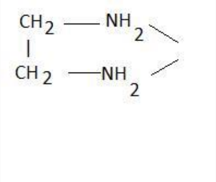
Examples : CN^-, OH^-,Cl^-,Br^-,NH_3:,H_2O,CO etc

- **Di-dentate**: if it has two donor atoms

Examples



(OXALATE ION)

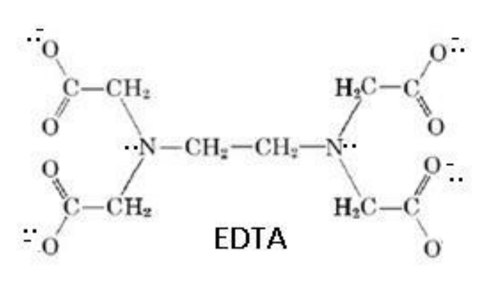


(ethylene diamine)

- **Polydentate** : if it has 3 or more donor atoms in it DIETHYLENE TRIAMINE (tridendate)

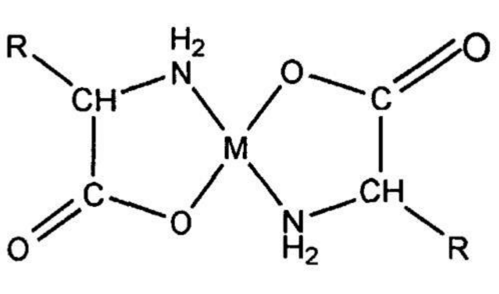
NH_2-CH_2-CH_2-NH-CH_2-CH_2-NH_2

Hexadentate: ethylene diamine tetra acetic acid (EDTA)



chelate: when the ligand has two or more donor atoms and they are arranged in such a way that they give rise to a ring like structure than the effect is called chelating and the ring formed is chelate .

For example:



uses of chelates:

- They are used in softening of hard water
- In qualitative analysis for detection of metal
- In separation of lanthanoids and actinoids

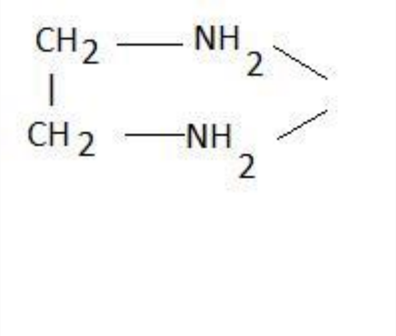
Ambidentate ligand: that have two donor atoms but doesn't show chelation. This group bond at a time by one atom.

For example: CN^-,NO_2 etc

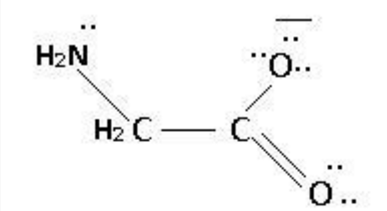
Symmetrical and unsymmetrical ligands :

Symmetrical ligands: if ligands attached to central atom are of same type

Example: ethylenediamine etc.



Unsymmetrical ligands: if ligands attached are of different type.



Glycinate ion

Example: glycinate ion etc.

Coordination number: it is the number of ligands bonded with the central metal atom for example: IN $[Ag(CN)_2]^-$"the no. Of ligands attached are 2 therefore coordination no. is 2 ".

Oxidation number: it is the residual chargeleft on the atom when all other atoms are removed from it .it is calculated by assigning appropriate charges to ligands and then equating the sum of the charges on the central atom and the ligands equal to the charge on the coordination sphere.

For example: $[Co(NH_3)_6]Cl_3$ in this oxidation state of NH_3 is 0 and for Cl is -1, and ooxidation state of Co is taken as x then

$$(x-3) \times 1=0 \text{ or } \quad x=+3$$

another example: $[Cu(CN)_4]^{3-}$ in this oxidation state of Cu is taken as x, CN as -1 so,

$$x + (-1 \times 4) = -3 \text{ or } x=+1$$

Homo-leptic and hetero-leptic compounds

Homoleptic: are those which have same kind of ligands attached to central metal atom

Example:in $[Co(NH_3)_6]Cl_3$ is homoleptic as ligands are same

terolyptic: when ligands attached are of different type

Example: in $[CoCl_3(NH_3)_3]^{3+}$ is heterolytic because ligands attached are of different types.

Nomenclature of coordination compounds

Like for ionic compounds the naming is done by writing first cation name and then naming anion.

For example: NaCl is ionic and written as sodium chloride that is in name first part is cationic and other is anionic.

In the same way coordination compounds consist of two parts:Cation and anion. While naming,the name of cationic part is written first followed by anionic part. There are certain set of rules that are followed while writing name of cation.

Naming for cationic species: in which coordination sphere is positively charged

- Name of cation is written first

Let's say the coordination sphere is cationic that is with positive charge for example $[Co\ (NH_3)_6]\ Cl_3$ for the naming of coordination entity is done first and later the counter ion .so in given complex the name of $[Co\ (NH_3)_6]$ is written first than the counter ion Cl

- In case of coordination entity: the name of ligands is written first and then the central metal atom. Forexample, in this $[Co\ (NH_3)_6]$the name of NH_3 is written first than for Co.
- If the ligands are homoleptic than you can write in any manner but if they are heterodetic than the alphabetical order is followed

For example: in complex $[Co\ (NH_3)_5CL]$ the name of ligands is written in alphabetical order that is for ammine firstand then chloro.

Rules for writing the name of the ligand:

- If the ligand names end with 'ate' or 'its'than e is replaced by o

Like for oxalate it is written as oxalate, sulphite as sulphito

- If ligand name end with' ide 'than ide is replaced by 'o '

Example for chloride it becomes chlorido

- Neutral ligands are name as such like for water it is aqua, for ammonia it is ammine
- If more than one ligand is present than alphabetical order is followed and di,tri, tetra is prefixed before the name of ligand.

For example: in complex [Co $(NH_3)_6$] ligand name will be hexamine that is hexa for 6

- For polydentate ligands they include numerical prefix –like di is replaced by bi, tri is replaced by tris, tetra is replaced bytetra is so on

For example: $[CoCl_2(en)_2]$ Cl in this the ligands are dichlorobisethylenediamine

In case of Central metal atom:

Oxidation state of central metal atom is written in numeral after the name of central metal atom

For example: in complex [Co $(NH_3)_6$] Cl_3 it is hexamine cobalt (III) that is cobalt (III) is central metal atom with its Oxidation state in numeral

- if complex is cationic than normally the name is used: example is same as given above
- if complex is anionic than metal atom name ends with ate

for example: in complex $K_3[fe(CN)_6]$ in this the name is written as potassium hexacyanoferrate(III) that is in this example coordination entity is anionic complex and the name of central metal atom is written with ate followed by Oxidation state in numeral

- if complex is neutral than the normal central metal atom name is used

some commonly used ligands:

- bromo Br^-
- floro F^-
- oxo
- hydroxo OH^-
- cyano CN^-
- carbonato CO_3^{2-}
- acetate CH_3COO^-
- ammine NH_3
- aqua H_2O
- nitrosyl NO
- carbonyl CO
- dioxygen O_2
- dinitrogen N_2
- pyridine C_5H_5N
- ethylene diamine $H_2NCH_2CH_2NH_2$

some examples of iupac naming:

1. **$[Cr (NH_3)(H_2O)_3]Cl_3$**

Triaminetriaquachromium(III)chloride

2. **$[Co(en)_3]_2(SO_4)_3$**

Trisethylenediaminecobalt(III)sulphate

3. **$[Ag(NH_3)_2][Ag(CN)_2]$**

Diamine argentum(i)dicyanoargentate(i)

4. **$[Pt (NH_3)_2Cl (NO_2)]$**

Diaminechloronitroplatinum(III)

5. **$K_3[Cr(C_2O_4)_3]$**

Potassiumtrioxalatochromate(III)

Isomerism in Coordination Compounds

Isomerism is the phenomenon in which compounds have same molecular formula but different structures and these different structures are called as isomers. Isomers are those that have different physical and chemical properties.

There are two types of isomers:

- Structural isomerism
- Stereoisomerism

Structural isomerism: Different types are as follows:-

- ionization isomerism
- Hydrate isomerism
- Coordination isomerism
- Linkage isomerism

Stereoisomerism: Different types are as follows:-

- geometrical isomerism
- Optical isomerism

Structural isomerism:The compounds have same molecular phenomenon but different structures

- **Ionization isomerism**: they differ in productions of ions in aqueous solution

For example:à $[CoBr(NH_3)_5]SO_4$ and $[Co (NH_3)_5SO_4]Br$ are ionization isomers when dissolved in water

$[CoBr(NH_3)_5]SO_4$ à$[CoBr(NH_3)_5]^{2+}$ + SO_4^{2-}

$[Co\ (NH_3)_5SO_4\ ]Br$àà$[CoSO_4\ (NH_3)_5]^{2+}$ + Br^-

- **Hydrate or solvate isomerism:** in this they differ in number of molecules of water of crystallization

For example: $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2H_2O$are hydrate isomers

When dissolved in water

$[Cr(H_2O)_6]Cl_3$à$[Cr(H_2O)_6]$ + $3Cl^-$ (no water molecule)

$[Cr(H_2O)_5Cl]Cl_2H_2O$à$[Cr(H_2O)_5Cl]+2Cl+H_2O$(will give one water molecule)

- **Coordination isomerism**: they differ in coordination entities

For example:$[Co(NH_3)_6]$ $[Cr(CN)_6]$ and :$[Co(CN)_6]$ $[Cr(NH_3)_6]$ are coordination isomers

- **Linkage isomerism**: it is in case of ambidentate ligands and in this they differ in the point of attachment.

For example, in case of CN(cyano) and in case of NC (isocyano)

- **Stereoisomerism**: in these compounds have same molecular formula but differ in spatial arrangements of ligands.

It is of two types:

- Geometrical isomerism
- Optical isomerism

Geometrical isomerism: it is due to difference in the geometrical arrangements of ligands around central metal atom.

it is of further two types :

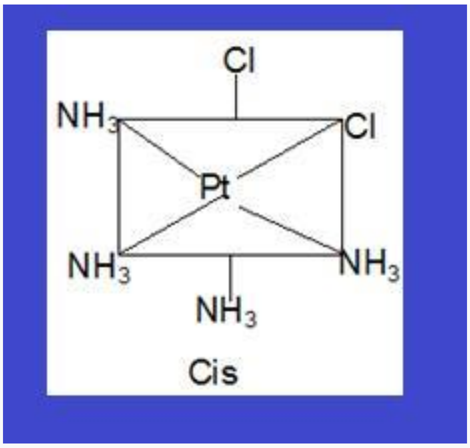
- Cis
- Trans

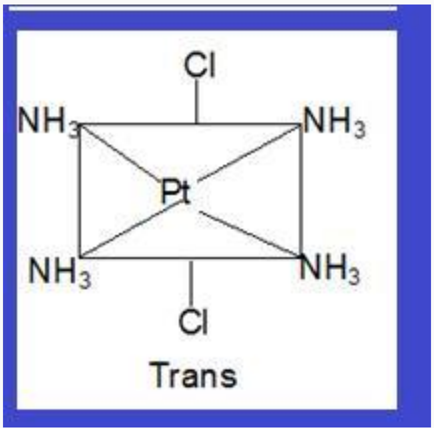
Cis : when the similar ligands are on adjacent position

Trans : when the similar ligands are on opposite positions

Cis and trans isomers are shown below (this is shown by compounds with coordination number 4 and 6

Example: $[Pt\ (NH_3)_4Cl_2]$





- Another type of Geometrical isomerism that occurs in octahedral compounds in Ma_3b_3 like $[Co(NH_3)_3(NO_3)_3]$.

It can be of two types :

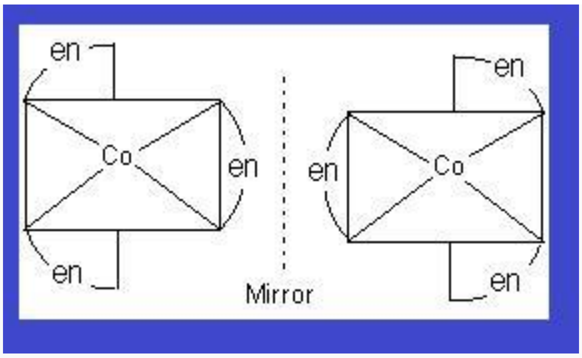
- Facial
- Meridional

Fac :In this three donor atoms of same ligands occupy adjacent positions at corners of an octahedral face

mer :In this three donor atoms of same ligands occupy positions around the meridian of an octahedron.

- **Optical isomers:**they can also show optical isomerism if chiral center is present in them .if they possess chiral center they can rotate the plane of polarized light .

Example: $[Co(en)_3]$



Bonding in coordination compounds

The first theory in order to explain it was given by **Alfred Werner in 1892.**

He performed various experiments to show that the surrounding atoms exist around central atom. He actually conducted ppt. studies

$CoCl_2+NH_3$à$CoCl_3.6NH_3$

When $CoCl_3.6NH_3$ was precipitated with $AgNO_3$ it gave 3 moles of AgCl this shows that 3 Chloride ions are not directly bonded with cobalt that is why it was precipitated with silver nitrate which gave him the idea about primary and secondary valances' and accordingly he postulated his theory.

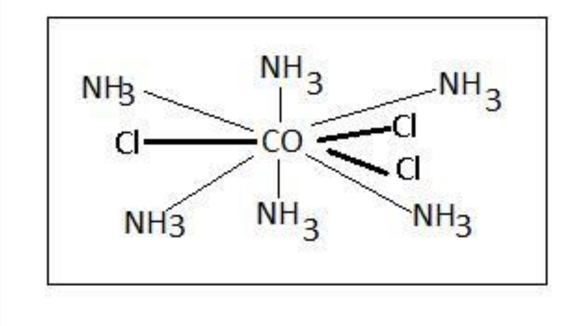
Werner's theory

According to the theory the postulates are:

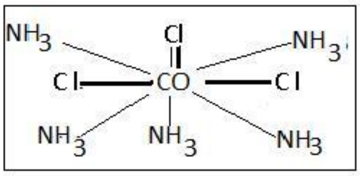
1. Metal exhibit 2 types of vacancies: primary valency and secondary valency
2. Primary valency gives the information about oxidation state and secondary valency gives the information about coordination number
3. Primary valency is variable whereas secondary valency is always fixed
4. Secondary valency that is coordination number determines the geometry of molecule or we can say polyhedral of the molecule.
5. Metal stabilize all its vacancies

<u>Depending upon this theory various structures of coordination compound was explained :</u>

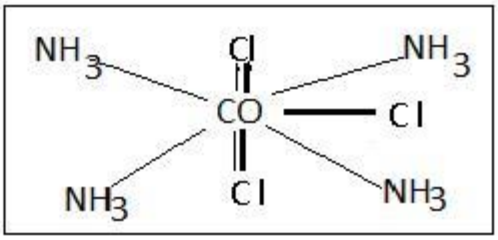
In $CoCl_3.\ (NH_3)_6$à In this NH_3 is secondary valency and Cl is primary valency



In $CoCl_3.(NH_3)_5$ the ionizable chlorides are only 2



In $COCl_3.(NH_3)_4$ the ionizable ions are only one chloride ion



Please note the dark lines shows ionizable part and light lines show non ionizable part in all the figures.

Limitations of Werner's theory:

He was able to explain many facts about coordination compounds but failed to give any information about why only certain elements participate in coordinate bond, why the coordination entity has special geometry …

Due to these reasons other theory was proposed that is valence bond theory

Valence bond theory

It was given by Pauling in 1931

1. He proposed the idea of donating lone pair to central metal atom.
2. Bonding in coordination compound occur due to overlap of orbital of ligand with vacant orbital of central metal atom
3. All the vacant d orbitals have same energy. but the degeneracy of d orbital breaks when ligand approaches
4. Hybridization is considered while drawing polyhedral
5. Metal ions in presence of ligands can use their (n-1)d ns np or ns np Nd.

If the inner d orbital is used than the complex is regarded as inner orbital complex and if outer d orbital is used than the complex is outer orbital complex.

6. The ligands decide which orbitals out of these to be used and accordingly the geometry is decided.

If hybridization

- sp^3- tetrahedral

- dsp^2-square planar
- Sp^{3}d-trigonal bipyramidal
- Sp^{3}d^2- octahedral
- d^{2}sp^3-octahedral

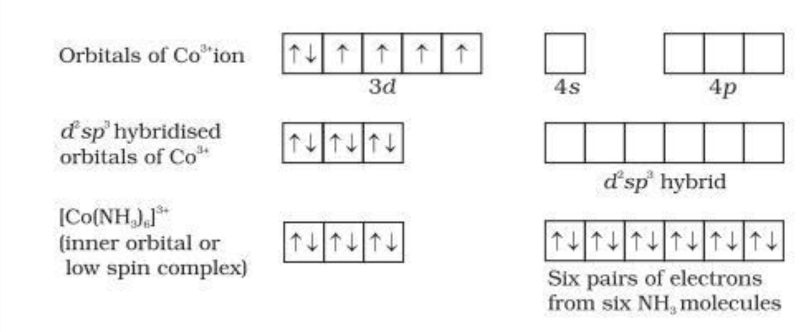
For example:

For any coordination compound: To find the shape using valence bond theory following steps to be followed

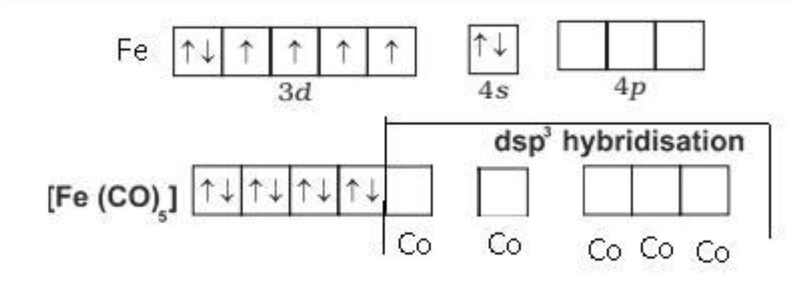
1. Remove the electrons from the metal and form it the ion
2. Rearrange metal electrons if necessary
3. Hybridization
4. Overlapping of hybrid orbitals of metal with ligand

Let us take one example: of example $[Co(NH_3)_6]^{3+}$. In this central metal atom Co atomic no. is 27. The electronic configuration of Co = $(Ar)^{18}3d^7 4s^2$

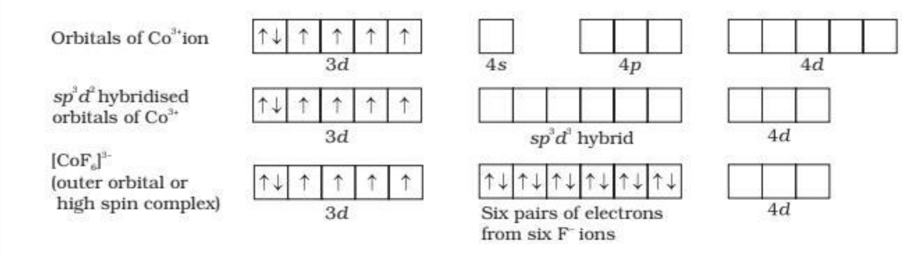
$Co^{3+}=(Ar)^{18}3d^6$



Example $[Fe(Co)_5]$: (inner orbital complex and diamagnetic)



EXAMPLE: in $[CoF_6]^{3-}$…… (outer orbital complex and paramagnetic)



Drawbacks of valence bond theory:

1. This theory couldn’t have valid reason behind that why some complexes of metal oxidation state is inner orbital while in some other complexes the same metal atom ion in same state form outer orbital complex.
2. The magnetic behavior explained wasn’t satisfactory
3. This theory couldn’t give the information about color of compounds
4. This theory failed to distinguish between strong and weak ligand

TO OVERCOME THE SHORT COMINGS A NEW THEORY WAS PROPOSED: CRYSTAL FIELD THEORY

Crystal field splitting theory

It was given by Hans Bethe Ans John van vleck

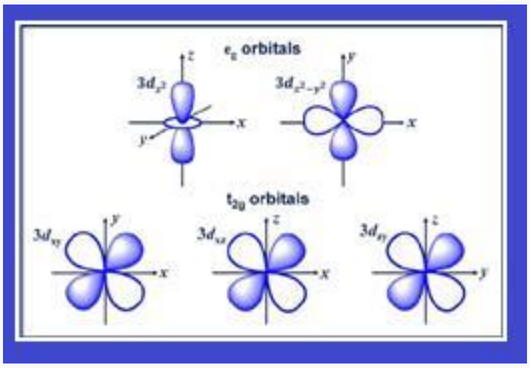
Postulates

1. It assumes the central metal atom and ligands as point charges
2. When a complex is formed: central metal atom positive charge

Ligands –have negative charge

3. This theory considers the interaction between central metal atom and ligand is purely electrostatic
4. When a complex is formed the central metal atom is surrounded by oppositely charged ligands
5. No hybridization takes place
6. To form a bond the ligand molecule must approach towards central metal atom
7. In absence of external magnetic field, the d orbital of central metal atom is degenerate but this degeneracy breaks when ligand approaches.
8. The d orbital splits into two sets:

Axial set	non-axial set
d_{xy},d_{yz}, d_{zx}	$d_{x^2-y^2}$,d_{z^2}

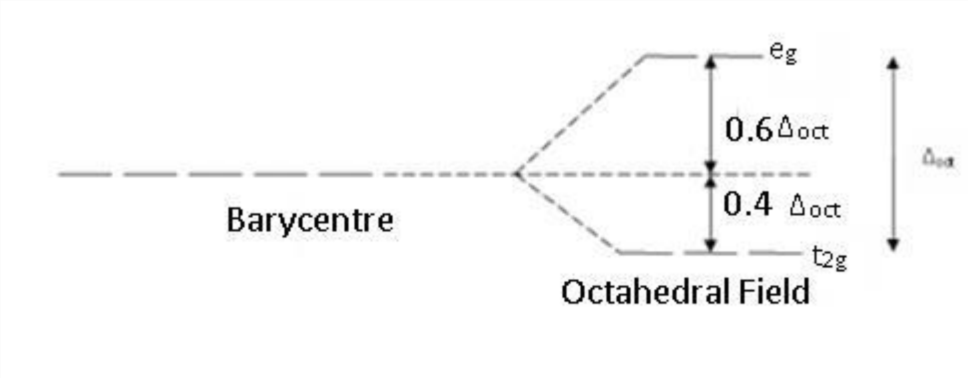


This is crystal field splitting.

9. Repulsive forces occur between electrons of metal and with lone pair ligands due to which energy of electron fluctuate or changes.

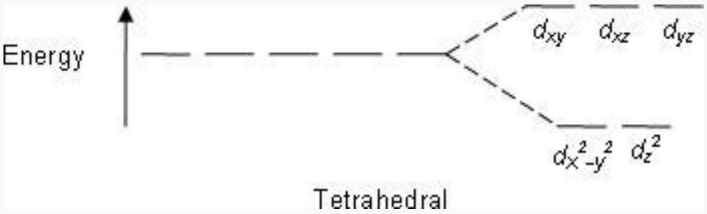
For octahedral complexes

To form octahedral complex the ligands, have to approach central metal atom along the coordination axis. During the approach the d orbitals whose lobes lie along the axis will experience more repulsion due to this their energy will increase and the other non axial set will suffer less repulsion. as a result, the non-axial will have less energy as compare to axial set (e_g greater than t_{2g})



Tetrahedral complex:

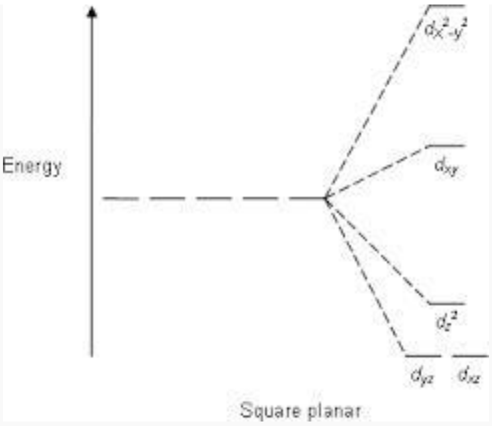
The ligands have to approach central metal atom in between the coordinationaxis. during the approach the d orbital's whose lobes lie along the axis will experience less repulsion due to this their energy will increase and the other non axial set will suffer more repulsion. as a result, the non-axial will have more energy as compared to axial set (t_{2g} greater than e_g)



square planar complex:

In the different order is seen i.e

d_{x^2}-y^2,d_{xy},d_{z^2},d_{yz},d_{zx}



Please note for all the complexes:

for strong ligands : the CFSE is more therefore pairing will occur

for weak ligands : the CFSE Is less

Organo-metallic compounds

They are those compounds in which metal or metalloid or a non-metal is directly linked to carbon atom of a hydrocarbon.

For example: $(C_2H_5)_2Zn$ etc

Please note that metal cyanides and metal carbides are not organometallic compounds as in them carbon atom is not directly joined to metal.

Types of organometallic compounds:

- Sigma organometallic compounds
- Pi organometallic compounds

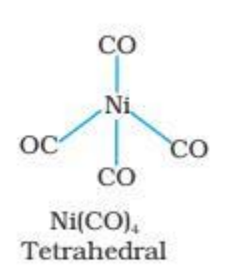
Sigma and pi organometallic compounds In detail:

- Sigma organo-metallic compounds: these are the compounds obtained by bonding of non-metal with metalloid elements with carbon. forexample:RMgX, $(CH_3)_3Al$ etc.
- Pi organo- metalliccompound: these compounds are formed mainly by transition elements. Normal sigma bond is formed through the pi electron cloud of organic molecule. Forexample : ferrocene ,zeisse's salt etc
- Sigma and pi organo-metaliccompound: these compounds are formed by transition metal carbonyls .for example : $Ni(CO)_4$,$Fe(CO)_5$ etc

Shapes of these structures are shown below:

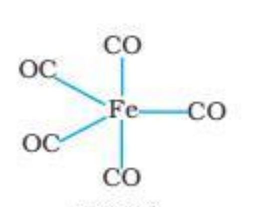
For example :

1. **Shape of [Ni(Co)$_4$]**



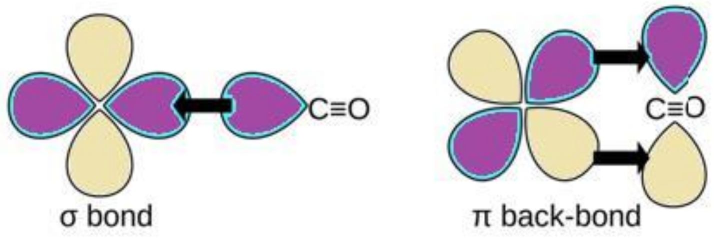
Ni(CO)$_4$
Tetrahedral

Shape of [Fe(Co)$_5$]



Fe(CO)$_5$
Trigonal bipyramidal

Considering bonding in metal carbonyls: these compounds possess both s and p characters. The M-C sigma bond is formed by donation of lone pair if electrons on the carbonyl carbon into a vacant orbital of metal. The M-C pi bond is formed by the donation of pair of electrons from the filled d orbital of metal into vacant antibonding pi orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and metal as shown below:-



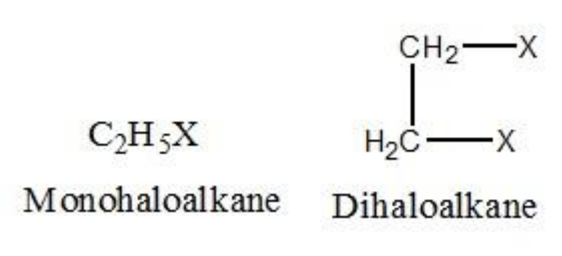
Applications of coordination compounds

1. They are used in estimation of hardness of water as calcium and, magnesium ions form complexes with EDTA.
2. It is used in estimation and detection of metal ions. for example: Ni^{2+}ions is estimated using dimethyl glyoxime
3. It is used in Extraction of metals
4. It is used in medicines like cis platin is used in treatment of cancer
5. It is used in animal and in plant world like hemoglobin is a complex of iron, chlorophyll is a complex of magnesium and so on

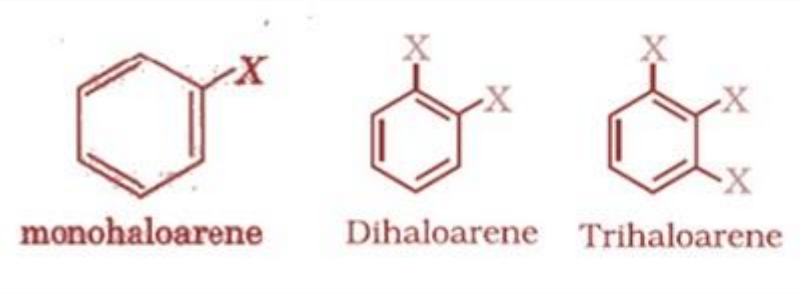
10.Haloalkanes and Haloarenes

Introduction

Halo alkanes are the compounds containing halogen atom attached to the sp^3 hybridized carbon atom of an alkyl group.

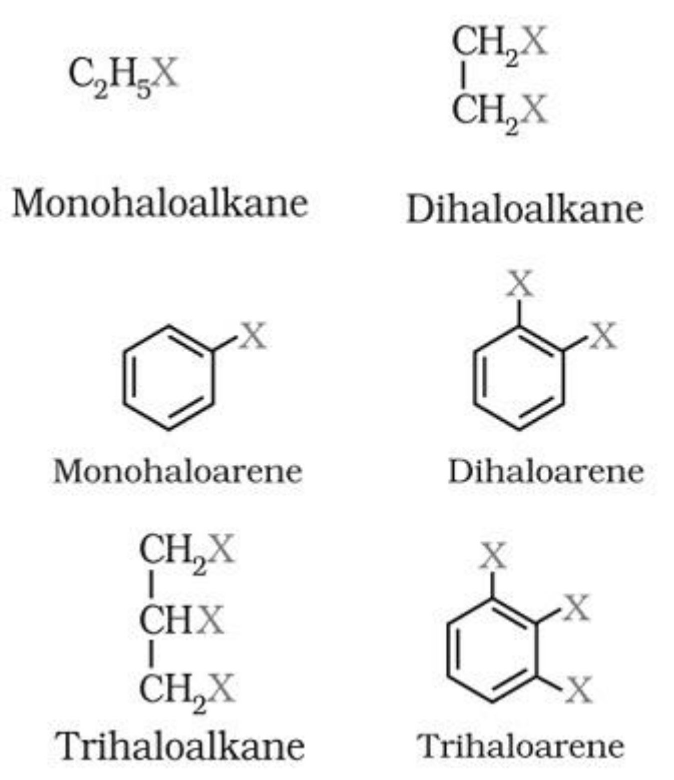


Haloarenes are the compounds containing halogen atom attached to sp^2 hybridized carbon atom of an aryl group.



Classification of halo alkanes and halo arenes On the Basis of number of halogen atoms

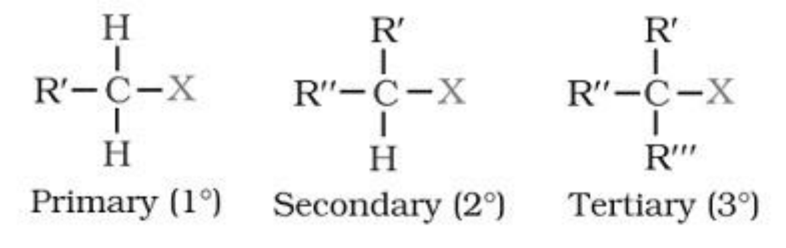
Depending on number of halogen atoms present in halo alkanes and halo arenes they can be classified as mono (one atom), di (two atoms), or Polyhalogen (tri- (three atoms), tetra- (four atoms), etc.) compounds.



Classification of halo alkanes and halo arenes on the basis of compounds containing sp3C—X Bond

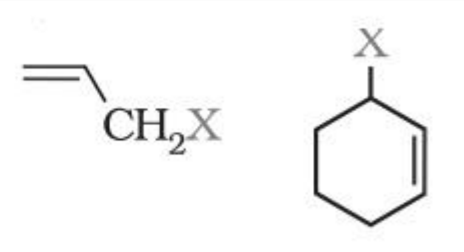
(a) Alkyl halides or halo alkanes (R—X)

They create a homologous series represented by $C_nH_{2n+1}X$ and can be further classified as primary, secondary or tertiary.



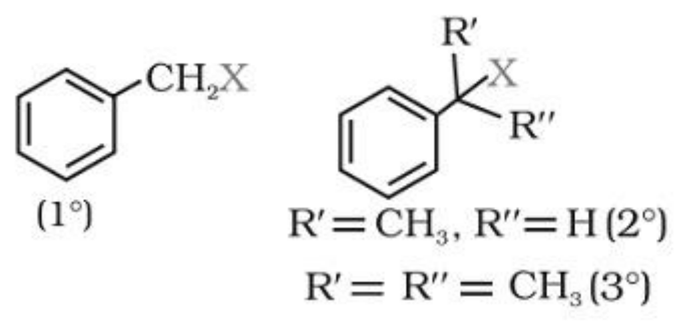
(b) Allylic halides

The compounds with halogen atoms bonded to *sp3*-hybridised carbon to carbon-carbon double bond (C=C) *i.e.* to an allylic carbon.



(c) Benzylic halides

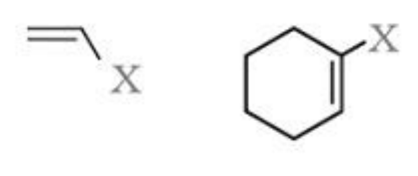
The halogen atom of these compounds is bonded to *sp3*-hybridised carbon atom placed next to an aromatic ring.



Classification of halo alkanes and halo arenes on the basis of compounds containing sp_2 c—x bond

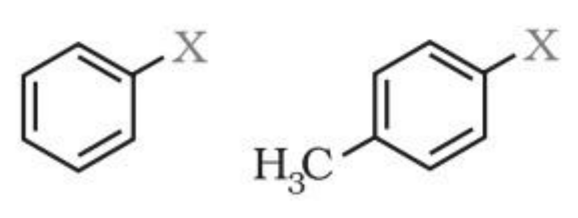
- ***Vinylic halides***

The halogen atom of these compounds is bonded to sp^2-hybridised carbon atom of a carbon-carbon double bond (C = C).



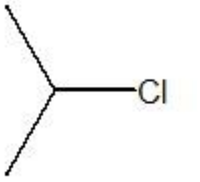
(b) Aryl halides

The halogen atom of these compounds is bonded to the *sp2*-hybridised carbon atom of an aromatic ring.



Nomenclature

- Nomenclature of halo alkanes
- Select the longest chain of carbon that contains the halogen atom.
- Give least possible number to the halogen atom.
- The carbon containing double or triple bond is given the least number.
- Place the suitable suffix like di, tri, tetra for 2, 3, 4 halogen atoms respectively.
- Name the compounds as halo alkanes, halo alkenes or halo alkynes.
- For example,



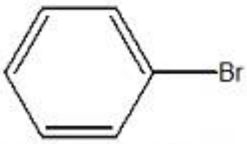
2-chloropropane

1-Bromobutane

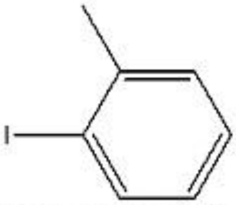
1,2-Dibromoethane

1,2-dichloroethane

- Nomenclature of halo arenes
- Commonly they are termed aryl halides.
- Numerical prefixes (1,2) ; (1,3) ; (1,4) for [for positions of the compound with respect to halogen atom.
- The halogen atom is given the least number.
- For example,



BROMOBENZENE



1-IODO-2-METHYL BENZENE

Problem:

Give the IUPAC names of the following compounds:

(i) $CH_3CH(Cl)CH(Br)CH_3$

(ii) $CHF_2CBrClF$

(iii) $ClCH_2C{\equiv}CCH_2Br$

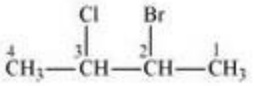
(iv) $(CCl_3)_3CCl$

(v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$

(vi) $(CH_3)_3CCH{=}CClC_6H_4I\text{-}p$

Solution:

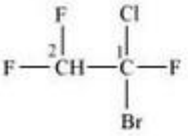
(i)



$\overset{4}{C}H_3-\overset{3}{C}H(Cl)-\overset{2}{C}H(Br)-\overset{1}{C}H_3$

2-Bromo-3-chlorobutane

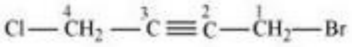
(ii)



$F-\overset{2}{C}H(F)-\overset{1}{C}(Cl)(Br)-F$

1-Bromo-1-chloro-1, 2, 2-trifluoroethane

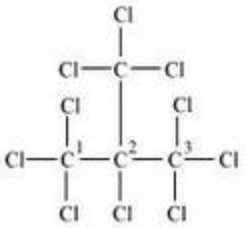
(iii)



$Cl-\overset{4}{C}H_2-\overset{3}{C}{\equiv}\overset{2}{C}-\overset{1}{C}H_2-Br$

1-Bromo-4-chlorobut-2-yne

(iv)

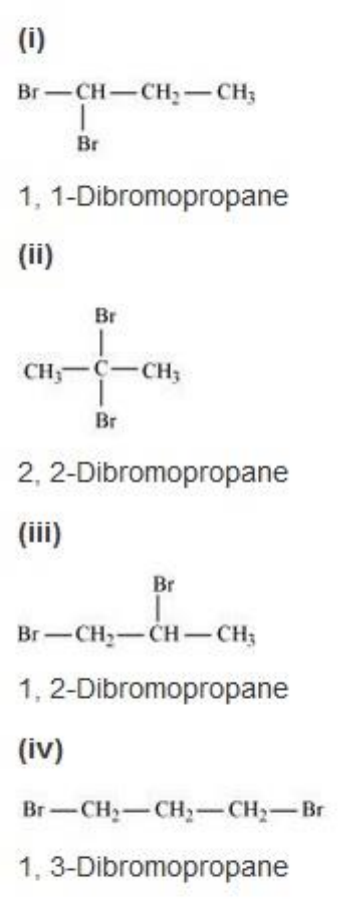


2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

Problem:

Write structures of different dihalogen derivatives of propane.

Solution:



(i)

$Br-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3$

1, 1-Dibromopropane

(ii)

$CH_3-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-CH_3$

2, 2-Dibromopropane

(iii)

$Br-CH_2-\overset{\overset{Br}{|}}{CH}-CH_3$

1, 2-Dibromopropane

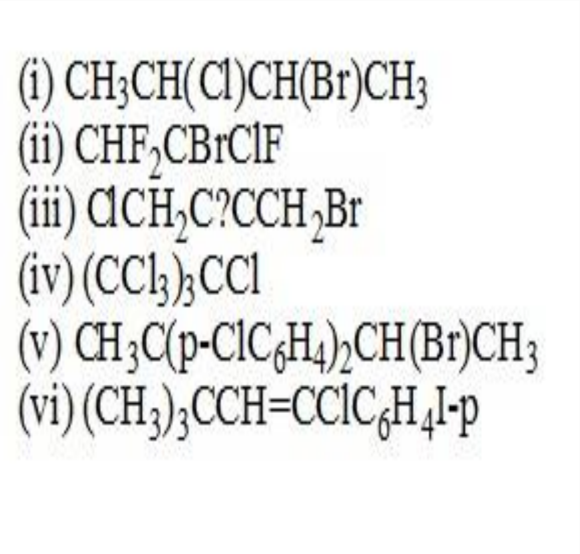
(iv)

$Br-CH_2-CH_2-CH_2-Br$

1, 3-Dibromopropane

Problem:

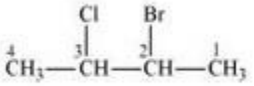
Give the IUPAC names of the following compounds:



(i) $CH_3CH(Cl)CH(Br)CH_3$
(ii) $CHF_2CBrClF$
(iii) $ClCH_2C?CCH_2Br$
(iv) $(CCl_3)_3CCl$
(v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$
(vi) $(CH_3)_3CCH=CClC_6H_4I\text{-}p$

Solution:

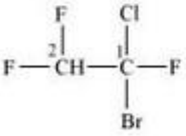
(i)



$\overset{4}{C}H_3-\overset{3}{C}H(Cl)-\overset{2}{C}H(Br)-\overset{1}{C}H_3$

2-Bromo-3-chlorobutane

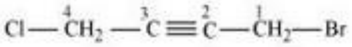
(ii)



$F-\overset{2}{C}H(F)-\overset{1}{C}(Cl)(Br)-F$

1-Bromo-1-chloro-1, 2, 2-trifluoroethane

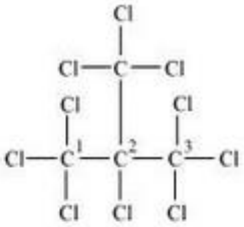
(iii)



$Cl-\overset{4}{C}H_2-\overset{3}{C}\equiv\overset{2}{C}-\overset{1}{C}H_2-Br$

1-Bromo-4-chlorobut-2-yne

(iv)

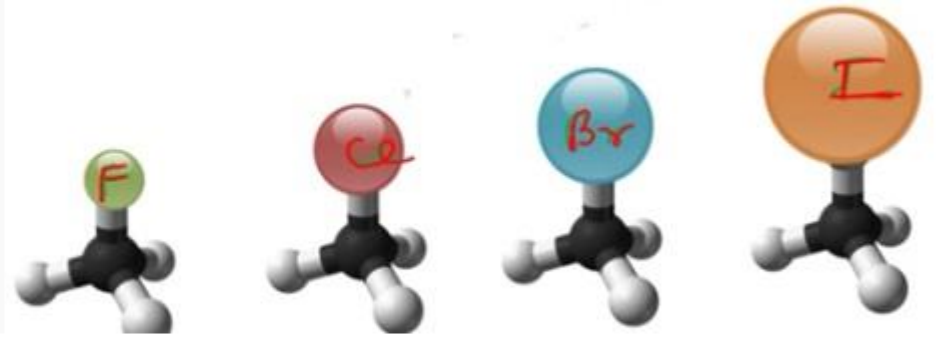


2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

Nature of C-X Bond

- Halogen atoms being more electronegative than carbon possess a polarized bond between the carbon halogen of alkyl halide.
- The carbon atom of the alkyl halide possesses a partial positive charge. The halogen atom on the other hand possesses a partial negative charge.

- The carbon-halogen bond length increases from C—F to C—I due to the increase in the size of halogen atom while going down the group in a periodic table from fluorine to iodine atom.



- Consequently the carbon-halogen bond length also increases from C—F to C—I.

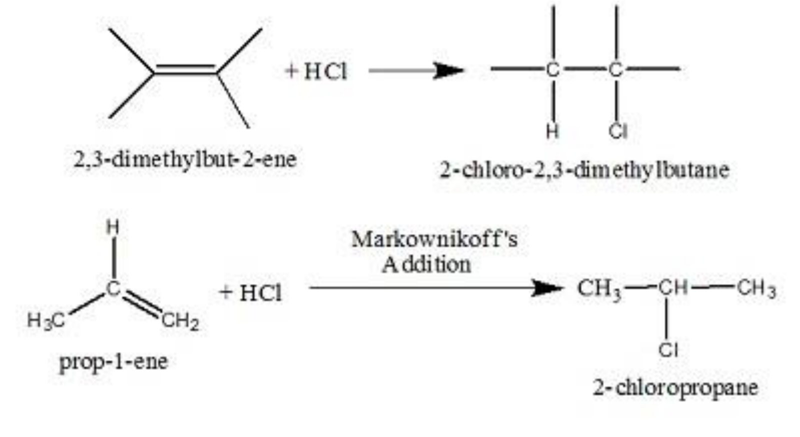
Bond	Bond length/pm	C-X Bond enthalpies/ kJmol⁻¹
CH_3–F	139	452
CH_3– Cl	178	351
CH_3–Br	193	293
CH_3–I	214	234

Methods of Preparation of haloalkanes

- **By halogenations of alkanes in presence of light, catalyst or heat:**

$$\underset{\text{Ethane}}{C_2H_6} + Cl_2/hv \longrightarrow \underset{\text{Chloroethane}}{C_2H_5Cl} + HCl$$

- **By halogenations of alkenes with HX :**

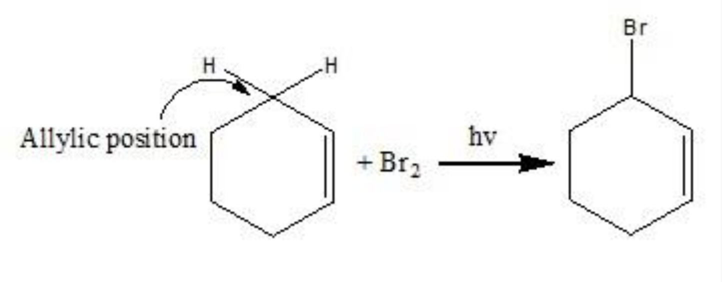


- **Hunsdiecker reactions:**

The Hunsdiecker reaction is an instance of a halogenation reaction which involves an organic between silver salts of carboxylic acids and halogens resulting in the formation of organic halides.

$$RCOOAg + Br_2 \longrightarrow RBr + CO_2 + AgBr$$

Allylic halogenations:



- **Preparation of alkyl halides from alcohols:**

Treatment of alcohol with HCl in the presence of anhydrous $ZnCl_2$ phosphorous pentachloride, PX_3(P_4 + X_2)or $SOCl_2$ leads to the preparation of alkyl halide.

1. By the action of halogen acids:

$$\underset{\text{Ethanol}}{CH_3CH_2OH + HCl} \xrightarrow{ZnCl_2} \underset{\text{Chloroethane}}{CH_3CH_2Cl + H_2O}$$

1 and 2 degree alcohols require anhydrous $ZnCl_2$ while alcohols do not require $ZnCl_2$. Mixture of conc. HCl and anhydrous $ZnCl_2$ is called Lucas reagent.

Primary and secondary alkyl chlorides are prepared from their respective alcohols by using HCl gas and anhydrous $ZnCl_2$.

1. By the action of phosphorous halides:

$3ROH + PX_3$ à $3RX + H_3PO_3$.

Alkyl chlorides can be synthesized by the action of PCl_3 or PCl_5.

1. Darzen method:

Darzens halogenation is a chemical processs involving the preparation of alkyl halides from alcohols by treating with reflux of thionyl chloride or bromide (SOX_2) in the presence of small quantity of a nitrogen base like tertiary amine or pyridine, or the equivalent hydrochloride.

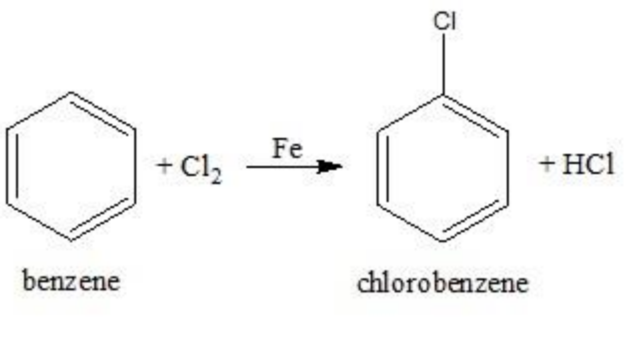
Alkyl bromides and iodides cannot be prepared by this method. The reason behind this is that thionyl bromide is unstable and thionyl iodide does not exist. This method is preferred for preparing alkyl chlorides because here by-products are gaseous SO_2 and HCl which escape easily. But this does not happen in the method involving phosphorous chloride; hence it is not used for preparing alkyl chlorides.

$$ROH + SOCl_2 \xrightarrow[\text{Reflux}]{\text{Pyridine}} RCl + SO_2 + HCl$$

Methods of Preparation of aryl halides

- **Nuclear halogenations:**

This method can be used to prepare aryl chlorides and bromides. This is done by treatment of arene with chlorine or bromine in the absence of sunlight and in the presence of halogen carrier like $AlCl_3$, $FeCl_3$ etc. at low temperatures. It is an electrophilic substitution.



- **From phenol:**

$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow[\text{or } SOCl_2]{HX,\ PX_3} \text{No Reaction}$$

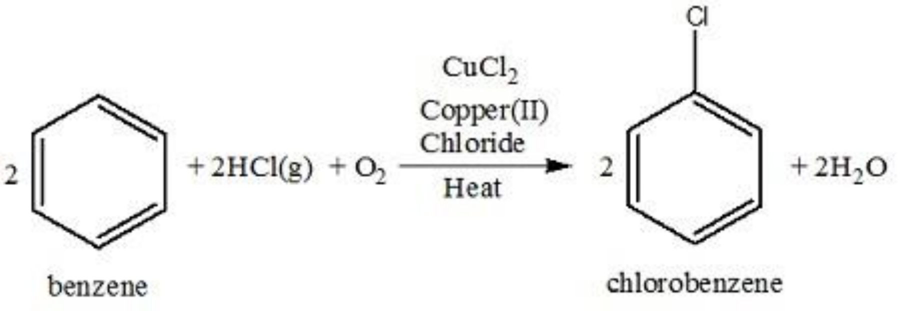
$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\substack{\text{Phosphorus}\\ \text{pentachloride}}}{PCl_5} \longrightarrow \underset{\text{chlorobenzene}}{C_6H_5Cl} + HCl + \underset{\substack{\text{Phosphoryl}\\ \text{Chloride}}}{POCl_3}$$

However the yield of Chlorobenzene is very poor as the main product is Triphenyl phosphate.

- **By Hunsdiecker reaction:**

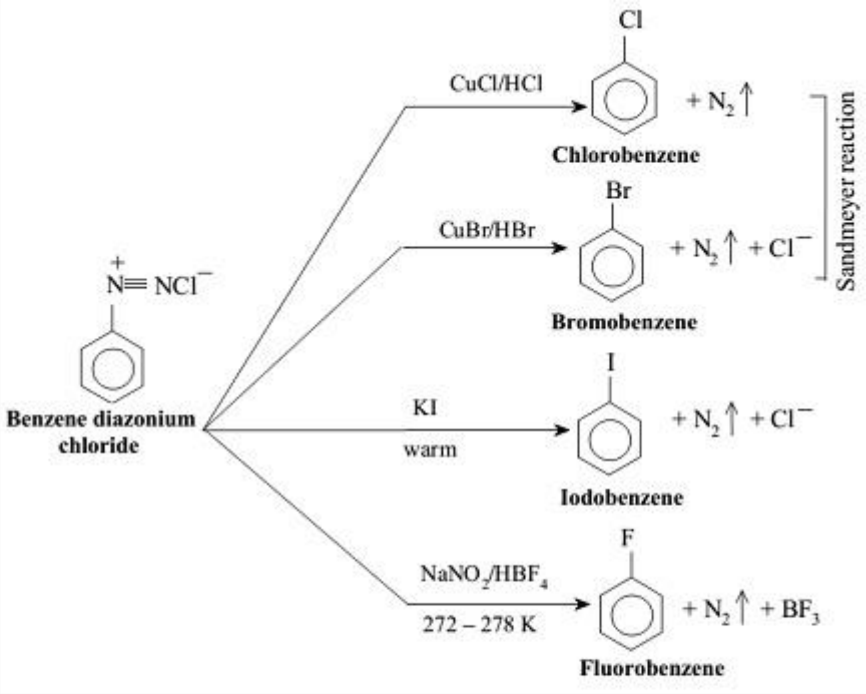
$$\underset{\text{Silver propionate}}{C_2H_5COOAg} + Br_2 \xrightarrow[CCl_4 \text{ as solvent}]{\text{Acetone or}} \underset{\text{Bromoethane}}{C_2H_5Br} + CO_2 + \underset{\text{Silver bromide}}{AgBr}$$

- **Raschig process:**



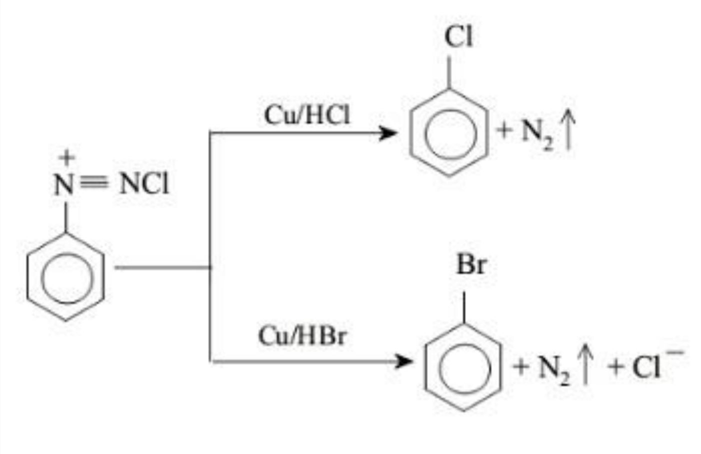
Sandmeyer reaction

Diazonium salts are highly reactive compounds used to prepare arene derivatives. Treating diazonium salt with copper (I) chloride (Cu_2Cl_2) or copper (I) bromide (Cu_2Br_2) leads to the formation of corresponding haloarene. This reaction is known as Sandmeyer reaction.



Gattermann reaction

Haloarenes can also be prepared by reaction of benzene diazonium chloride with copper powder in the presence of corresponding halogen acid. This reaction is termed as **Gattermann reaction**.

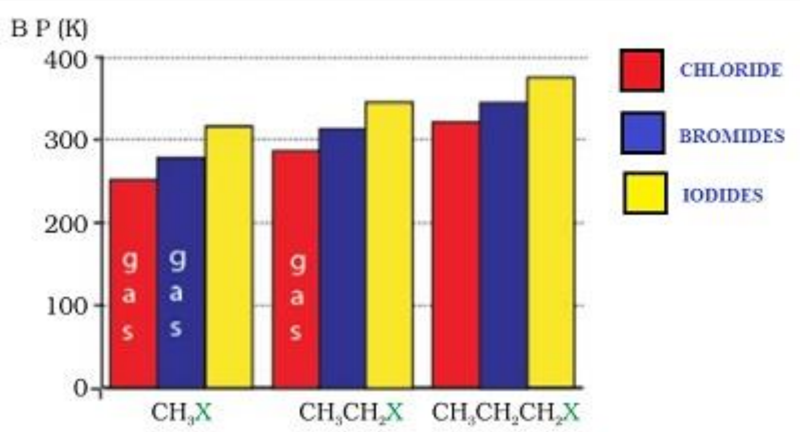


Physical Properties of halo alkanes

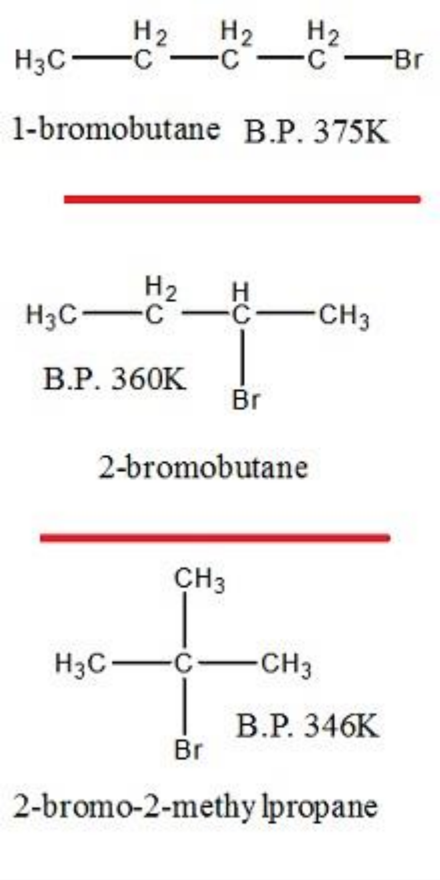
- Alkyl halides are colorless in pure state. Bromides and iodides cultivate colour on exposure to light
- Volatile halogen compounds possess a sweet smell.
- Intermolecular forces of attraction of halogen derivatives are stronger due to greater polarity and molecular mass as well compared to the parent hydrocarbon thereby resulting in higher boiling

points of chlorides, bromides and iodides compared to hydrocarbons of equivalent molecular mass.

- The boiling points of alkyl halides for same alkyl group follow the order: RI> RBr> RCl> RF due to the increase in size and mass of halogen atom thereby increasing the extent of van der Waal forces.



- In isomeric haloalkanes the boiling points decreases with increase in branching.



- *Para*-isomers possess high melting point compared to *ortho* and *meta*-isomers due to the symmetry of *para*-isomers fitting in crystal lattice better than *ortho*- and *meta*-isomers.
- Density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms. Consequently the density of Bromo, iodo and polychloro derivatives of hydrocarbons is greater than water.
- The haloalkanes are only very slightly soluble in water due to release of less energy during the setup of new attractions between the haloalkane and the water molecules which in turn is insufficient to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules.
- Haloalkanes dissolves easily in organic solvents due to the new intermolecular forces of attractions between haloalkanes and solvent molecules having equivalent strength as the one that is broken in separate haloalkane and solvent molecules.

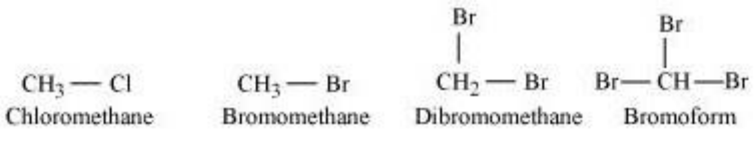
Problem:

Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

Solution:



Substitution reaction in halo alkanes

Nucleophilic substitution reactions are most common reactions of alkyl halides.

The most common nucleophiles are OH$^-$, CN$^-$, NO$_2^-$, SH$^-$, NH$_2^-$, OR$^-$ and RCOO$^-$

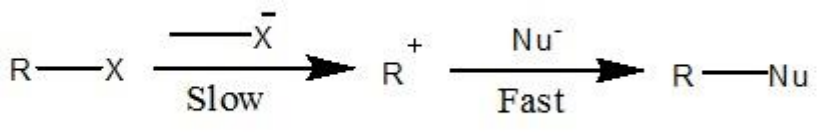
Following are some examples:

Nucleophilic substitution may take place in two ways:

1. SN1 Mechanism

2. SN2 Mechanism

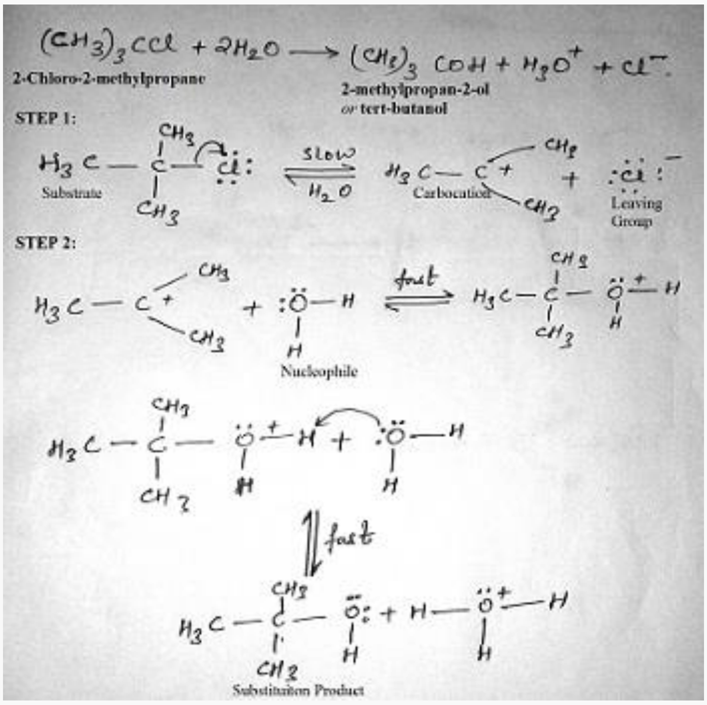
S$_N{}^1$ mechanism



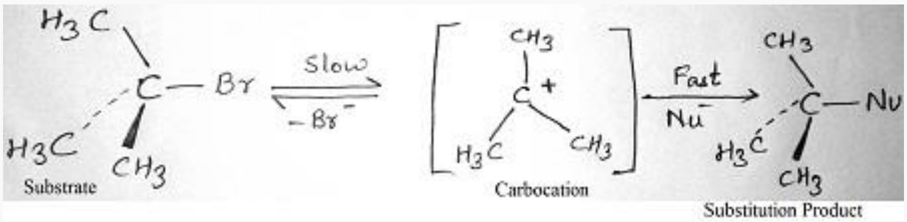
The tertiary alkyl halides react by S$_N{}^1$ mechanism via formation of carbocation as intermediate. The reactivity order for S$_N{}^1$ reaction is

Benzyl > Allyl > 3° > 2° > 1° > CH$_3$X.

A mechanism for the reaction of tert-butyl chloride with water apparently involves two steps:



Stereochemistry of SN^1:



Key features:

More stable will be the carbocation intermediate; faster will be the SN^1 mechanism.

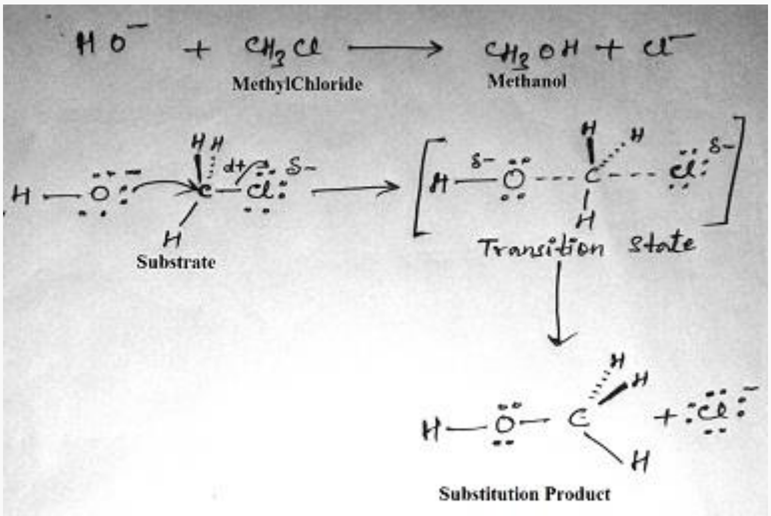
Polar solvents lead to polar transition state which in turn accelerates the SN^1 reaction.

If the initial compound is chiral then SN^1 reaction ends up with racemization of the product.

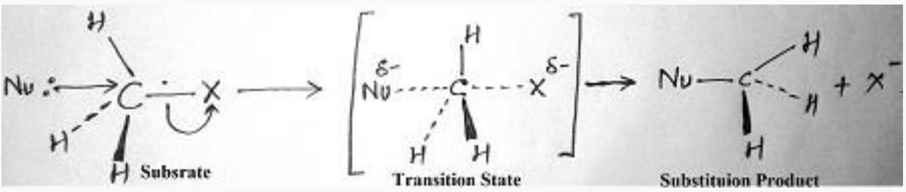
Weaker bases being leaving group favor SN^1 reaction.

S_N^2 mechanism

In case of S_N^2 reactions the halide ion leaves from the front side whereas the nucleophiles attacks from the back side; due to this reason S_N^2 reactions are always accompanied by the inversion of configuration. Thus formation of another enantiomer is lead by S_N^2 reaction of an optically active halide i.e. optical activity is retained but with opposite configuration.



Stereochemistry of SN^2:



Key features:

In SN^2 reaction the stereochemistry around carbon atom of the substrate undergoes inversion and is known as walden inversion.

The rate of reaction depends on the steric bulk of the alkyl group.

Increase in the length of alkyl group decreases the rate of reaction. Alkyl branching next to the leaving group decreases the rate drastically.

Under the following conditions S_N^1 and S_N^2 reactions take place:

- The alkyl is secondary and tertiary.
- The solvent is Protic or Aprotic.
- To stabilize the intermediate stage.

S_N^2 reaction and conditions required for it

Alkyl halide: S_N^2 reaction will be slowed down if there exists steric congestion around the carbon atom undergoing the inversion process.

$CH_3X > RCH_2X >> R_2CHX >>> R_3CX$

i.e. we conclude that if there is less congestion then the reaction will be faster.

Leaving group: the leaving group with a full negative charge is always expelled out. As a result the best leaving groups are those that can best stabilize an anion.

Solvent: Surroundings which the solvent surrounds can cause a reaction to go faster or slower. Solvent are of two types:

Protic solvent: Nucleophile suffers salvation in which Protic solvent hydrogen bonds with anion that tries to attack the alkyl halide thus creating a shield around the nucleophiles. As a result reaction is slowed down. E.g. Alcohol, water

Aprotic (polar) solvent: Aprotic solvents are those not capable of donating H's. Due to which it's favorable in SN^2 reaction because it's a 1step reaction and it doesn't require forming or having H's to stabilize the Carbocation step. E.g. Acetone, DMSO.

S_N^1 reaction and conditions required for it

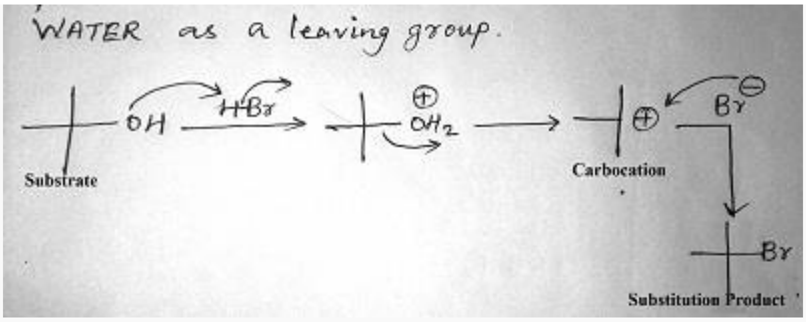
Alkyl halide:

S_N^1 reaction occurs faster if the carbocation intermediate is more stable and has a lower activation barrier.

3° carbocation > 2° carbocation > 1° carbocation.

Leaving group:

The leaving group with a full negative charge is always expelled out. As a result the best leaving groups are those that can best stabilize an anion. In this reaction, it will not be odd to consider water as a leaving group.



Solvent:

When a carbocation undergoes solvation it allows the carbocation to get surrounded by more electron density thereby making the +ve charge more stable. The solvent can be protic or Aprotic but it must be polar.

Nucleophiles:

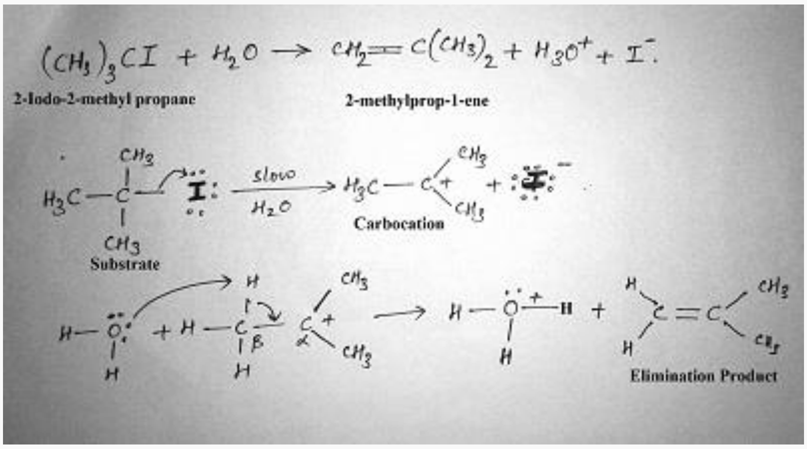
Those nucleophiles that undergo $S_N{}^1$ mechanism are weak neutral molecules. Any nucleophiles stronger than this is also a strong base that results in elimination reactions.

1. **Elimination reactions**:
2. This reaction involves the loss of two atoms or groups from the substrate as by product with formation of pi-bond. A halogen along with a hydrogen atom is removed from adjacent carbon atoms to form a double bond. This elimination introduces multiple bonds. It can be classified into E1 and E2 reaction.

E1 reaction

It is a unimolecular reaction. Rate determining step consist of formation of carbocation intermediate. Stability of carbocation intermediate determines the reactivity of E1 reaction.

Order of reactivity for E1 reaction is $3^0 > 2^0 > 1^0$. Both elimination and substitution reaction involves the use of (same reactive intermediate) carbocation. Therefore both the products are formed in comparable amount. This reaction is favored by entropy of reaction therefore increase in temperature favors the E1 reaction.



Stereochemistry of E1 reaction:

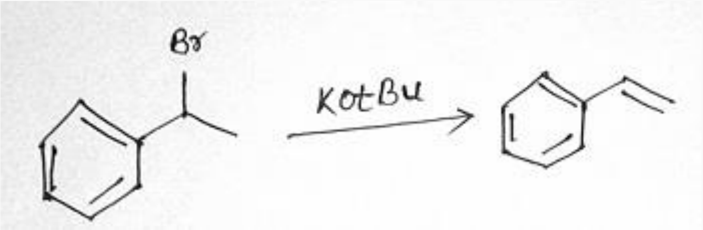
E1 eliminations generally lead to the more stable stereochemistry.

The rate of the E1 reaction depends only on the substrate, therefore more stable the carbocation is, faster will be the reaction. Slowest step is the formation of the carbocation. Alkenes formation doesn't require strong base, since there is no leaving group that needs to be displaced. So there is no requirement for the stereochemistry of the starting material;

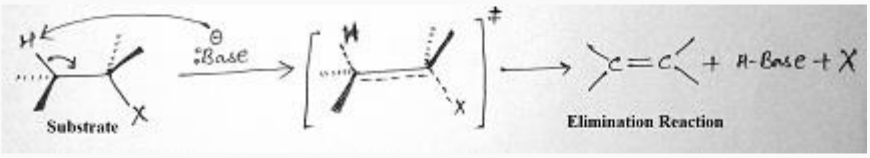
E2 reaction

It's a biomolecular reaction. It is a single step reaction whose rate depends on the concentration of base and substrate. Reactivity depends on both strength of base and nature of alkyl halide. Order of reactivity for E1 reaction is $3^0 > 2^0 > 1^0$. This reaction proceeds at room temperature.

Example:

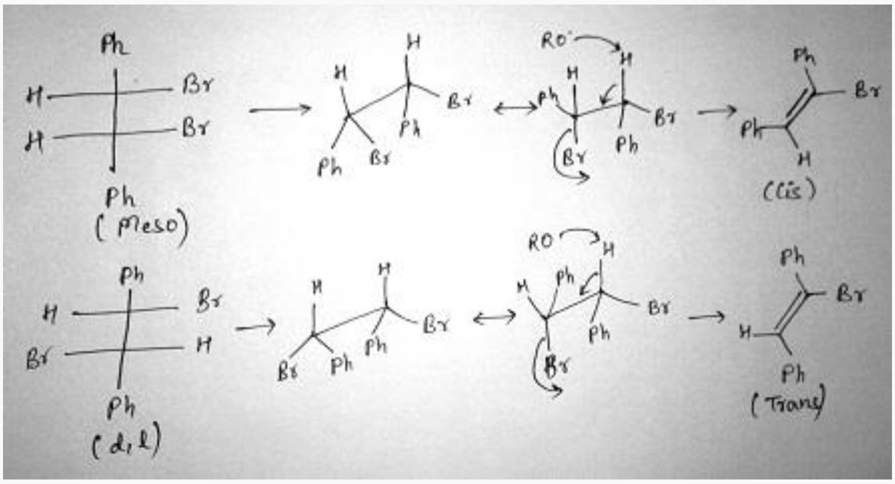


General mechanism:



Stereochemistry of E2 reaction:

E2 eliminations may or may not lead to the more stable stereochemistry. Initial material for this reaction has two sp^3 hybridized carbons which on rehybridization forms two sp^2 hybridized carbons. The C-X bond and the C-H bond lines up in the same plane and faces in anti directions to each other.



Conditions of E2 reaction:

The conditions favoring S_N^2 reaction favors E2 reactions which are as follows:

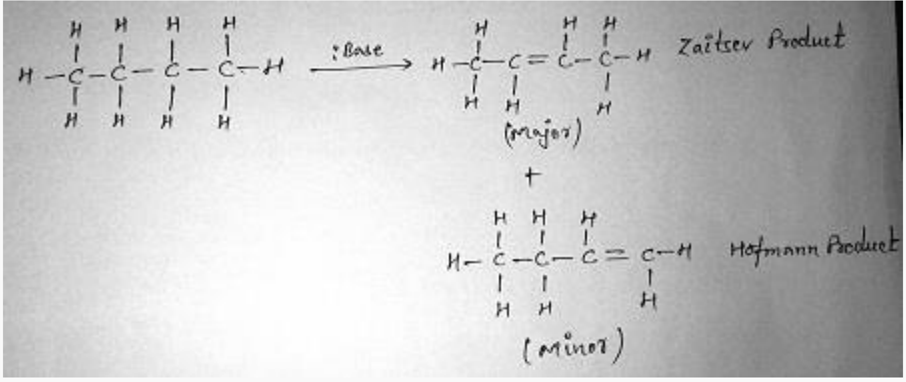
Alkyl halide: S_N^2 reaction will be slowed down if there exists steric congestion around the carbon atom undergoing the inversion process.

i.e. we conclude that if there is less congestion then the reaction will be faster.

$CH_3X > RCH_2X >> R_2CHX >>> R_3CX$

Leaving group: the leaving group with a full negative charge is always expelled out. As a result the best leaving groups are those that can best stabilize an anion.

Solvent: Surroundings which the solvent surrounds can cause a reaction to go faster or slower. Solvent are of two types:

1. Protic solvent: Nucleophile suffers salvation in which protic solvent hydrogen bonds with anion that tries to attack the alkyl halide thus creating a shield around the nucleophiles. As a result reaction is slowed down. E.g. Alcohol, water
2. Aprotic (polar) solvent: Aprotic solvents are those not capable of donating H's. Due to which it's favorable in SN^2 reaction because it's a 1step reaction and it doesn't require forming or having H's to stabilize the Carbocation step. E.g. Acetone, DMSO.
3. <u>**Saytzeff's rule of elimination:**</u>
4. According to this rule although alkene synthesis leads to the formation of more than one product, the more substituted alkene is the major product.
5. 

<u>Conditions of E1 reaction:</u>

The factors that favors S_N^1 reaction also favors E1 reaction which are as follows:

Alkyl halide:

E1 reaction occurs faster if the carbocation intermediate is more stable and has a lower activation barrier.

3° carbocation > 2° carbocation > 1° carbocation.

Leaving group:

The leaving group with a full negative charge is always expelled out. As a result the best leaving groups are those that can best stabilize an anion. In this reaction, it will not be odd to consider water as a leaving group.

Solvent:

When a carbocation undergoes solvation it allows the carbocation to get surrounded by more electron density thereby making the +ve charge more stable. The solvent can be protic or Aprotic but it must be polar.

Nucleophiles:

Those nucleophiles that undergo E1 mechanism are weak neutral molecules. Any nucleophiles stronger than this is also a strong base that results in elimination reactions.

Like the E2 reaction, the E1 favors the Zaitsev product (always).

Comparison of S_N^1, S_N^2, E1 and E2

1. **E1 and E2**

E2 reaction is favored by strong base whereas strength of base doesn't determine whether the reaction will be favored or not.

Order of reactivity is same for both the reaction i.e. 3° > 2° > 1°.

E1 reaction is favored by polar protic solvent because it accelerates the reaction by solvating halide ion forming carbonium ion whereas E2 reaction is decelerated by polar protic solvent.

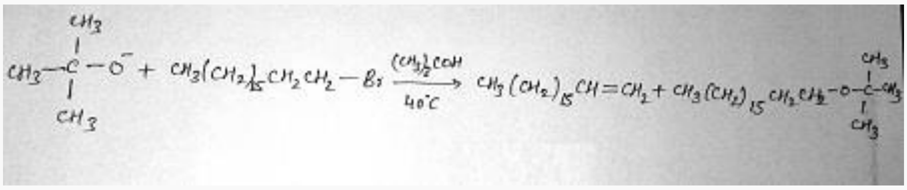
E2 reaction is favored at room temperature whereas E1 reaction requires little higher temperature.

2. **S_N^2 and E2**

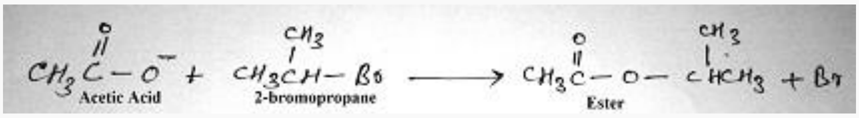
High concentration of a strong nucleophiles or base favors both the reactions.

Increase in temperature favors elimination over substitution. They are entropically favored over substitution due to the fact that products of elimination are greater in number than the reactants and increase in temperature increases the entropy effect. This is due to the relation $\Delta G^0 = \Delta H^0 - T\Delta S^0$.

Another way to influence the elimination reaction is to strong sterically hindered base. In the reaction mentioned below E2 reaction is 85 % whereas S_N^2 is 15%



Using a strong and slightly polarized base such as amide ion, alkoxide ion influences the elimination reaction.



3. **S_N^1 and E1**

E1 reactions are favored by the use of substrates that can form stable carbocation. They are also favored by the use of polar solvents. At lower temperature S_N^1 is favored over E1 reaction.

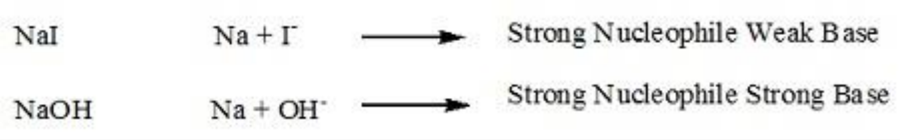
Strong nucleophile & Weak Nucleophile

Strong nucleophile

Usually anions with a full negative charge and no steric hindrance. Nucleophilicity increase with increase in charge density. For example, NaOR, RLi, NaOH or KOH, NaCN or KCN, NaCCR, $NaNH_2$, NaNHR, NaI, LiBr, KI, NaN_3.

Weak Nucleophile: Neutral. For example,

Basicity and Nucleophilicity essentially describe same phenomenon, except basicity concerns donation of lone pair of hydrogen and Nucleophilicity concerns donations of lone pair to all other atoms.



NaI	$Na + I^-$	$\longrightarrow$	Strong Nucleophile Weak Base
NaOH	$Na + OH^-$	$\longrightarrow$	Strong Nucleophile Strong Base

Organometallic Compounds

Most organic chlorides and iodides react with certain metals to give compounds containing carbon-metal bonds called organo-metallic compounds.

For example, RMgX is referred to as Grignard Reagent in 1900 by Victor Grignard.

Carbon-magnesium n=bond is covalent but highly polar.

Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons.

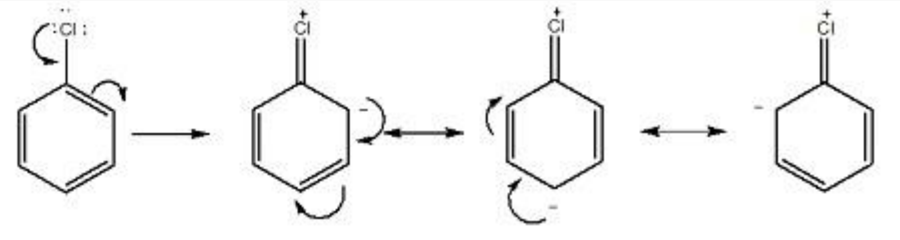
Chemical properties:

It involves

1. Nucleophile Substitution
2. Elimination Reaction
3. Reaction with metals

Nucleophilic Substitution: Resonance effect

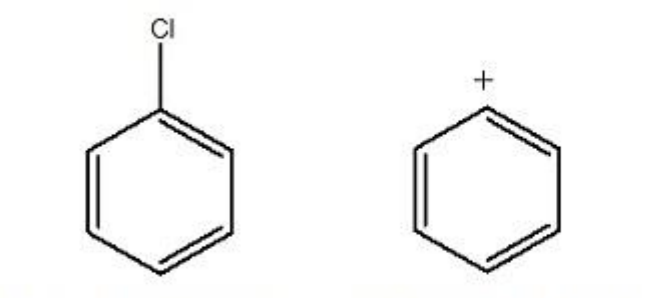
Aryl halides are extremely less reactive towards Nucleophilic substitution reactions. Let us now discuss resonance effect.



Nucleophilic Substitution:sp_2 hybridised

C-X bond in halo alkane is 177 Pico meter. Whereas C-X bond in haloarenes is 169 Pico meter. Therefore the C-x bond in haloarenes is strong and stable and hence difficult to break. Hence the Nucleophilic substitution in haloarenes is difficult.

Nucleophilic Substitution: unstable cation



Resonating Structure
Stable

No resonating Structure
Unstable

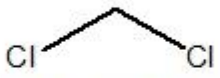
In figure II resonance structure is not possible. Cation formation is not possible as the cation is unstable.

This shows that S_N^1 is totally ruled out.

S_N^2 is possible.

Polyhalogen Compounds

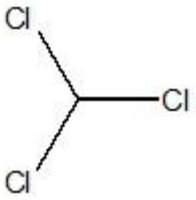
Dichloromethane **(Methylene chloride)**



Methylene chloride

- It is used as solvent, paint remover, propellant in aerosols, process solvent in the manufacture of drugs.
- It is used as metal cleaning and finishing solvent.
- But human beings can be adversely affected when exposed to Methylene
- It causes harm to human mental health.
- Human exposure to even lower levels of mythlene chloride in air can lead to dizziness, nausea, tingling, numbness in fingers and toes, etc.
- Direct exposure to Methylene **chloride** can cause intense burning and mild redness in the skin.
- Cornea of eyes can be adversely burnt on direct exposure to Methylene

Trichloromethane **(Chloroform)**



Chloroform

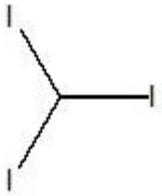
- Chloroform is a sweet smelling, heavy and colorless liquid. It has low B.P. of 61°
- It is insoluble in water but soluble in organic solvents.
- If it is inhaled it causes unconsciousness.

- It is used as anesthetic because when pure chloroform is inhaled it affects the heart due to which after mixing with ether and other suitable anesthetics chloroform can be used as anesthetic.
- Chloroform on oxidation in air leads to the formation of phosgene which is a poisonous gas due to which it should be stored in a dark colored bottle.

$$CHCl_3 + 1/2\ O_2 \xrightarrow{\text{light}} COCl_2 + HCl$$

- Before using chloroform as an anesthetic it is tested with $AgNO_3$. Poisonous chloroform gives white precipitate with $AgNO_3$.

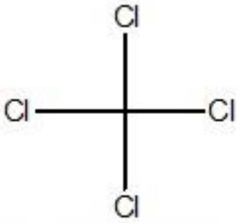
Triiodomethane **(Iodoform)**



Iodoform

- They are used as an antiseptic due to the liberation of free iodine. It is not because of Iodoform itself.
- But due to the offensive smell it was replaced by some other solutions that contain iodine.

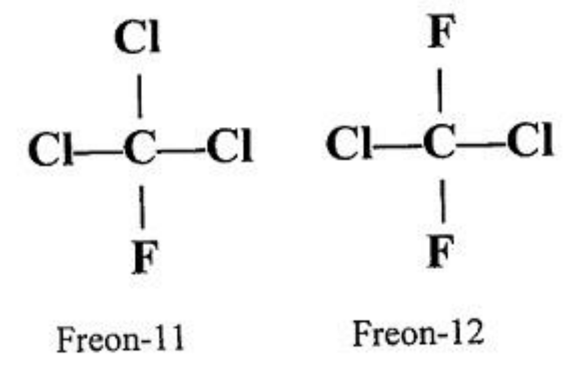
Tetra chloromethane **(Carbon tetrachloride)**



Carbon tetrachloride

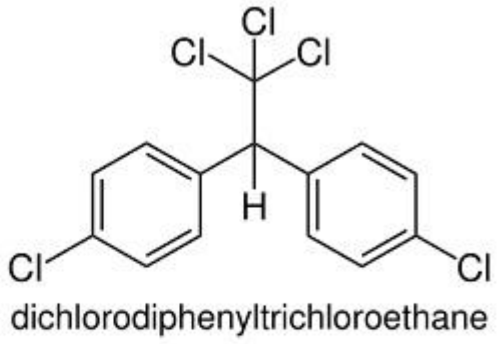
- They are used in manufacturing refrigerants and propellants for aerosol cans.
- They are also used for the synthesis of chlorofluorocarbons, pharmaceutical etc.
- It was extensively used as cleaning agent in industry and as a degreasing agent at home as well.
- It is also used as a spot remover and fire extinguisher.
- Exposure to $CCl4$ can adversely affect the heart beat and make it beat irregularly or make it permanently stop.
- Exposure to eyes can cause irritation.
- Exposure to atmosphere can lead ozone depletion that may lead to rise in the level of exposure to ultraviolet rays. This in turn leads to increased risk of skin cancer, eye diseases and other disorders as well as weakened immune system.

Freons



- The chlorofluorocarbon compounds of methane and ethane are jointly called freons.
- They are very stable, non-corrosive, non-toxic, and unreactive liquefiable gases.
- Freon 12 (CCl_2F_2) is most commonly used Freons in industrial sector.
- Freons are manufactured from tetra chloromethane using Swarts reaction.
- Freons are extensively used in aerosol propellants, refrigerants and air conditioners.

***p,p’*-Dichlorodiphenyltrichloroethane(DDT)**



- DDT stands to be the first chlorinated organic insecticides originally discovered in 1873 which was then further studied and it was 1939 when Paul Muller discovered the effectiveness of DDT as an insecticide.
- It is highly poisonous to all living organisms as it does not get metabolized rapidly by animals and gets deposited and stored in the fatty tissues.

Problem:

Write structures of the following compounds:

(i) 2-Chloro-3-methylpentane

(ii) 1-Chloro-4-ethylcyclohexane

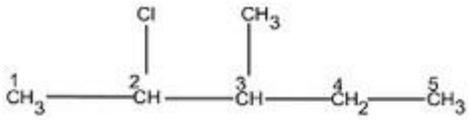
(iii) 4-tert. Butyl-3-iodoheptane

(iv) 1,4-Dibromobut-2-ene

(v) 1-Bromo-4-sec. butyl-2-methylbenzene

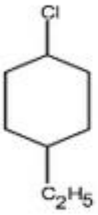
Solution:

(i)



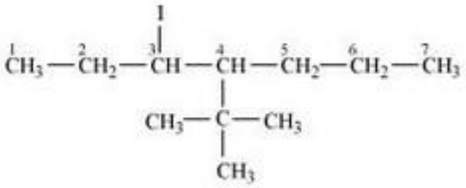
2-Chloro-3-methyl pentane

(ii)



1-Chloro-4-ethylcyclohexane

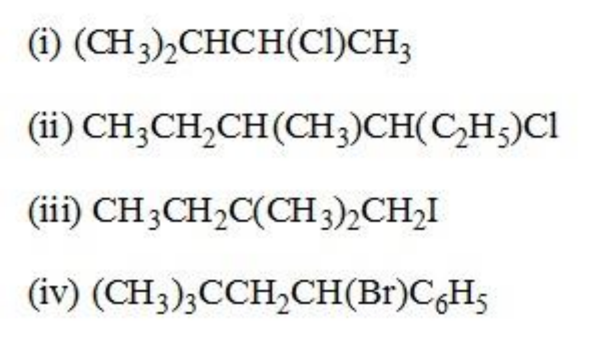
(iii)



4- tert-Butyl-3-iodoheptane

Problem:

Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:



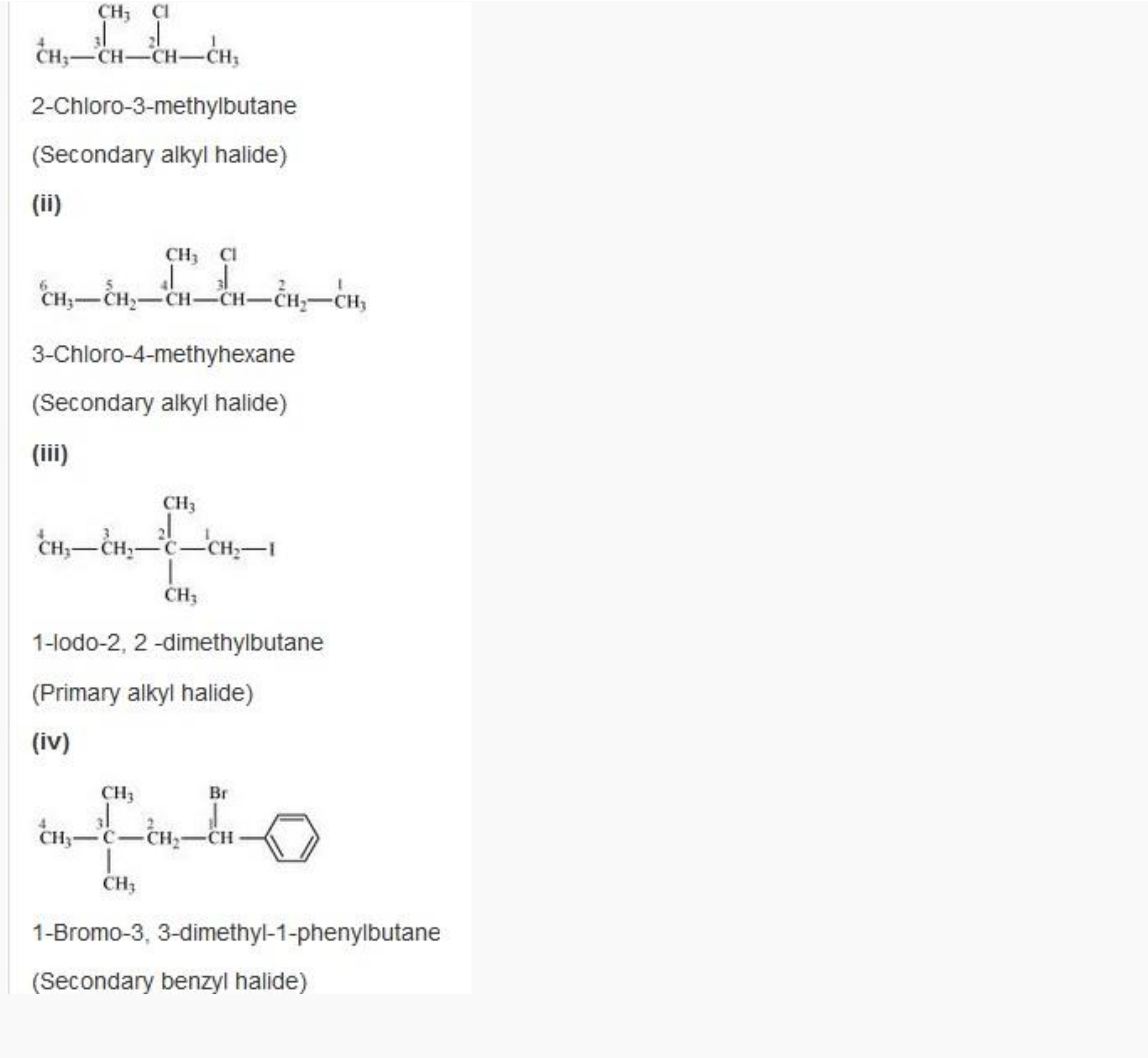
(i) $(CH_3)_2CHCH(Cl)CH_3$

(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$

(iii) $CH_3CH_2C(CH_3)_2CH_2I$

(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$

Solution:



$\overset{4}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{3}{C}}H-\overset{\overset{Cl}{|}}{\overset{2}{C}}H-\overset{1}{C}H_3$

2-Chloro-3-methylbutane

(Secondary alkyl halide)

(ii)

$\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{\overset{CH_3}{|}}{\overset{4}{C}}H-\overset{\overset{Cl}{|}}{\overset{3}{C}}H-\overset{2}{C}H_2-\overset{1}{C}H_3$

3-Chloro-4-methyhexane

(Secondary alkyl halide)

(iii)

$\overset{4}{C}H_3-\overset{3}{C}H_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{2}{C}}}-\overset{1}{C}H_2-I$

1-Iodo-2, 2 -dimethylbutane

(Primary alkyl halide)

(iv)

$\overset{4}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{3}{C}}}-\overset{2}{C}H_2-\overset{\overset{Br}{|}}{\overset{1}{C}}H-C_6H_5$

1-Bromo-3, 3-dimethyl-1-phenylbutane

(Secondary benzyl halide)

11. Alcohols, Phenols and Ethers

Introduction of alcohol

It belongs to category of groups which when attached to a carbon chain governs the properties of organic compound or in other words we can say it is a functional groups. They are indicated by presence of—OH group in a chain .This -OH is regarded as hydroxyl group.

Functional group – OH

Suffix used: “ol”

Examples: Its homologous series is :

Methanol (CH_3OH)

Ethanol (C_2H_5OH)

Propanol (C_3H_7OH)

Butanol (C_4H_9OH)

Pentanol ($C_5H_{11}OH$) and so on.

Classification of alcohols

We can classify alcohols on the basis of different factors:

- Number of hydroxyl groups attached , hybridization ,number of alkyl groups attached to alpha carbon (alpha carbon is that which has functional groups attached to it)

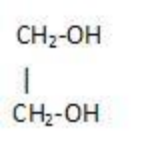
1. **On the basis of number of -OH(hydroxyl) group attached we have :**

- **Monohydric alcohols**: They are those that have only one hydroxyl group attached.

Example: methanol (CH_3OH) ethanol (C_2H_5OH) and more

- **Dihydric alcohols**: They have two hydroxyl groups attached.

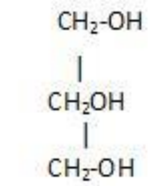
Example: ethylene-glycol



$$\begin{array}{l} CH_2\text{-}OH \\ | \\ CH_2\text{-}OH \end{array}$$

- **Polyhydric alcohol**: That have three or more hydroxyl groups in it.

Example glycerol



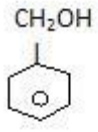
(propan -1,2,3- triol)

(2). Based on the type of hybridization:

- It can be sp^3 like ethanol - CH_3-CH_2-OH
- Another **example :**

It can be sp^2 like Benzyl alcohol-

In this second carbon is alpha carbon and that is sp^3



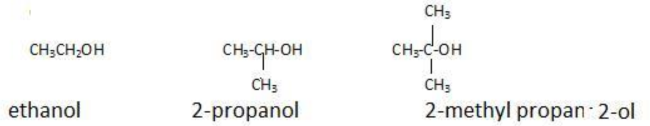
(Benzyl alcohol)

Allyl alcohol CH_2=CH- CH_2OH (In it also alpha carbon is sp^3 hybridised).

Another type of hybridization they possess is sp^2

Example: Phenol C_6H_5OH, Vinyl alcohol CH_3-CH_2=CH-OH etc

(c) Classification is on the basis of primary secondary or tertiary carbon atom (alpha carbon)



1^0 2^0 3^0

Preparation of alcohols:

It can be prepared by following methods:

1. **From Haloalkane:** When any haloalkane reacts with aqueous KOH it undergoes nucleophilic substitution and leads to the formation of alcohol and potassium halide .

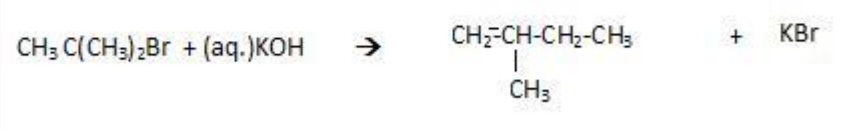
$$RX + KOH(aq.) \rightarrow ROH + HX$$

Example: $CH_3CH_2Br + (aq.)KOH \rightarrow CH_3CH_2OH + KBr$

(Bromoethane) (ethanol)

If we take secondary alcohol than secondary alcohol potassium halide and traces of alkenes is formed.

Example: If we take tertiary alkyl halide then on reacting with KOH we get alkene as major product and potassium halide.



$$CH_3C(CH_3)_2Br + (aq.)KOH \rightarrow \underset{\substack{|\\CH_3}}{CH_2{=}C}H\text{-}CH_2\text{-}CH_3 + KBr$$

(2-methyl butene)

2. **By reduction of aldehyde and ketones:** Whenever we reduce aldehyde or ketones in presence of reducing agent like Ni, Pd ,Pt, $LiAlH_4$ etc we get alcohol .

For example: $CH_3CHO + H_2 \rightarrow CH_3CH_2OH$

(ethanal) (ethanol)

$CH_3COCH_3 + H_2 \rightarrow CH_3\text{-}CH(CH_3)\text{-}OH$

(propanone) (2-propanol)

We can’t produce tertiary alcohol by this method.

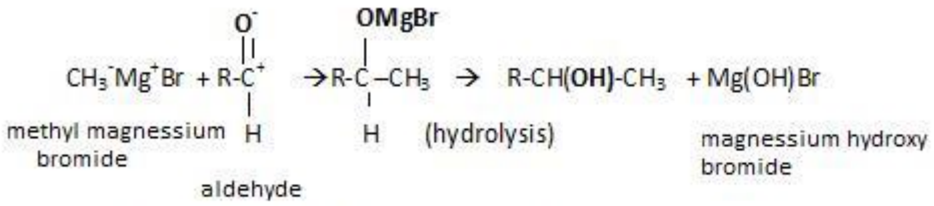
3. **By reduction of carboxylic acid:** Whenever we reduce carboxylic acid in presence of reducing agent it forms respective alcohol as shown

$RCOOH + H_2 \rightarrow RCOH$

$CH_3COOH + H_2 \rightarrow CH_3CH_2OH$

(ethanoic acid) (ethanol)

4. **From Grignard reagent i.e RMgX**



$$CH_3^-Mg^+Br + R\text{-}\overset{\overset{O^-}{||}}{\underset{\underset{H}{|}}{C^+}} \rightarrow R\text{-}\overset{\overset{OMgBr}{|}}{\underset{\underset{H}{|}}{C}}\text{-}CH_3 \rightarrow R\text{-}CH(OH)\text{-}CH_3 + Mg(OH)Br$$

Grignard reagent +HCHO → primary alcohol
(Formaldehyde)

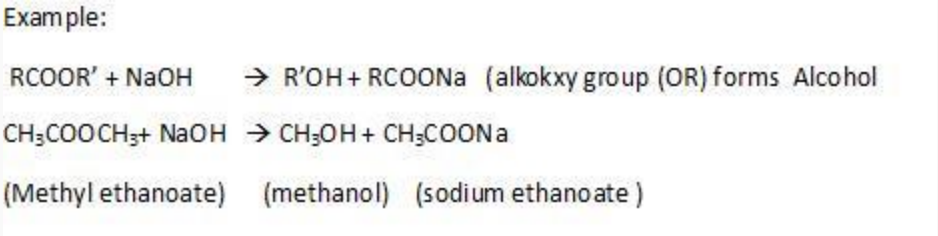
Grignard Reagent +any other aldehyde →secondary alcohol

Grignard Reagent + Ketone → 3^*alcohol,

$R^-Mg\,X + HCHO \rightarrow RCH_2OMgX \rightarrow CH_3CH_2OH$

- Please remember whenever Grignard reagent reacts with formaldehyde it forms primary alcohol.
- When Grignard reagent reacts with any other alcohol it forms secondary alcohol.
- When Grignard reagent reacts with ketone it forms tertiary alcohol.

5. **By hydrolysis of ester:** Whenever ester reacts with caustic soda or water it forms alcohol and sodium salt of carboxylic acid.



Example:

$RCOOR' + NaOH \rightarrow R'OH + RCOONa$ (alkokxy group (OR) forms Alcohol

$CH_3COOCH_3 + NaOH \rightarrow CH_3OH + CH_3COONa$

(Methyl ethanoate) (methanol) (sodium ethanoate)

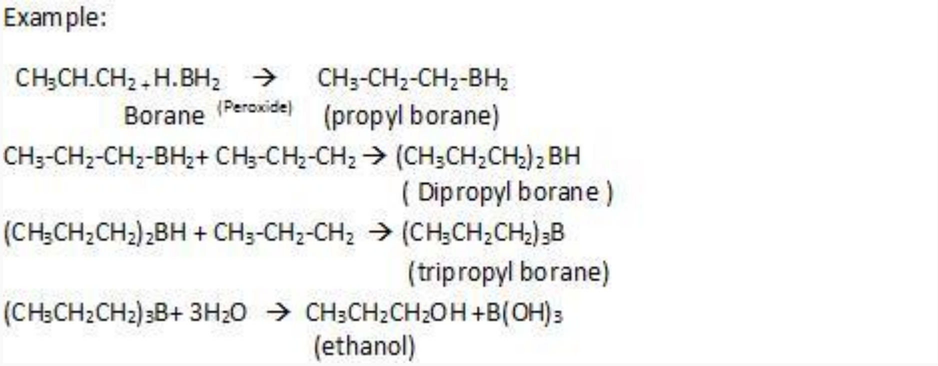
6. **From alkenes: by their acidic hydration**

$C_2H_4 + H_2O \rightarrow CH_3CH_2OH$

(Ethene) (H^+) (ethanol)

Another method employed for alkenes is: Hydroboration oxidation reaction

In this we add BH_3 to unsymmetrical alkenes:



Example:

$CH_3CH.CH_2 + H.BH_2 \rightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}BH_2$

Borane (Peroxide) (propyl borane)

$CH_3\text{-}CH_2\text{-}CH_2\text{-}BH_2 + CH_3\text{-}CH_2\text{-}CH_2 \rightarrow (CH_3CH_2CH_2)_2BH$

(Dipropyl borane)

$(CH_3CH_2CH_2)_2BH + CH_3\text{-}CH_2\text{-}CH_2 \rightarrow (CH_3CH_2CH_2)_3B$

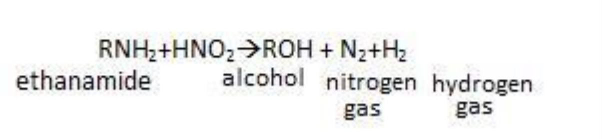
(tripropyl borane)

$(CH_3CH_2CH_2)_3B + 3H_2O \rightarrow CH_3CH_2CH_2OH + B(OH)_3$

(ethanol)

7. **From aliphatic primary amines:** Whenever amine reacts with nitrous acid in presence of $NaNO_2$ and HCl it forms respective alcohol and nitrogen gas and water.

Example:



$RNH_2 + HNO_2 \rightarrow ROH + N_2 + H_2$

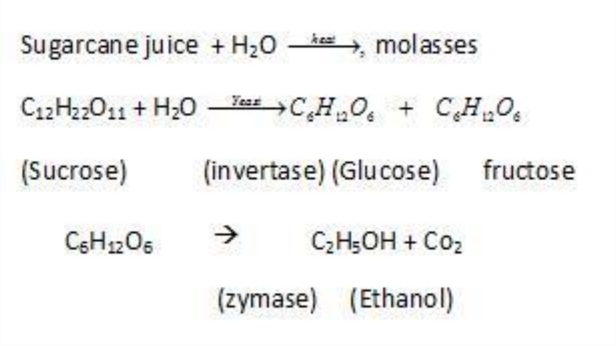
ethanamide alcohol nitrogen gas hydrogen gas

Industrial preparation of alcohol is by two methods: Hydration of alkene and fermentation of sugar (used in breweries)

1. **Fermentation** - Breakdown of complex substance into simple substance by action of enzymes released by anaerobic bacteria.

- By this method we can prepare only ethanol.
- In this firstly the sugarcane juice and water are mixed and heated to form sweet liquid called molasses.

- Then in presence of yeast and enzyme invertase it breaks in to glucose and fructose and then further glucose and fructose break into further simpler substances called ethanol and carbon dioxide.
- This method is generally carried out in breweries.



$$\text{Sugarcane juice} + H_2O \xrightarrow{heat}, \text{molasses}$$

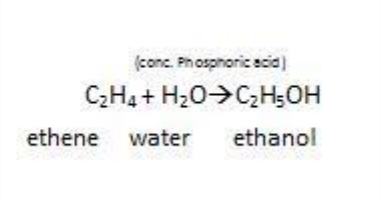
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Yeast} C_6H_{12}O_6 + C_6H_{12}O_6$$

(Sucrose) (invertase) (Glucose) fructose

$$C_6H_{12}O_6 \rightarrow C_2H_5OH + Co_2$$

(zymase) (Ethanol)

2. **Hydration of alkene**: This is a method by which any alcohol can be prepared and accordingly we take member of alkene. Suppose we need to prepare ethanol than we need to take ethene. When water is added to ethene in presence of some weak acid like phosphoric acid then ethene undergoes addition reaction and leads to formation of ethanol.



$$C_2H_4 + H_2O \xrightarrow{\text{(conc. Phosphoric acid)}} C_2H_5OH$$

ethene water ethanol

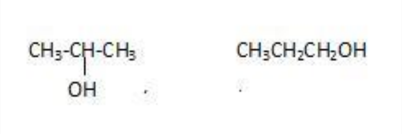
Isomerism in alcohols

Isomerism in alcohols: They basically show

- Position isomerism
- Chain isomerism
- Functional isomerism
- Optical isomerism

Position: In this the position of –OH group changes.

Examples:

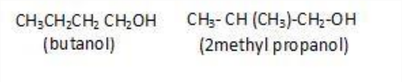


$$CH_3\text{-}\underset{|\\OH}{CH}\text{-}CH_3 \qquad CH_3CH_2CH_2OH$$

(2-propanol) (Propanol)

CHAIN ISOMERISM: In this the number of carbon atom in parent chain is going to be different.

Example



$CH_3CH_2CH_2CH_2OH$ (butanol) $CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}OH$ (2methyl propanol)

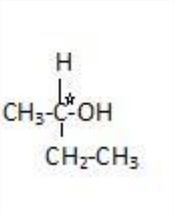
Functional isomerism: they are functional isomer of alcohol & ether

Example: $CH_3CH_2CH_2OH$ and $CH_3CH_2O\ CH_3$ are functional isomers

(Propanol) (Methoxy ethane)

Optical Isomerism: they also show optical isomerism but there should be a chiral centre

Like: in the given molecule of alcohol



$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_2-CH_3}{C^*}}-OH$$

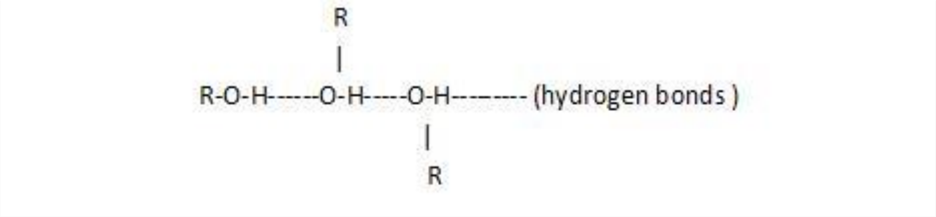
(2-butanol)

(In this there is the chiral centre marked as C* as it has different groups attached to it).

PHYSICAL PROPERTIES OF ALCOHOL

1. **State of existence:** Lower members are colorless liquids with characterize smell. Higher members with more than 12 carbons are solid
2. **Boiling point:** They have high boiling points due to hydrogen bonding.

- If we compare their boiling points with hydrocarbons they will possess higher boiling point because of existence of hydrogen bonds in them due to which they occur at associated molecules.



$$R-O-H\text{-----}\overset{\displaystyle R}{O}-H\text{----}\underset{\displaystyle R}{O}-H\text{--------}$$

- It is noted that boiling point increase with increase in carbons in chain: As no. of carbon atoms increases Vander wall force increases hence boiling point increases.

Example:

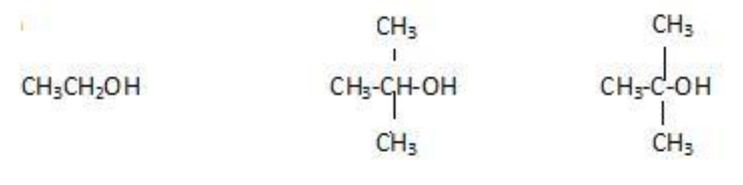
- If we look for the molecule of alcohol out of them with higher boiling point than :

$CH_3CH_2CH_2OH$ AND $CH_3CH_2CH_2\ CH_2CH_2OH$

The Second compound will definitely have the higher boiling point as it has more number of carbon atoms.

- Boiling point decreases with branching: as surface area gets reduced therefore Vander wall force decrease and boiling point also decreases.

Example: If we look for the molecule of alcohol out of them with higher boiling point than:



(Primary) (Secondary) (Tertiary)

The one degree will have higher boiling point as it has more surface area.

3. **Solubility:** They are soluble in water due to formation of hydrogen bonds in them .However solubility decreases with increase in number of carbon atoms in chain as non polar part increases therefore solubility decreases.

Example: If we look for the molecule of alcohol out of them with higher solubility than:

$CH_3CH_2CH_2OH$ and $CH_3CH_2CH_2 CH_2CH_2OH$

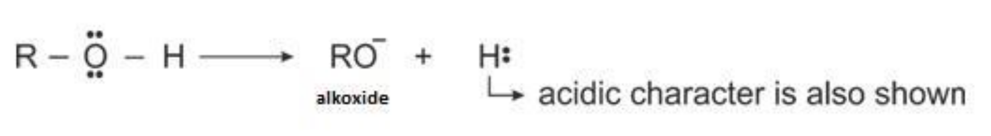
The second one will have lower solubility because the non polar part is more in it.

Chemical properties of alcohols

Alcohol is most versatile organic compound. They can behave in different manner to give different reaction. Three type of reaction we will study

1. Alcohol behaves as nucleophiles

They are electron rich species



2. Alcohols behave as electrophile

Electron deficient

Carbocation is formed

R-OH --> R^+ + OH^-

alcohol carbocation Hydroxide ion

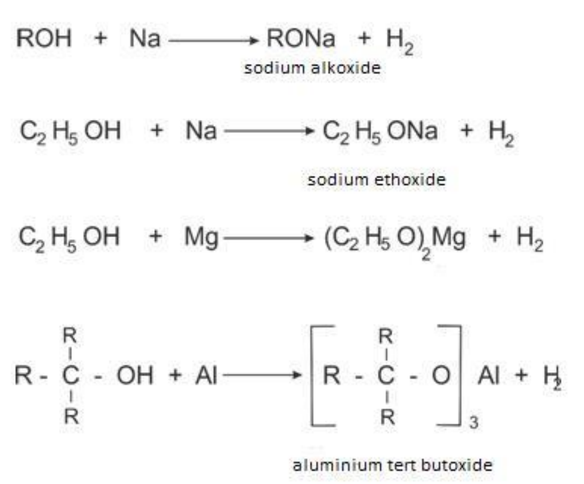
Mixed reaction

Involving alkyl and OH group

1. **Reaction as nucleophiles**

It shows their acidic character.

1. Reaction with active metals



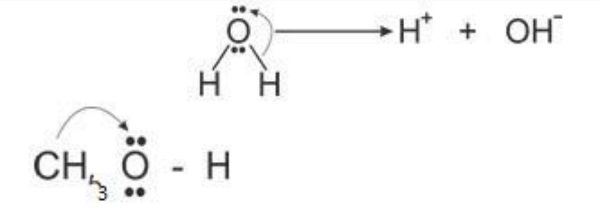
$$ROH + Na \longrightarrow \underset{\text{sodium alkoxide}}{RONa} + H_2$$

$$C_2H_5OH + Na \longrightarrow \underset{\text{sodium ethoxide}}{C_2H_5ONa} + H_2$$

$$C_2H_5OH + Mg \longrightarrow (C_2H_5O)_2Mg + H_2$$

$$R-\overset{R}{\underset{R}{C}}-OH + Al \longrightarrow \underset{\text{aluminium tert butoxide}}{\left[R-\overset{R}{\underset{R}{C}}-O\right]_3 Al} + H_2$$

Comparison of acidic character of H_2O with alcohol.



In alcohols R is electron releasing group which increases electron density on oxygen and pass of electron from O-H bond to O becomes difficult due to +inductive effect. Therefore water is more acidic than alcohols.

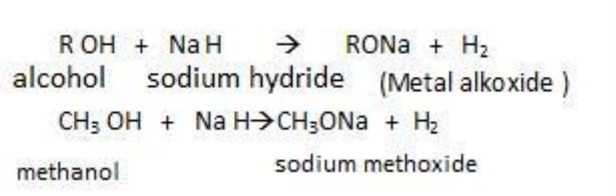
Order of reactivity as nucleophile /acidic strength

1. If we compare acidic strength of primary, secondary and tertiary alcohols we found that more the alkyl groups attached, more they release electrons and more is the difficulty in loosing H^+

Primary Alcohols (Less Acidic), Secondary Alcohols(Acidic) and Teritary Alcohols(Most Acidic)

Here are some reactions showing acidic strength of alcohols:

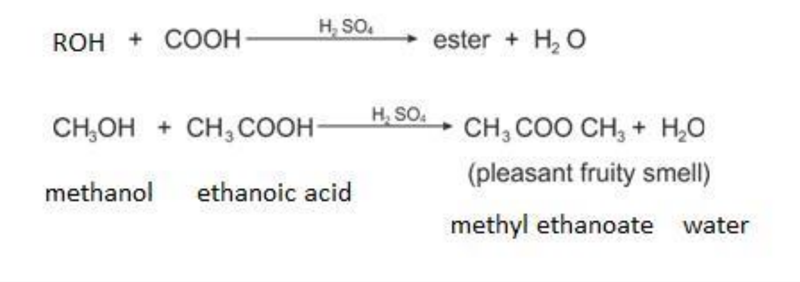
- **Reaction with metal hydrates**



$$\underset{\text{alcohol}}{ROH} + \underset{\text{sodium hydride}}{NaH} \rightarrow \underset{\text{(Metal alkoxide)}}{RONa} + H_2$$

$$\underset{\text{methanol}}{CH_3OH} + NaH \rightarrow \underset{\text{sodium methoxide}}{CH_3ONa} + H_2$$

- **Reaction with carboxylic acid : Esterification**



$ROH + COOH \xrightarrow{H_2SO_4} \text{ester} + H_2O$

$CH_3OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COO\,CH_3 + H_2O$

methanol ethanoic acid (pleasant fruity smell) methyl ethanoate water

- Order of reacting of alcohols towards esterification :

$CH_3\,OH > 1^0 > 2^0 > 3^0$ (alcohol)

- Order of reactivity of carboxylic acid towards esterification:

$H\,COOH > CH_3COOH > (CH_3)_2\,CH\,COOH > (CH_3)_3\,COOH$

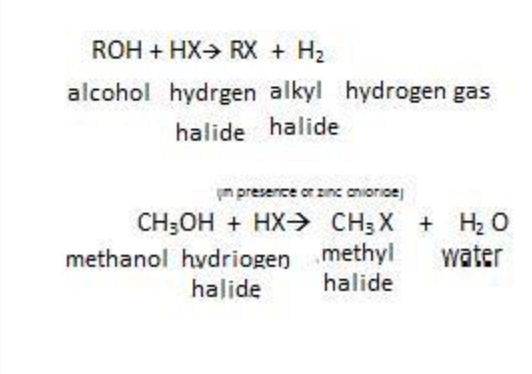
Less number of alkyl groups attached, more is the acidic strength that is release of hydrogen ion becomes easy.

2.Alcohol behave as electrophiles

In this the bond break in such a way that electrophile is generated

$R\text{-}OH \dashrightarrow R^+ + OH^-$

- Reaction with HX: This reaction takes place in presence of zinc chloride and the equation involved is given below.



$ROH + HX \rightarrow RX + H_2$

alcohol hydrgen halide alkyl halide hydrogen gas

(in presence of zinc chloride)

$CH_3OH + HX \rightarrow CH_3X + H_2O$

methanol hydriogen halide methyl halide water

The order of reactivity of different halogen acids towards this reaction is :

$HI > HBr > HCl > HF$

In this HI is most reactive towards this reaction as the bond that exist between H and I is weak bond whereas HF do not participate in this reaction as the bond between them is strong enough due to comparable sizes .

- Reaction With PCl_5 and PCl_3

$ROH + PCl_5 \dashrightarrow RCl + POCl_3 + H_2O$

Alcohol PhosphorousPentachloride ChloroAlkane PhosphorylChoride

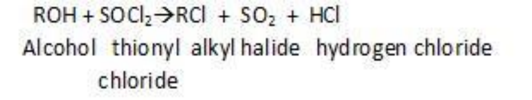
ROH + PCl_3 ---> RCl + H_3PO_3

Alcohol Phosphoroustrichloride AlkylHalide Phosphoric Acid

- Reaction With $SOCl_2$

2. **Clevage of both alkyl group and hydroxyl group**

- Acidic dehydration of alcohols

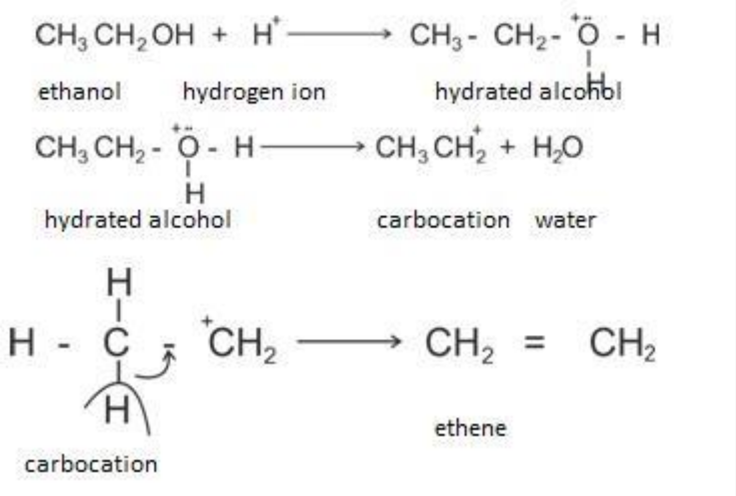


$ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$

Alcohol thionyl chloride alkyl halide hydrogen chloride

(Ethanol) (ethene)

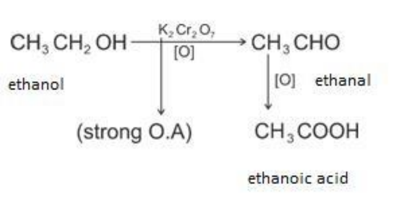
Mechanism:



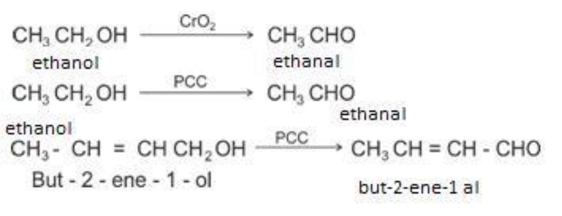
- Dehydrogenation - It is also called as oxidation reaction.

In this primary alcohols give aldehydes in presence of oxidizing agent acid

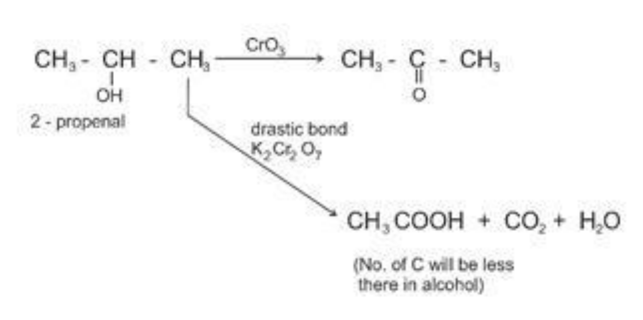
- Acidified $K_2Cr_2O_7$, CrO_3, Collins-reagent, CrO_3-pyridine,PCC (pyridinium chlorochromate), PDC (Pyridium dichromate).



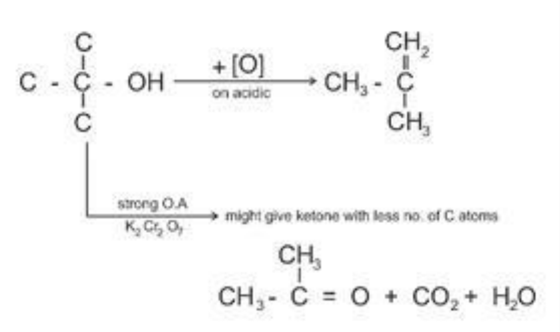
Please note: If we want to stop the reaction at stage of aldehyde, we can use mild oxidizing agent. It is to be noted that primary alcohols give aldehyde and secondary alcohols give ketones.



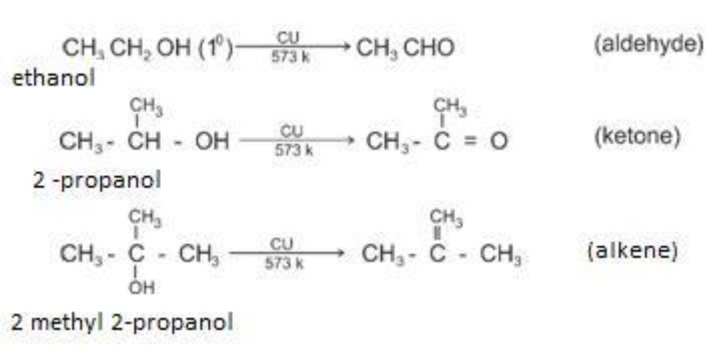
We have reactions where you will see that secondary alcohols gives ketones but under drastic conditions like use of potassium dichromate it gives carboxylic acid with less number of carbon atom than in alcohol.



Tertiary alcohols – Gives alkenes because they do not have H atom so oxidation is not possible and they show elimination reaction.



- Dehydrogenation - removal of Hydrogen.



- Please note that C_2H_5OH is used for drinking purpose are beverage but

CH_3 OH is not good to consume. When in C_2H_5OH, CH_3OH is added it becomes denatured alcohol if it is consumed by anyone it causes death. It hits the nervous system and can cause blindness.

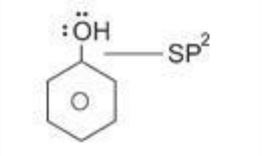
Partial Oxidation

CH_3OH --> HCHO

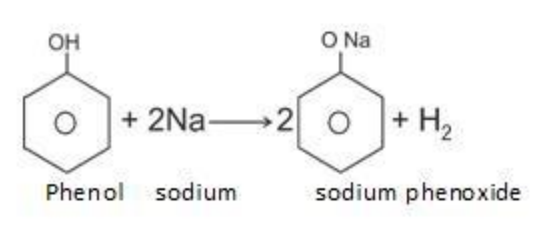
Methanol Methanal

Chemical properties of phenols

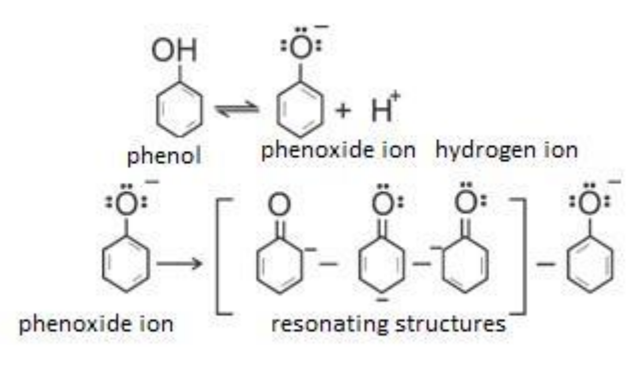
1. Acidic nature of phenols –



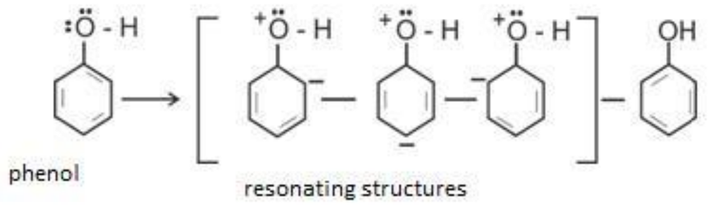
- It is sp^2 hybridized that is it has 33% s character and 67% p character that shows it is more electronegative . As a result electron density on oxygen decreases and Polarity of O – H bond increase therefore Hydrogen is not easily removed.
- Although phenol is acidic but it is less acidic than carboxylic acid therefore It doesn't react with Na_2CO_3 and $NaHCO_3$ but reacts with sodium metal as shown below.



- As compared with alcohol, phenol is more acidic than alcohol. Because in alcohol it is sp^2 hybridised in phenol and Sp^3 hybridised C atom in alcohol.
- The phenoxide ion is resonantly stabilized due to resonance as shown :



In this only one negative charge is getting dispersed.



On the other hand:

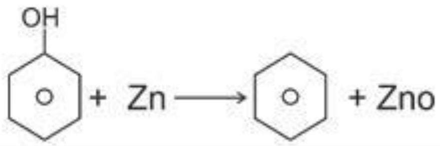
C_2H_5OH --> $C_2H_5O^-$ + H^+

ethanol ethoxide ion

No such resonance is possible therefore stability of alkoxide is less than phenoxide as a result phenol has more tendency to form phenoxide ion due to which phenol is more acidic than alcohols.

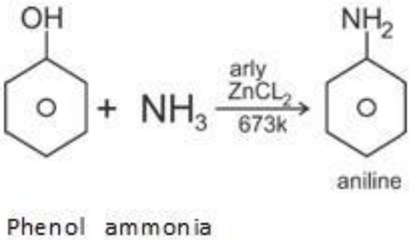
If electron withdrawing group is present at ortho or para position like NO_2 , CN , Cl etc then they disperse this negative charge and will enhance acidic strength, whereas if electron donating group's like CH_3, alkyl group, NH_2 (amine) or OR etc are present they decrease the acidic strength.

1. Reacting with zinc dust: Benzene is formed .

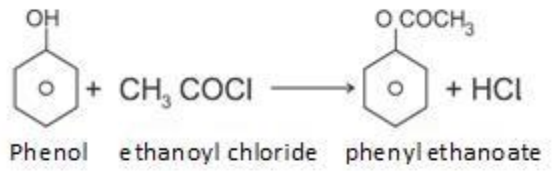


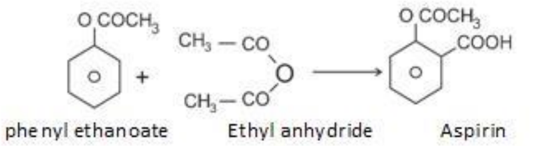
(phenol) (Zinc) (benzene)

2. Reaction with NH_3: aniline is formed



3. Reaction with Acid chloride: Phenyl ethanoate is formed .The reaction is called as acetylation. If we react this phenyl ethanoate with ethyl anhydride then we get aspirin :

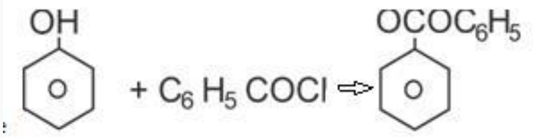




3. Fries rearrangement

Phenyl ethanoate O – (hydroxy acetophenone)

5. Shorten baumem reaction



(Phenol) (benzoyl chloride) (phenyl benzoate)

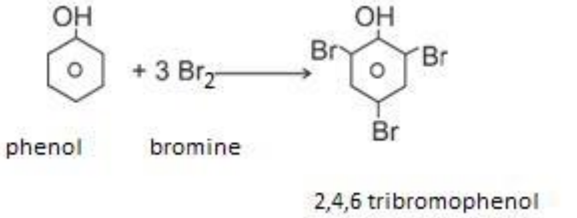
In all these reaction cleavage takes place between O and H.

Reactions of benzene ring

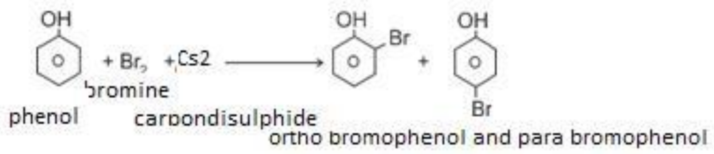
In this Electrophile substitution reaction takes place .As we know OH- group is Ortho and Para directing so according to resonating structures the negative charge is on the Ortho and Para position. Therefore Electrophile attacks at O and P position.

Reactions involved:

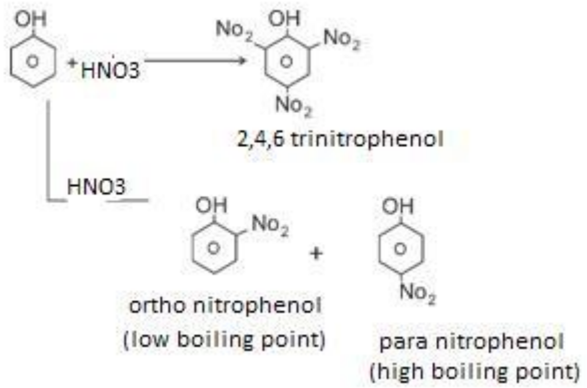
1. Bromination: Substitution by bromine



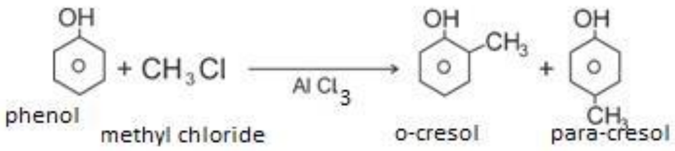
If it occurs in presence of CS_2 then mixture of ortho and para isomers are formed:



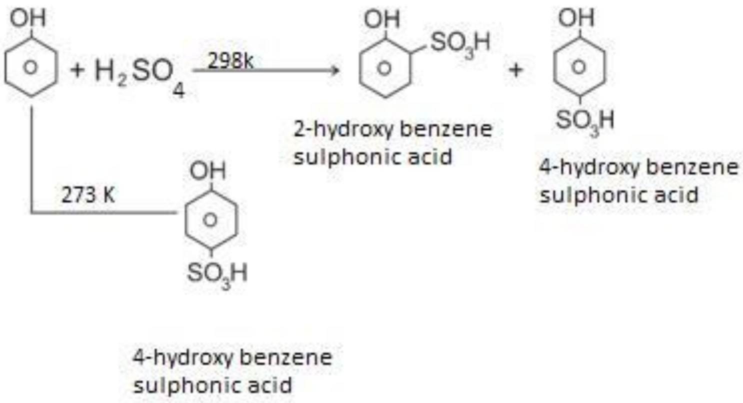
1. Nitration: Substitution by nitro group by adding nitric acid. If we use Concentrated HNO_3 we get tri-substituted



2. Friedel craft alkylation reaction

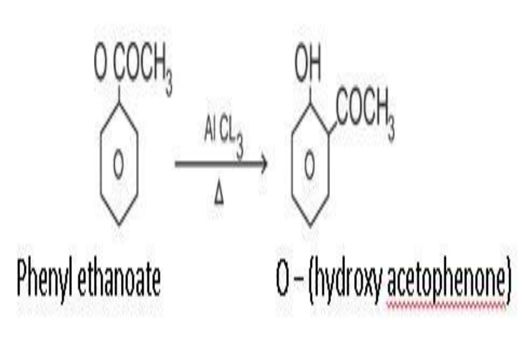


3. Sulphonation: Substitution by SO_3H group.



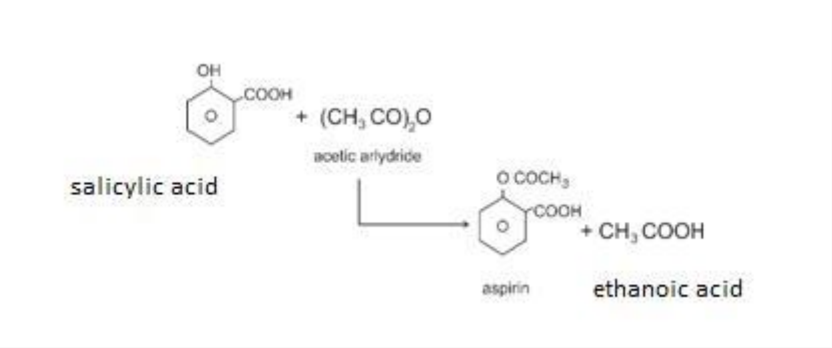
There are certain reactions that phenol undergoes –

- Kolbe’s reaction

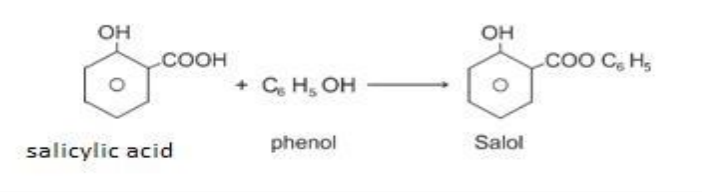


By **this** Aspirin and salol can be formed a shown :

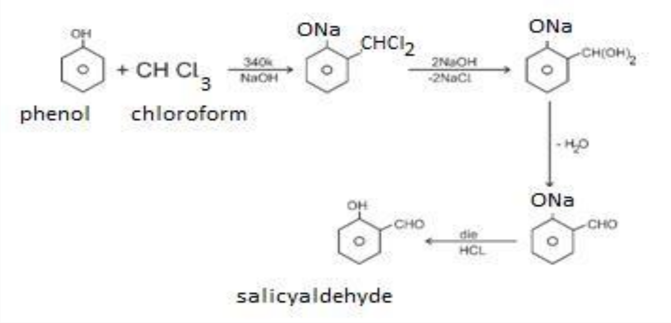
- Aspirin :



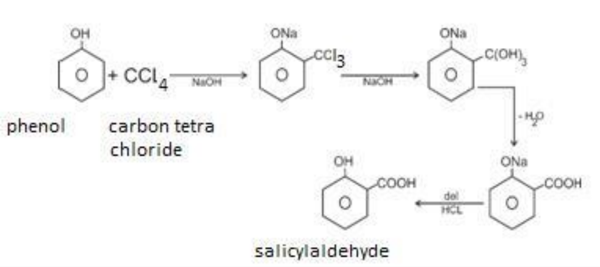
- Salol – phenyl salicylate



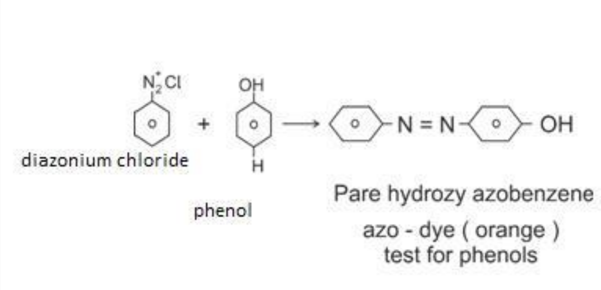
- **Reimer – tieman reaction –**



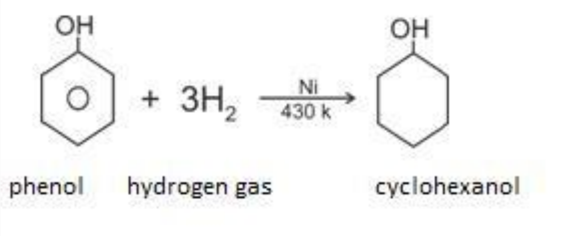
Reaction with carbon tetra chloride



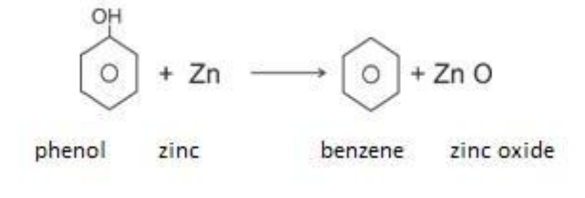
- **Coupling reaction** – in this we get dyes of different colours.



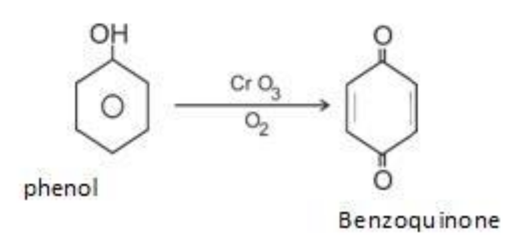
- **Hydrogenation reaction** –



- **With Zn dust**



- **Oxidation reaction**



Test to distinguish between 1^0 and 2^0 and 3^0alcohol

- First test :Lucas test

1. Primary alcohol + HCl($ZnCl_2$ / warm) ----> Turbidity appears on warm

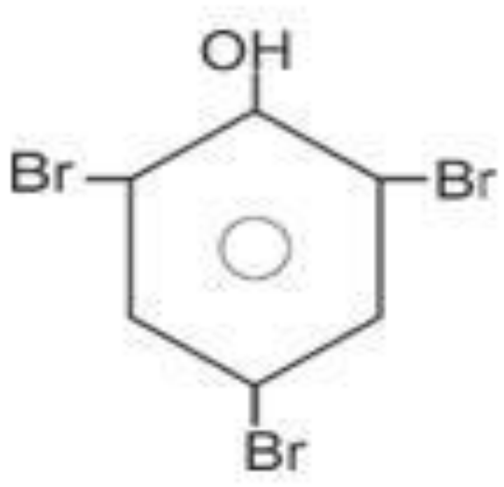
   Less reactive

2. Secondary alcohol + HCl ($ZnCl_2$ / NO warming) -->Turbid on standing
   On its own.

3. Tertiary alcohol + HCl ($ZnCl_2$) ---> immediate turbid

- Second test

  Victor Mayer's test



2,4,6 tribromophenol

Test to distinguish between alcohol and phenol

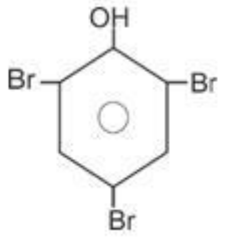
1. Litmus test: Phenol turns blue litmus red, whereas alcohols have no effect.

2. Coupling reaction – azo dye test

Phenol give orange colour, alcohol do not give any reaction.

3. Bromine water test

When Phenol is added to Br_2water they give white ppt. Due to formation of 2,4,5 tri nitro phenol
But alcohol do not give any such test.



2,4,6 tribromophenol

$CH_3-O-\overset{CH_3}{\overset{\vert}{CH_2}}$	1^0	ethyl methyl ether
$CH_3-\overset{CH_3}{\overset{\vert}{CH}}-O-CH_3$	2^0	propyl methyl ether
$CH_3-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-O-CH_3$	3^0	isobutyl methyl ether

Introduction

They are functional isomers of alcohols .The functional group in them is ROR and are represented as ROR where R is alkyl group.

Depending upon the type of alkyl group on both sides we can classify ethers as:

1. Symmetrical ethers: When it has same R on both sides.

Like: $CH_3\ OCH_3$ $C_2\ H_5OC_2\ H_5$

Di methyl ether Diethyl ether

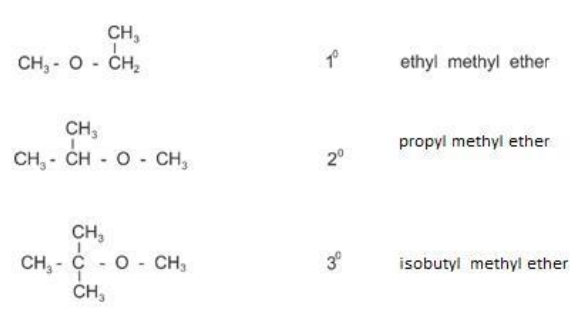
2. Unsymmetrical ethers: They have different R on both sides.

Like: $CH_3OC_2\ H_5$

Ethyl methyl ether

Depending upon the number of alkyl groups present we can classify ethers as:

1. Primary ,secondary and tertiary ethers



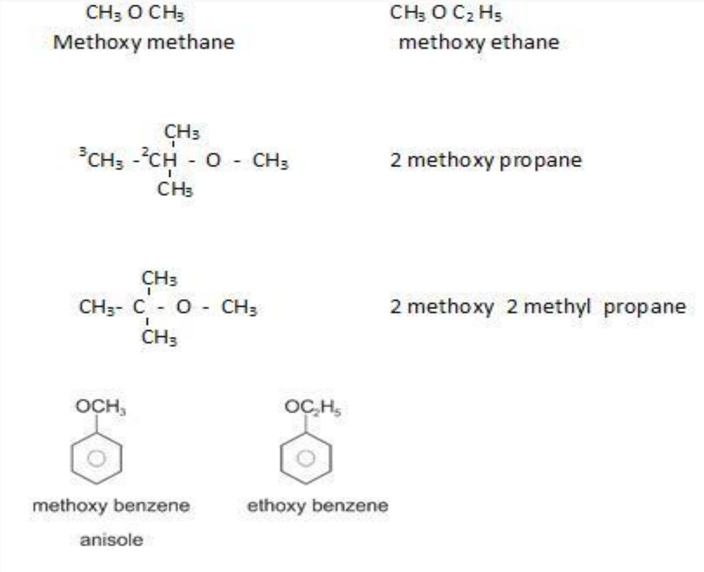
$CH_3-O-CH_2(CH_3)$

$CH_3-CH(CH_3)-O-CH_3$

$CH_3-C(CH_3)_2-O-CH_3$

IUPAC:

The common name used for them is alkoxy alkane. In this smaller group is written as alkoxy group and bigger group is written as Alkane.



$^3CH_3-{}^2CH(CH_3)-O-CH_3$

$CH_3-C(CH_3)_2-O-CH_3$

Isomerism in ethers

1. Chain isomerism: In this chain is going to be different.

$CH_3\ O\ CH_2CH_2CH_2\ CH_3 \rightarrow CH_3-O-CH(CH_3)-CH_2-CH_3$

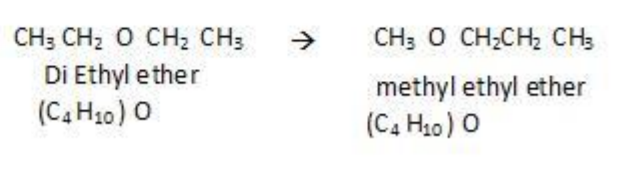
2. Functional Isomerism: In this the functional group changes.

$CH_3\ O\ CH_3 \rightarrow CH_3\ CH_2\ O\ H$

Ether ethanol

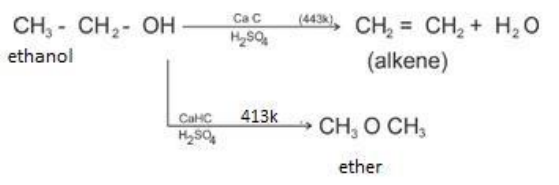
$(C_2\ H_6)\ O$ $(C_2 H_6)\ O$

3. Metamerism: it is shown by only ethers , ester and ketones.



Preparation of ethers

1. By dehydration of alcohol : by this method only primary ethers can be prepared but not tertiary or unsymmetrical ethers .the reaction involved is shown below .



1. **The Conditions required to form ether from alcohol**

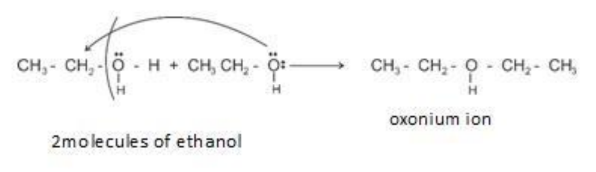
- Temperature must be maintained at 413k.
- Large amount of alcohol should be used as we will see in the mechanism we need more alcohol as shown below in second step of mechanism.
- Alkyl group should be unhindered.

Mechanism: Protonation and deprotonation

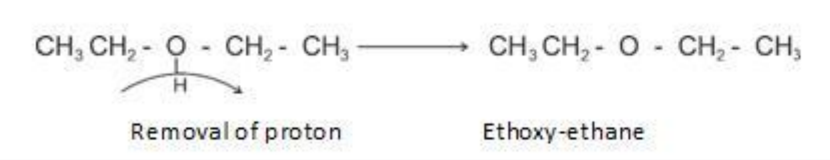
(a)From of protonated alcohol

Ethanol hydrogen ion (protonated alcohol)

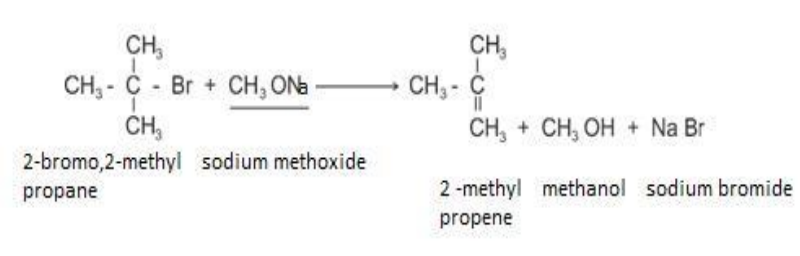
(b)Another molecule of alcohol also react



(c)De protonation: removal of proton

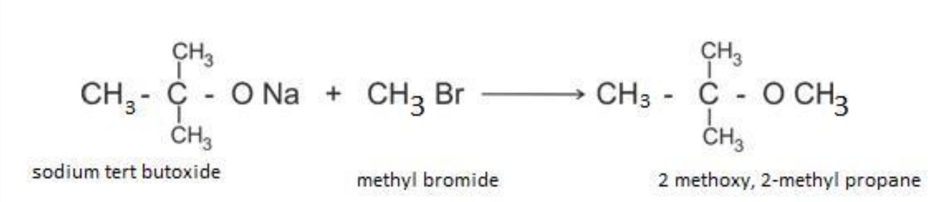


3. **Williamson's synthesis** - By this method tertiary ether ,unsymmetrical ether can be prepared .The reaction involved is given .

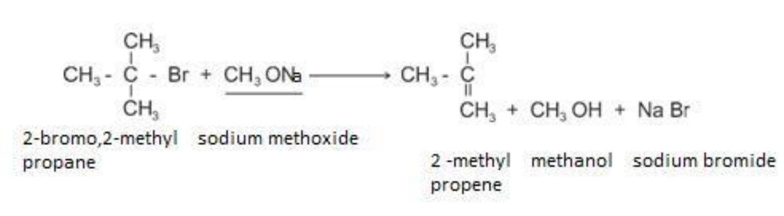


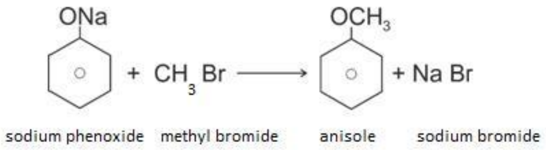
Key points –

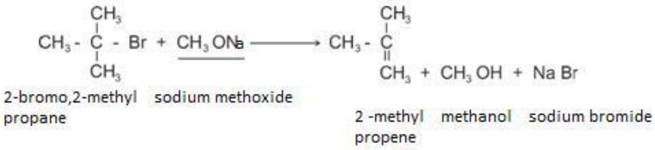
- If secondary or tertiary ether have to formed than the RX should be

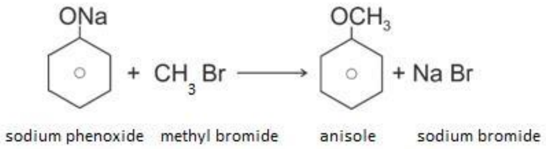


- From secondary or tertiary RX we get alkenes instead of ether.









4. **From alkyl halides by treating with dry silver oxide**

$$2(CH_3CH_2Br) + Ag_2O \rightarrow CH_3CH_2OCH_2CH_3 + AgBr$$

Ethyl bromide silver oxide Ethoxy ethane silver bromide

5. **By action of diazomethane on alcohol**

$$CH_3CH_2OH + CH_2N_2 \xrightarrow{HBF_4} CH_3CH_2OCH_3 + N_2$$

ethanol diazomethane methoxyethane nitrogen gas

<u>Physical properties of ethers</u>

1. Existence: Lower members are gases and higher members may be liquids or solid due to increase in the Vander wall force.
2. Dipole moment: Ethers have higher dipole moments because of electro negativity difference and structure is bent.

- They have larger bond angles than alcohol. Alcohol have one hydrogen and ether there are two bulky groups so, repulsion between bulky groups are more therefore Bond angle will increase.
- More the bulky group's, lower is the value of dipole moments.

$CH_3 - O - CH_3$	$C_2H_5OC_2H_5$
1.3D	1.18D

3. Boiling point: Ethers have low boiling point because of less polarity.

$CH_3CH_2OCH_2CH_3$	$CH_3CH_2CH_2CH_2OH$
Boiling point – 307.6k	boiling point – 390k

"more polarity"

4. Solubility: lower members are more soluble .

Example – C_2H_5OH CH_3OCH_3] same solubility

- But as number of Carbon atoms increase, solubility decrease because non polar part increase.

Chemical properties of ethers

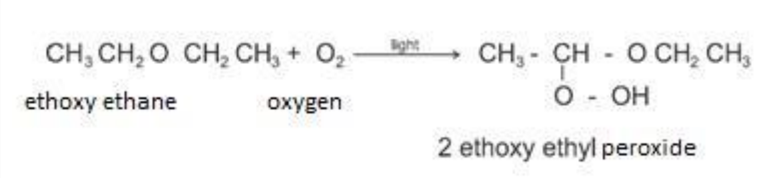
Ethers are very stable compounds –therefore they are least reactive among all functional groups .still we have few reactions lets study them.

1. **[Reaction of ethereal oxygen]**

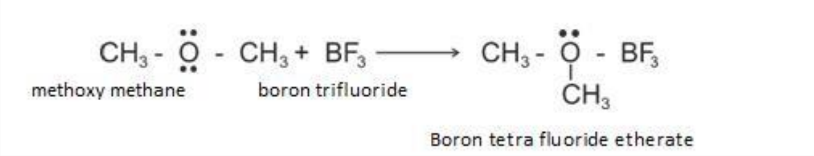
ROR (ether)

CH_3OCH_3 (methoxy methane)

1. Action of air on ether



1. With Lewis acid

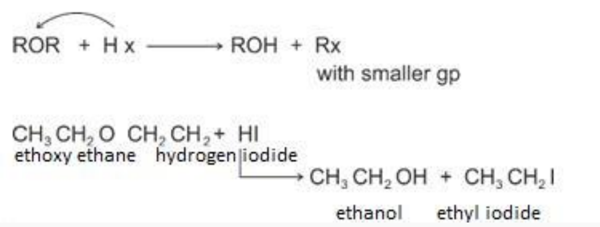


1. **Cleavage of C = O bond of ether**

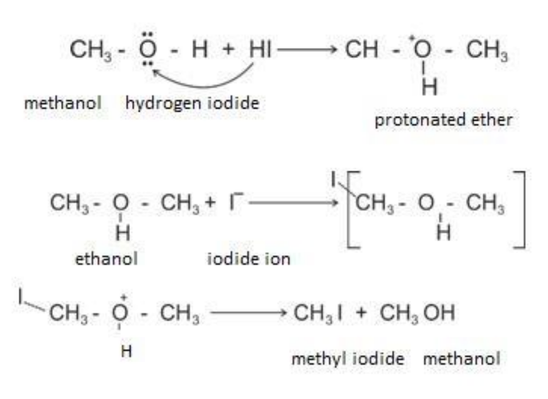
(a)Cleavage by halogen acids: The order of reactivity of halogen acids towards this reaction is:

HI > HBr > HCl > Hl

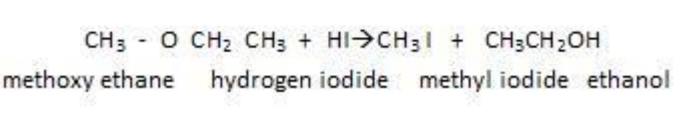
The HI bond is broken easily but HF bond can't be broken .The reaction involved is



The Mechanism involved:

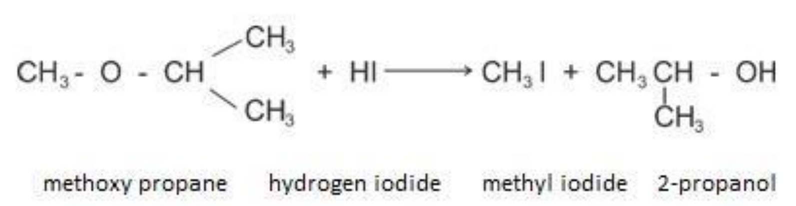


- In case of unsymmetrical ether :

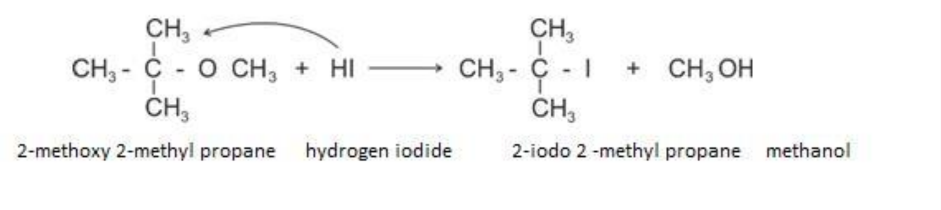


$CH_3 - O\ CH_2\ CH_3 + HI \rightarrow CH_3I + CH_3CH_2OH$

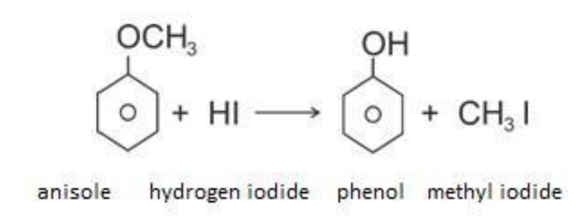
Another example:



- If we take tertiary than Iodide goes with tertiary group

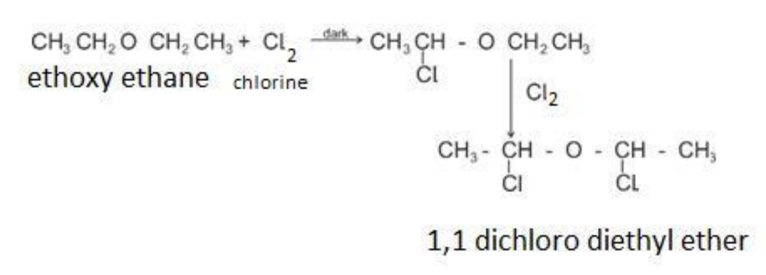


- More positive is the carbocation more is the tendency of iodine to attach.



2. **Reaction of alkyl groups**

Reaction taking place in dark in which chlorine molecule is added



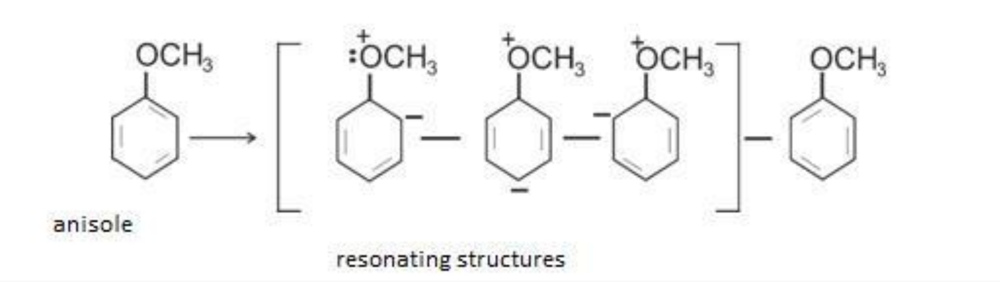
Reaction taking place in light in which chlorine molecule is added

$CH_3CH_2OCH_2CH_3Cl_2 \dashrightarrow CCl_3CCl_2OCCl_2CCl_3$

(Light) Perchloro diethyl ether

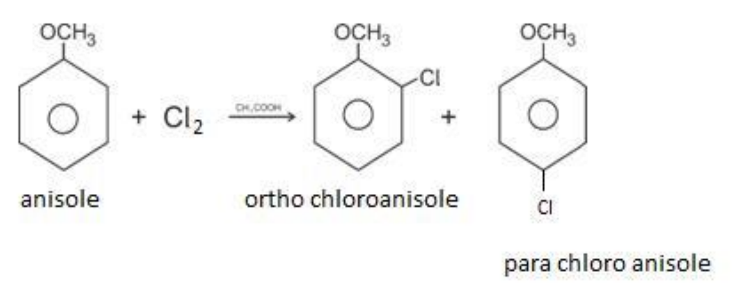
3. **Ring substitution reaction in ether**

If we look at resonance structures of ether ,we see that attack occur at ortho and para position because on those position electron density is high so attack of electrophile occur at ortho and para .



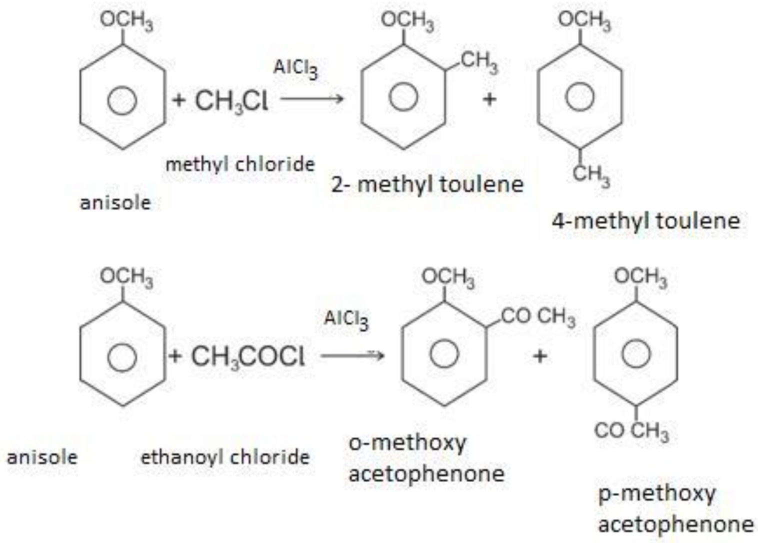
Halogenations: Attack of halogen.

- Chlorination



(B) Nitration: Reaction with nitric acid

- Friedel craft alkylation and acylation



Uses of ethers

Ethers are used as a refrigerant.

1. They are used as industrial solvent for fat and oils.
2. When mixed with alcohol they make alcohol denatured.
3. They are used in Perfumery like:

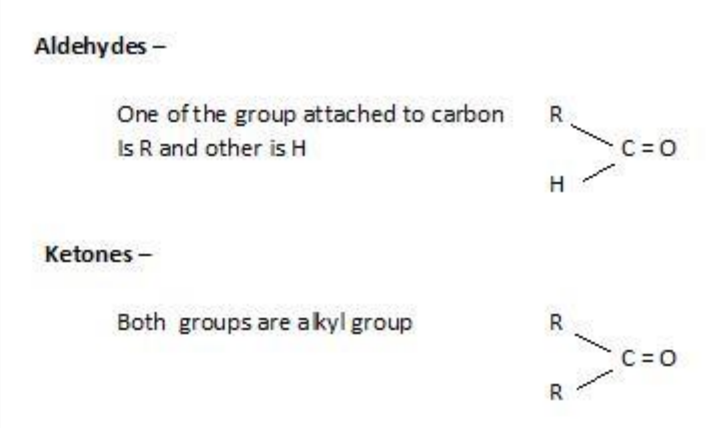
- In aniseeds – Anethol is present which is a phenyl ether.
- In clove oil – Eugenol is present.
- In vanilla extract vanillin is present.
- In mint – Thymol is present.

12.Aldehydes, Ketones and Carboxylic Acids

Introduction

Aldehydes and ketones

They are functional isomers of each other and collectively called as carbonyl compounds (C=O).



Aldehydes –

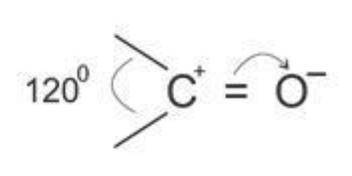
One of the group attached to carbon Is R and other is H

Ketones –

Both groups are alkyl group

Chemical properties of aldehydes and ketones

- **Structure of Carbonyl group**



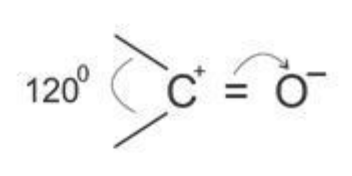
- If we look at structure ,multiple bonds are seen. Therefore ,they will show addition reactions .
- Oxygen being electronegative,attract electrons .
- As a result, partial negative charge is acquired on oxygen and partial postive on carbon .
- Therefore ,nucleophilic attack occur on carbon .So, in them common reactions that is seen is nucleophilic reactions.
- The electronegativity is same but due to approach of attacking agent temporary transfer of electrons occur .

Types of reactions shown

1. Nucleophilic addition reactions
2. Nucleophilic addition reactions followed by loss of water molecule
3. Oxidation reactions
4. Reduction reactions
5. Miscellaneous reactions

- **Nucleophilic addition reaction**

In this given structure



The nucleophile attack on the carbon atom and the reaction occur in a way as shown below:

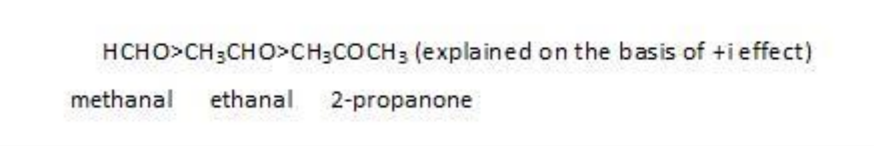
This reaction is acid catalysed reaction .Due to which hydroxyl group is formed from aldehyde.

Relative strength of Aldehydes and ketones

- **On the basis of Inductive effect**

If the magnitude of positive charge is more on carbon atom ,then more readily it shows nucleophilic addition reaction .So, out of all members HCHO shows this reaction more readily as it has no alkyl group(electron releasing group) present.

So, if we compare formaldehyde, ethanol and propanone, the order of their strength towards nucleophilic addition is:

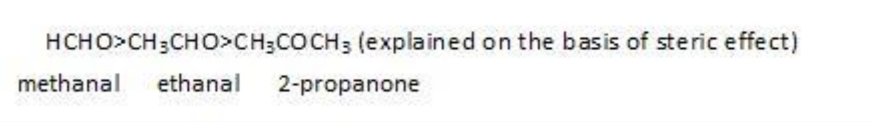


$HCHO > CH_3CHO > CH_3COCH_3$ (explained on the basis of +i effect)

methanal ethanal 2-propanone

- **It can also be explained on the basis of Steric effect**

More the bulky groups attached, less space will be available for nucleophile to attack. Therefore, reactivity will be less. So, this can also be the reason to explain the trend.



$HCHO > CH_3CHO > CH_3COCH_3$ (explained on the basis of steric effect)

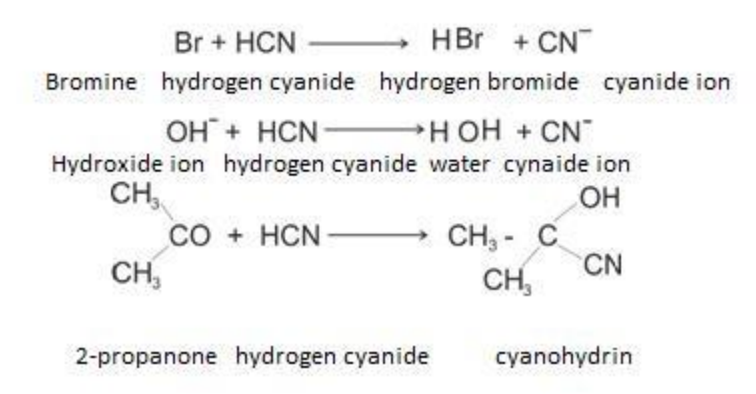
methanal ethanal 2-propanone

- If we compare Benzaldehyde with any other aldehyde, its strength towards nucleophilic addition is less. The reason is due to delocalisation of electron that takes place. Therefore, the charge is not so intensified.

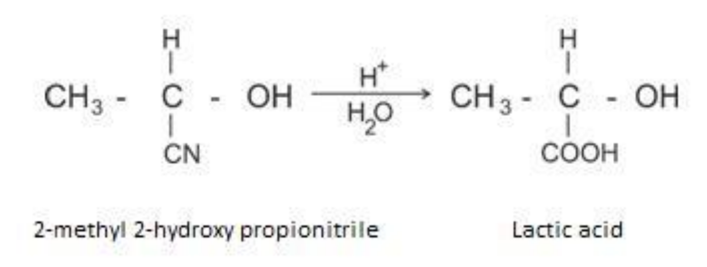
Let’s show some nucleophilic addition reactions:

(a)Addition of HCN (Cyanohydrins are formed)

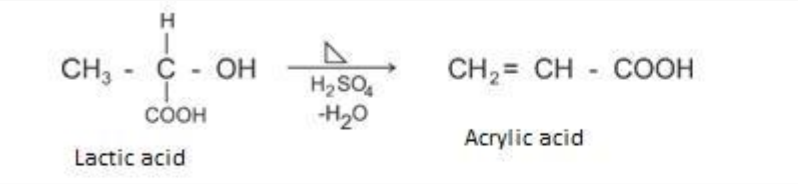
If only HCN is used, the reaction is slow. So, the base is used that help in removing hydrogen ion from HCN and sets the nucleophile free. As a result, reaction becomes fast. The base reacts as shown below:



If we carry out hydrolysis of the above compound, 2-methyl 2-hydroxy propionitrile, then the lactic acid is produced due to hydrolysis of CN group as shown below:

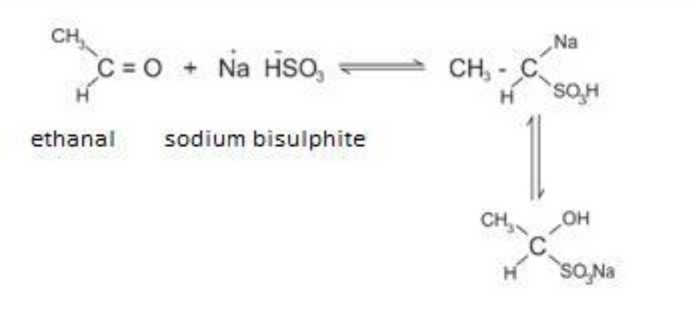


If we heat lactic acid, in presence of sulphuric acid then the water molecule gets removed and acrylic acid is formed as shown:



- **Addition of Sodium bisulphite (this reaction is used in separation of aldehyde and ketone)**

The reaction involved is given below:

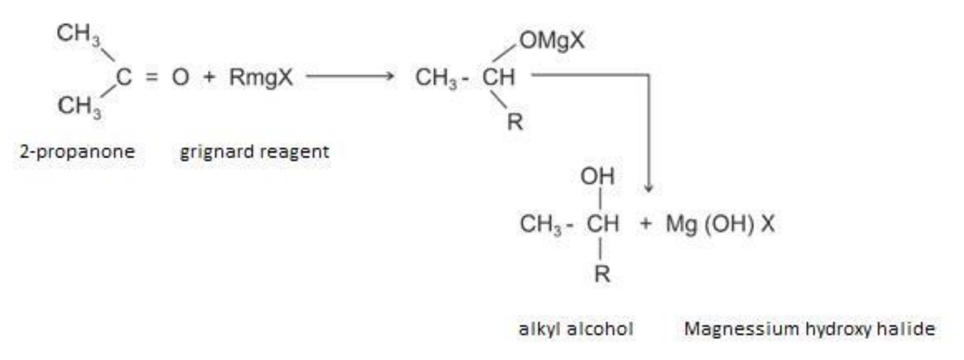


For aldehyde, the reaction goes in forward reaction and for ketone backside is favoured (as two methyl groups increase bulkiness and form unstable products).

Note: diethyl ketone, acetophenone and Benzophenone will not undergo these reactions because of bulkiness.

- **Addition of Grignard reagent**

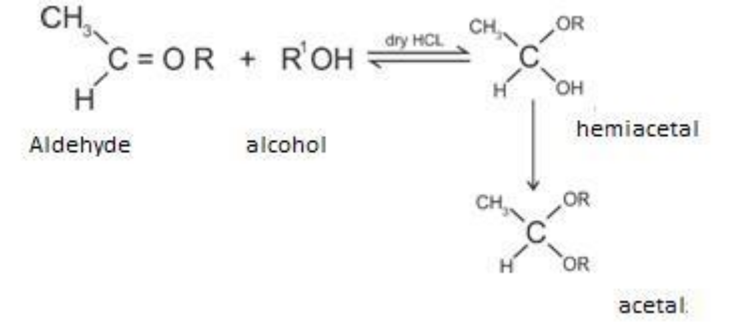
When Grignard reagent is added following reactions occur:



Please note: In this formaldehyde form primary alcohol, any other aldehyde form secondary alcohol and ketone forms tertiary alcohol.

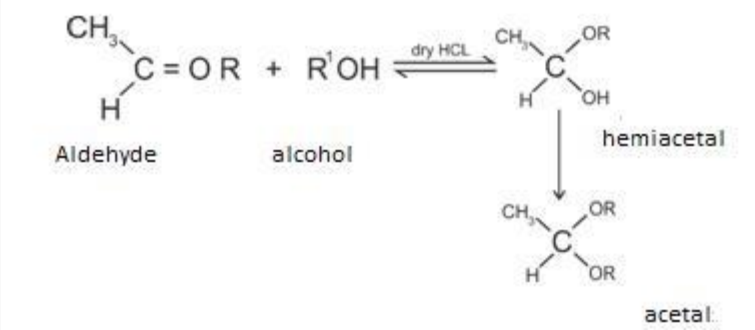
(d)Addition of alcohols: In this we get two products that are hemi-acetals and acetals from aldehyde. From ketone we get, ketals.

The reaction occurs as shown:

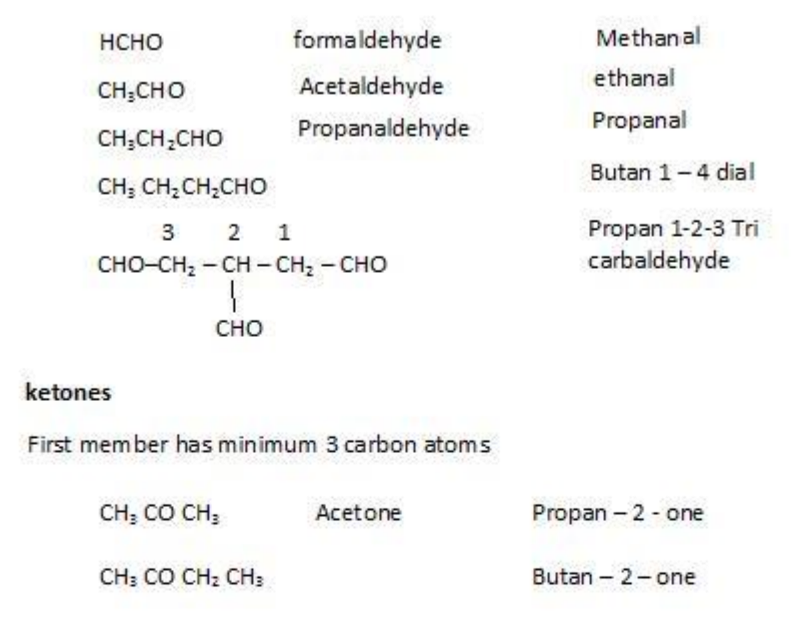


Please note in this we use dry HCl

- So as, to protonate the carbonyl oxygen. Therefore, increasing the electrophilicity of carbonyl carbon to enhance the attack of alcohol.
- It removes the water produced during the reaction and takes the reaction in forward direction.



Nomenclature



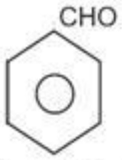
HCHO	formaldehyde	Methanal
CH_3CHO	Acetaldehyde	ethanal
CH_3CH_2CHO	Propanaldehyde	Propanal
$CH_3CH_2CH_2CHO$		Butan 1 – 4 dial
$\overset{3}{CHO–CH_2} - \overset{2}{\underset{\substack{\vert \\ CHO}}{CH}} - \overset{1}{CH_2} - CHO$		Propan 1-2-3 Tri carbaldehyde

ketones

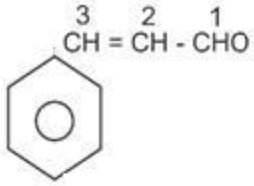
First member has minimum 3 carbon atoms

$CH_3\,CO\,CH_3$	Acetone	Propan – 2 - one
$CH_3\,CO\,CH_2\,CH_3$		Butan – 2 – one

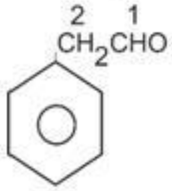
Aromatic compounds



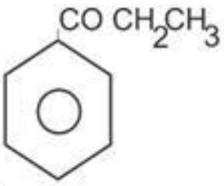
Benzaldehyde



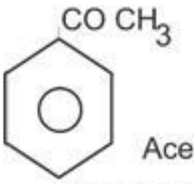
Cinamadehyde
3 Phenyl prop - 2 - one - al



2 - Phenyl ethanal



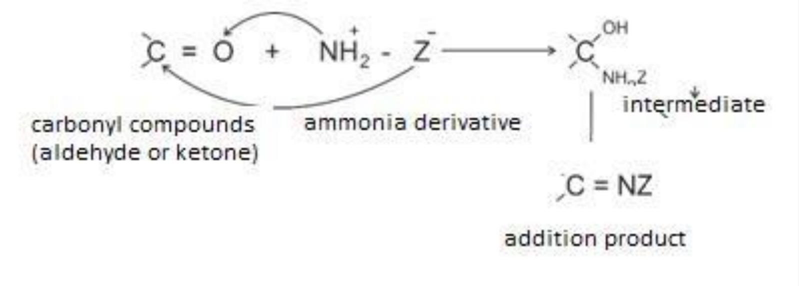
Propiophenone
Ethyl Phenyl Ketone



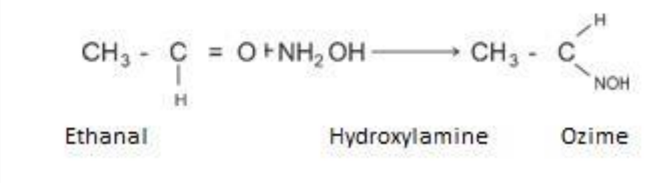
Acetophenone
Methyl Phenyl Ketone

- **Nucleophilic addition reaction with loss of water molecule**

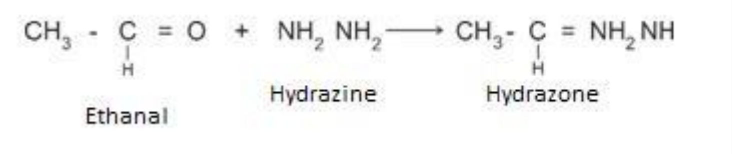
In these reactions, mainly the reaction occurs with ammonia and its derivatives. The general reaction involved is:



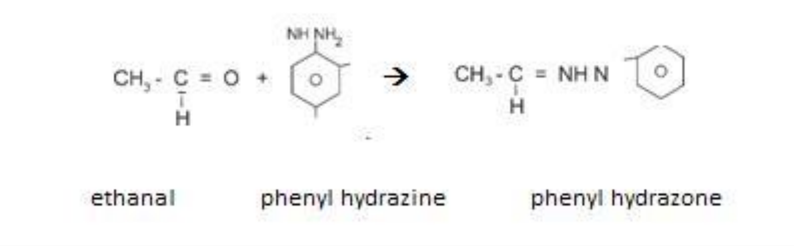
- **Reaction with hydroxylamine (NH_2OH): Oxime is formed**



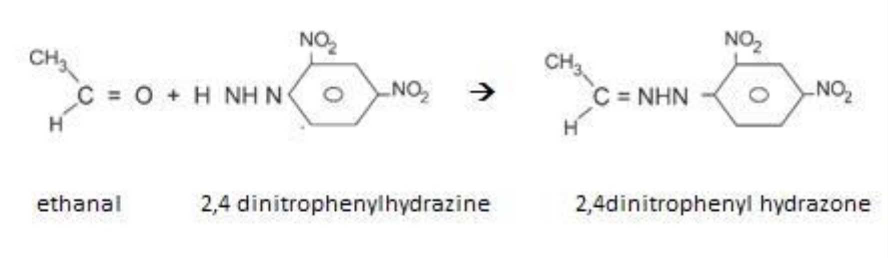
- **Reaction with hydrazine (NH_2NH_2):Hydrazones are formed**



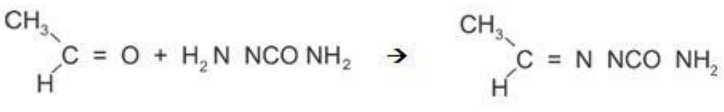
- **Reaction with phenyl hydrazine: (phenyl hydrazone is formed)**



- **Reaction with 2,4 dinitrophenylhydrazine: orange crystals are formed**



- **Reaction with semi carbazide ($NH_2NHCONH_2$):semi carbazone is formed**



ethanal semicarbazide semicarbazone

Isomerism

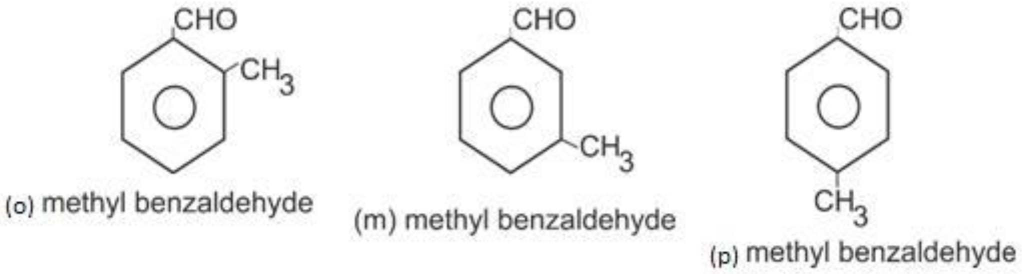
- **Chain isomerism**

$$CH_3CH_2CH_2CHO \qquad CH_3-\underset{CH_3}{\underset{|}{CH}}-CHO$$

(Butanal) 2 Methyl propanol

- **Position isomerism**

It is not shown by aliphatic compounds because CHO group is given least number.



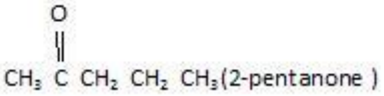
This is most common in ketones.

$$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_2CH_3 \qquad CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$$

Pentan- 3 – one Pentan-2 – one

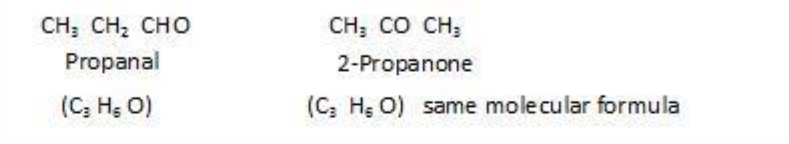
Metamerism

$CH_3\ CH_2\ CO\ CH_2\ CH_3$ (3-pentanone)



$CH_3\overset{\overset{O}{\|}}{C}CH_2\ CH_2\ CH_3$(2-pentanone)

- **Functional isomerism**

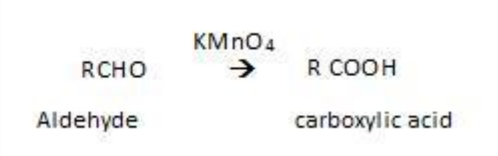


$CH_3\ CH_2\ CHO$ Propanal (C_3H_6O)

$CH_3\ CO\ CH_3$ 2-Propanone (C_3H_6O) same molecular formula

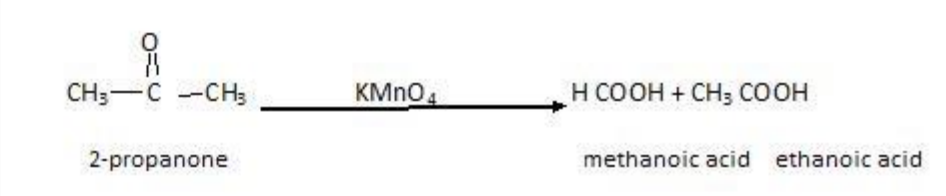
- **Oxidation**
- Aldehyde and ketones on oxidation give carboxylic acid .But this happens only,in presence of Oxidising agents like HNO_3 , $KMnO_4$, $k_2Cr_2O_7$, $Na_2Cr_2O_7$Collin's Fehling reagent and many more.

When we use $KMnO_4$ or $k_2Cr_2O_7$,the medium gets acidic. There is a trend, that when we carry oxidation of aldehyde or ketone it forms acid like –



$$\underset{\text{Aldehyde}}{RCHO} \xrightarrow{KMnO_4} \underset{\text{carboxylic acid}}{R\ COOH}$$

We get acid, irrespective of the alkyl group used. Likewise, ketones also give acids but we get mixtures.

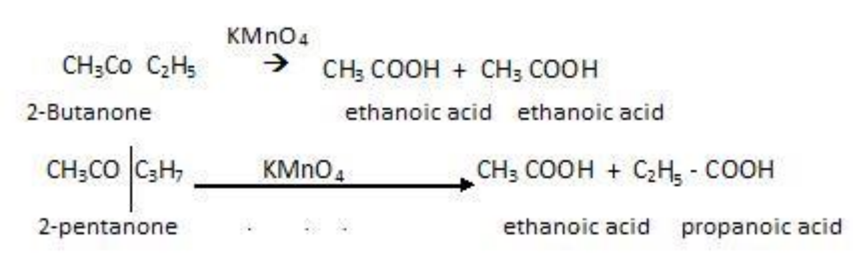


$$\underset{\text{2-propanone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow{KMnO_4} \underset{\text{methanoic acid}}{H\ COOH} + \underset{\text{ethanoic acid}}{CH_3\ COOH}$$

The product formed is in accordance with Popoff's rule.

According to it : "ketones get oxidised in such a manner that the keto group remains with smaller alkyl group.

Example:



$$\underset{\text{2-Butanone}}{CH_3Co\ C_2H_5} \xrightarrow{KMnO_4} \underset{\text{ethanoic acid}}{CH_3\ COOH} + \underset{\text{ethanoic acid}}{CH_3\ COOH}$$

$$\underset{\text{2-pentanone}}{CH_3CO|C_3H_7} \xrightarrow{KMnO_4} \underset{\text{ethanoic acid}}{CH_3\ COOH} + \underset{\text{propanoic acid}}{C_2H_5 - COOH}$$

Aldehyde

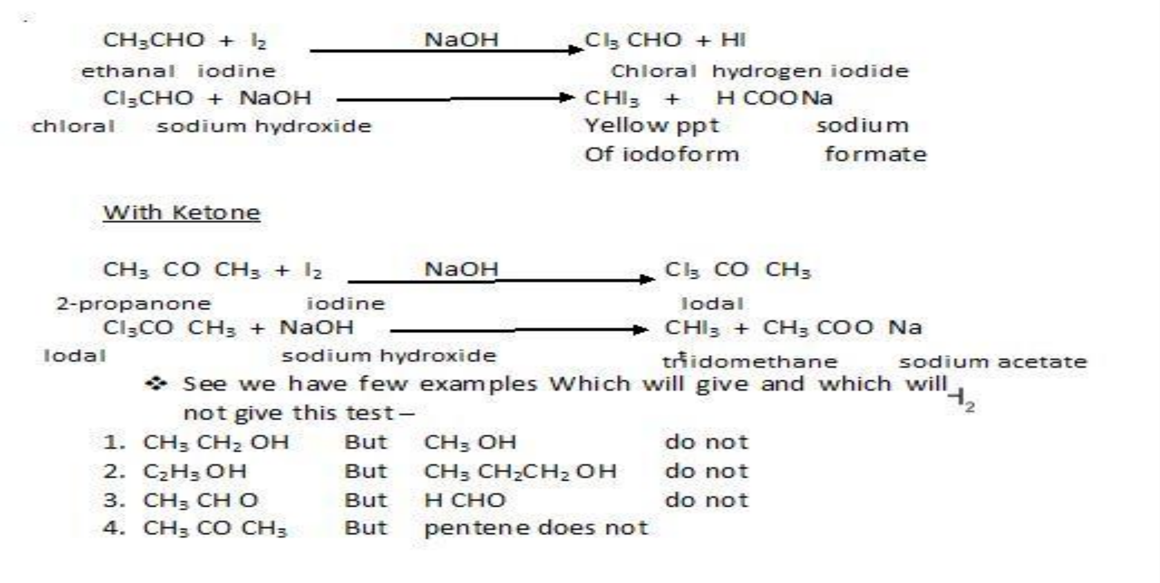
They are easily oxidised even with mild oxidising agents like Collin's, Fehling etc. They can be oxidised but in case of ketone we need to use strong oxidising agents .The use of weak and strong oxidising agents like Colin's, Fehling's can be used to distinguish between aldehydes and ketones.

Mild Oxidising agent: Used for oxidising aldehyde to carboxylic acids.

Mild Oxidising agents used are Tollen's reagent.

For aldehydes

- **Tollen's reagent** :It is a solution of Ammonical silver nitrate and it has formula [Ag $(NH_3)_2$ $]^+$ OH^-] .Now ,Let us take example of any aldehyde like :



$CH_3CHO + I_2 \xrightarrow{NaOH} CI_3\,CHO + HI$

ethanal iodine Chloral hydrogen iodide

$CI_3CHO + NaOH \longrightarrow CHI_3 + H\,COONa$

chloral sodium hydroxide Yellow ppt Of iodoform sodium formate

With Ketone

$CH_3\,CO\,CH_3 + I_2 \xrightarrow{NaOH} CI_3\,CO\,CH_3$

2-propanone iodine Iodal

$CI_3CO\,CH_3 + NaOH \longrightarrow CHI_3 + CH_3\,COO\,Na$

Iodal sodium hydroxide triidomethane sodium acetate

❖ See we have few examples Which will give and which will I_2 not give this test –

1. $CH_3\,CH_2\,OH$ But $CH_3\,OH$ do not
2. C_2H_3OH But $CH_3\,CH_2CH_2\,OH$ do not
3. $CH_3\,CH\,O$ But $H\,CHO$ do not
4. $CH_3\,CO\,CH_3$ But pentene does not

Therefore, it is called as "Silver mirror test". This test is known as silver mirror test and is not given by ketones.

- **Fehling solution test**
- It is prepared by missing equal amount of Fehling's Solution A and Fehling's solution B.

Has to be changed

(Aq. $CuSO_4$) (Sodium potassium Carbonate " Rochelle Salt")

- We take test tube and add both solutions A & B equally.
- The resulting solution is blue due to $CuSO_4$.
- Now when we add aldehyde this blue solution, it turns red. The medium is alkaline ketone due to Fehling solution B.
- The following reaction occurs.

RCHO + Cu^{2+} +5OH^- --> $RCOO^-$ + Cu_2O + $3H_2O$

(Aldehyde) Copper ion carboxylate ion (Cuprous oxide) (Reddish Brown ppt)

- Identification : Colour changes from blue to red .This test is not given by ketones.
- **Benedict's solution test-** It is alkaline solution of cupric ion complexed with citrate ions. When we react with aldehyde the following reaction occur:

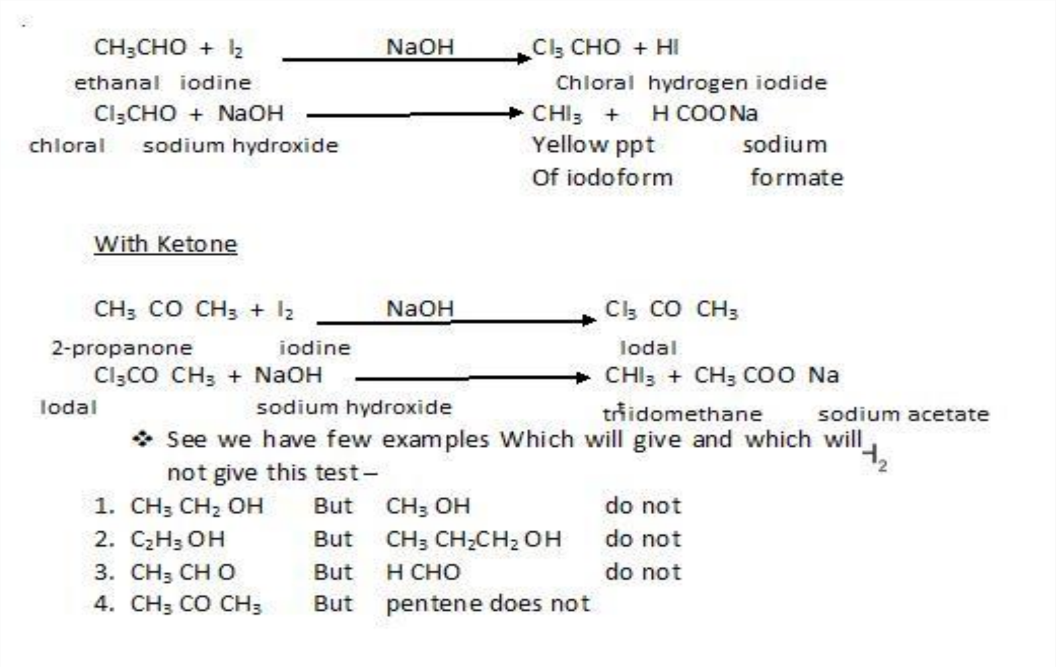
RCHO + Cu^{2+} +5OH^- --> $RCOO^-$ + Cu_2O + $3H_2O$

(Aldehyde) Copper ion carboxylate ion (Cuprous oxide) (Reddish Brown ppt)

for Ketones

- **Iodoform test**: By performing this test, we get yellow precipitate due to formation of iodoform.
- Limitation of this test: This is given only methyl ketones i.e. one of the R in ketone should be CH_3 and also by ethanol as it contains the methyl group.

In this, aldehyde reacts with I_2 in presence of NaOH. In this 3 hydrogen are substituted by Iodine as shown below:



$$CH_3CHO + I_2 \xrightarrow{NaOH} CI_3CHO + HI$$

ethanal iodine Chloral hydrogen iodide

$$CI_3CHO + NaOH \longrightarrow CHI_3 + HCOONa$$

chloral sodium hydroxide Yellow ppt Of iodoform sodium formate

With Ketone

$$CH_3COCH_3 + I_2 \xrightarrow{NaOH} CI_3COCH_3$$

2-propanone iodine Iodal

$$CI_3COCH_3 + NaOH \longrightarrow CHI_3 + CH_3COONa$$

Iodal sodium hydroxide triidomethane sodium acetate

❖ See we have few examples Which will give and which will not give this test – I_2

1. CH_3CH_2OH But CH_3OH do not
2. C_2H_3OH But $CH_3CH_2CH_2OH$ do not
3. CH_3CHO But $HCHO$ do not
4. CH_3COCH_3 But pentene does not

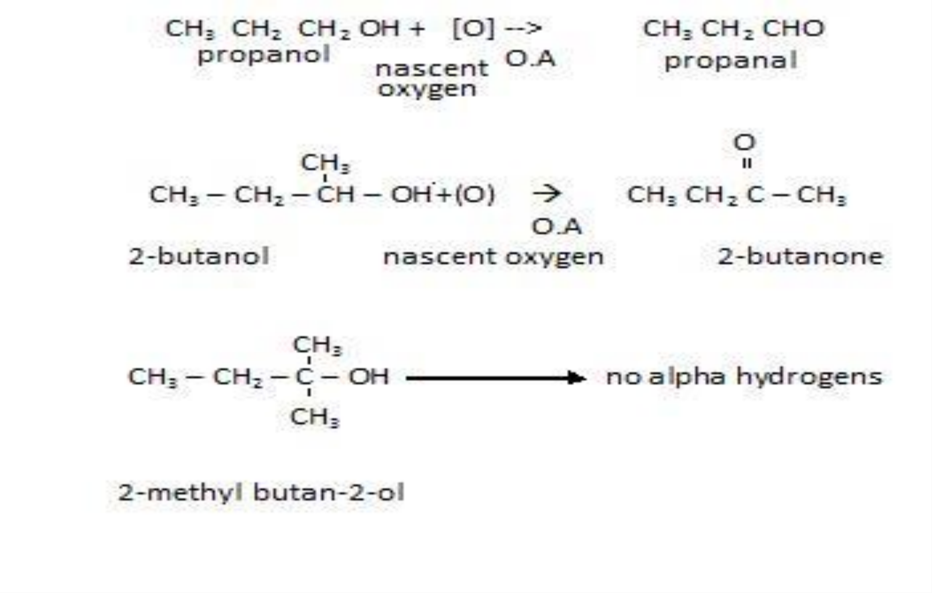
Methods of preparation

There are different methods for their preparation

1. Common Methods for both aldehyde and ketones
2. Preparation for Only aldehydes
3. Preparation for Only Ketones

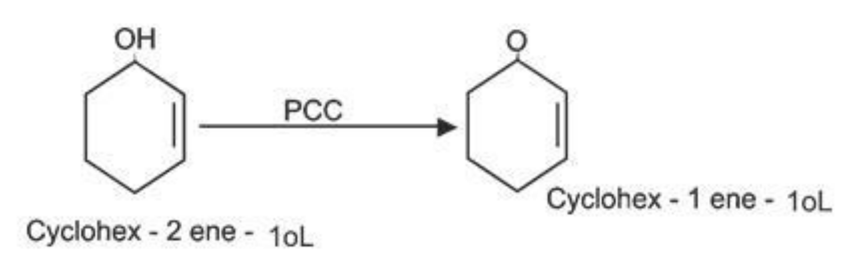
1. From alcohols

1. Oxidation of alcohols: It is prepared from oxidation of alcohols using Oxidising agents like $K_2Cr_2O_7$, $Na_2Cr_2O_7$, PCC , collins reagent (CrO_3 + pyridine). All of them are good oxidising agents. So, we need to poison in order to stop it at aldehydic stage.

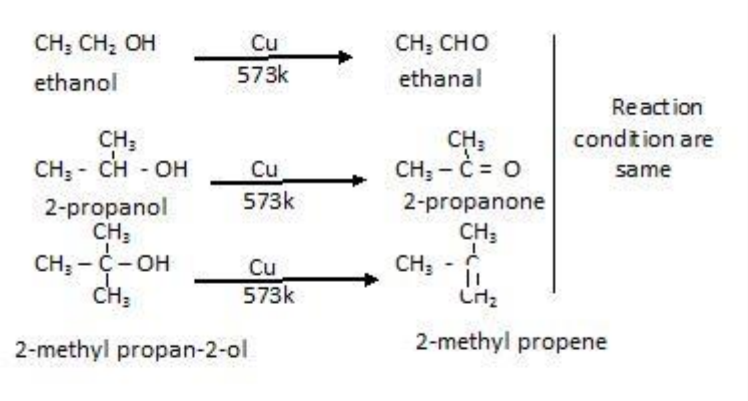


(From tertiary alcohol) : We can't get aldehyde from tertiary alcihols as there is no alpha hydrogen present. So ,in this case we get alkene.

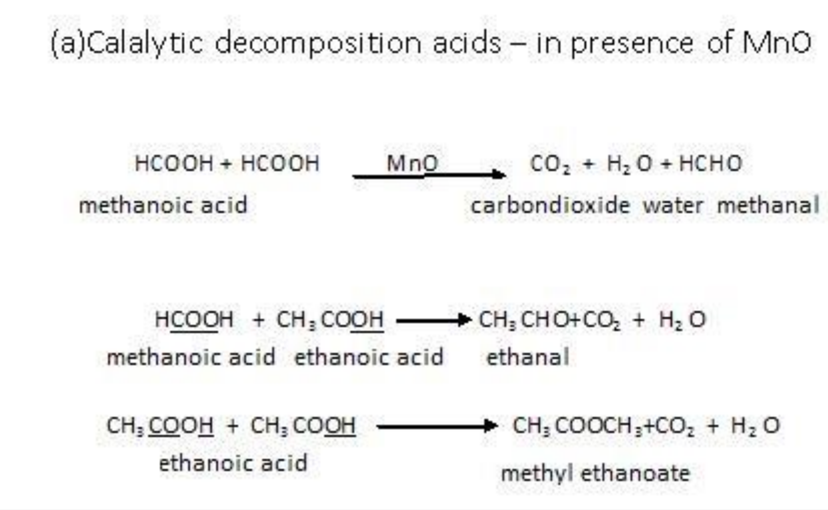
- If we have cyclohex – 2 ene –1ol



b.Dehydrogenation of alcohols – Cu (573k)



2. **FORM CARBOXYLIC ACIDS**



(a)Calalytic decomposition acids – in presence of MnO

$HCOOH + HCOOH \xrightarrow{MnO} CO_2 + H_2O + HCHO$

methanoic acid → carbondioxide water methanal

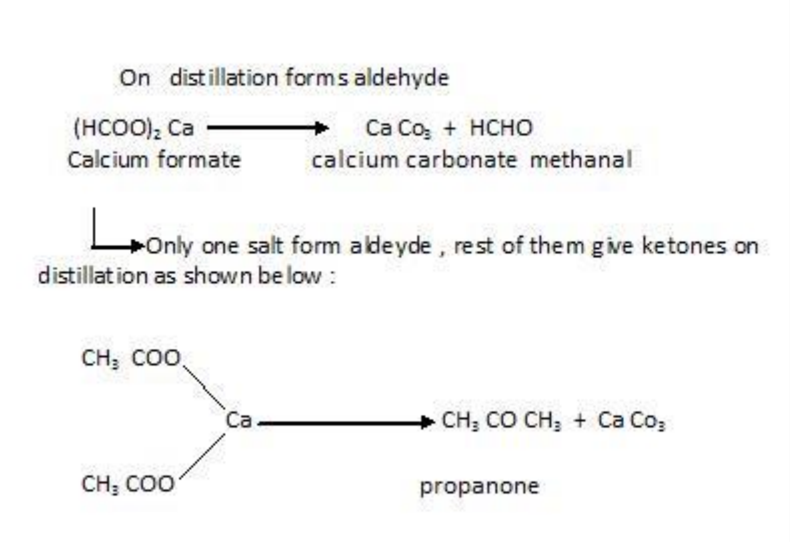
$HCOOH + CH_3COOH \longrightarrow CH_3CHO + CO_2 + H_2O$

methanoic acid ethanoic acid → ethanal

$CH_3COOH + CH_3COOH \longrightarrow CH_3COOCH_3 + CO_2 + H_2O$

ethanoic acid → methyl ethanoate

- Distillation of calcium salts of acids



On distillation forms aldehyde

$(HCOO)_2Ca \longrightarrow CaCO_3 + HCHO$

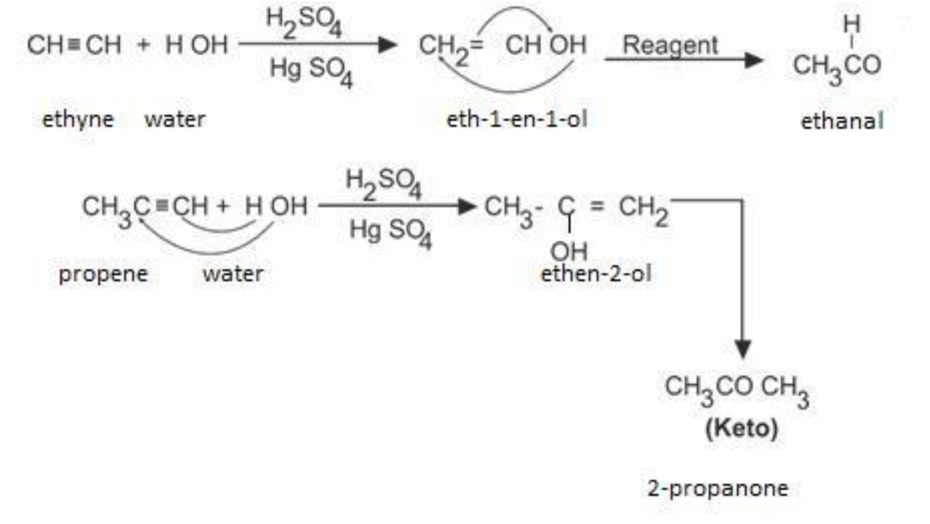
Calcium formate → calcium carbonate methanal

Only one salt form aldeyde , rest of them give ketones on distillation as shown below :

$(CH_3COO)_2Ca \longrightarrow CH_3COCH_3 + CaCO_3$

propanone

- **From hydrocarbons :**
- By acid hydration of alkynes



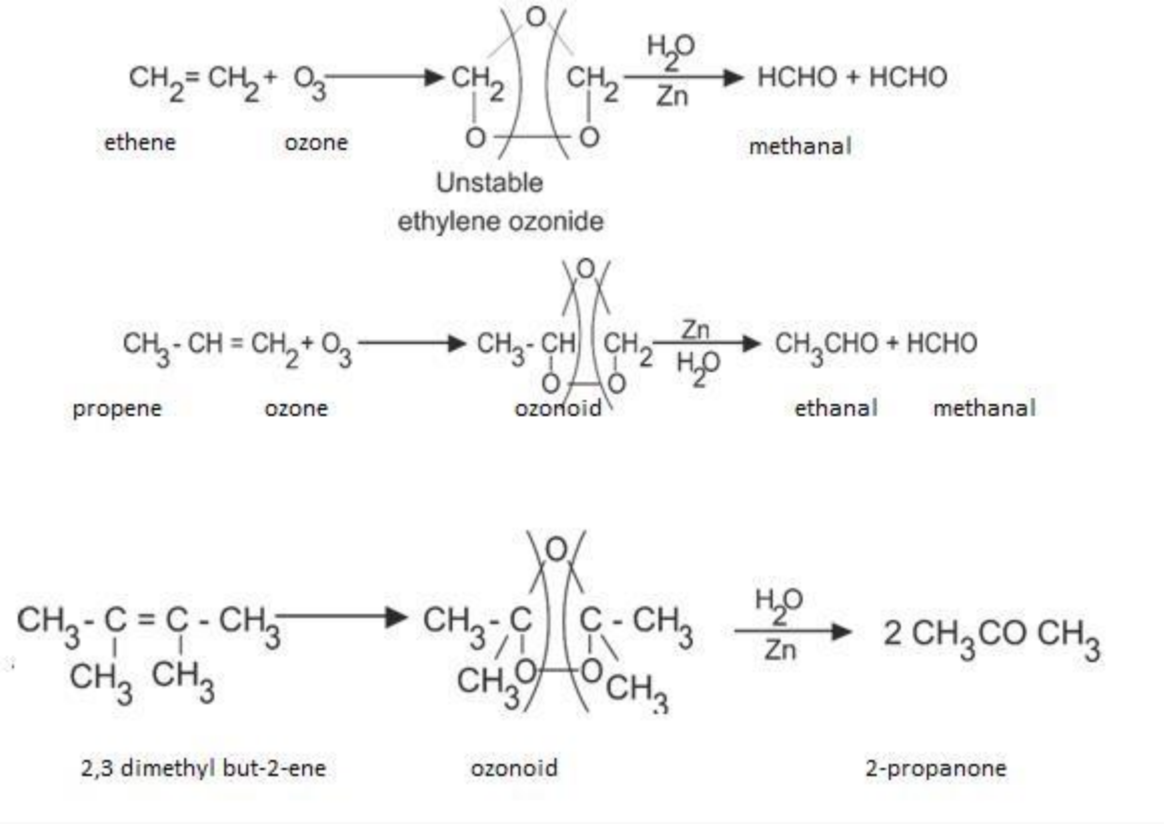
$CH{\equiv}CH + HOH \xrightarrow[HgSO_4]{H_2SO_4} CH_2{=}CHOH \xrightarrow{Reagent} CH_3CHO$

ethyne water → eth-1-en-1-ol → ethanal

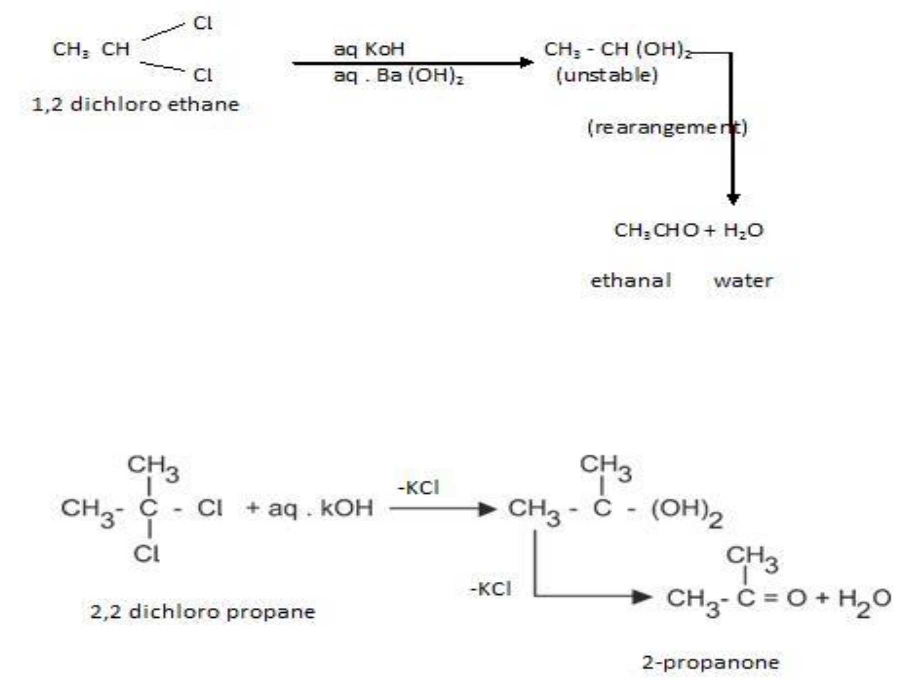
$CH_3C{\equiv}CH + HOH \xrightarrow[HgSO_4]{H_2SO_4} CH_3-C(OH)=CH_2 \longrightarrow CH_3COCH_3$

propene water → ethen-2-ol → (Keto) 2-propanone

- Ozonolysis of alkenes



- **From gem dihalide**



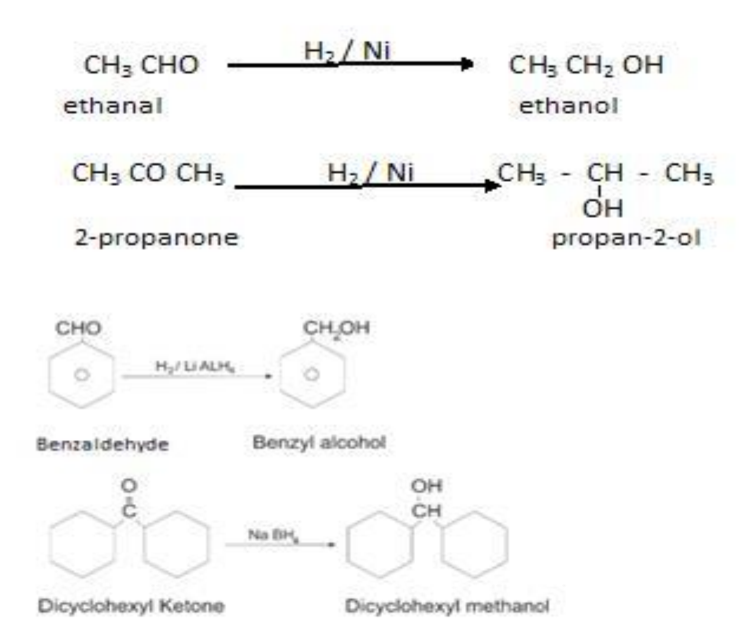
- **Reduction of Aldehyde and Ketone**

The major product on reduction is alcohol.

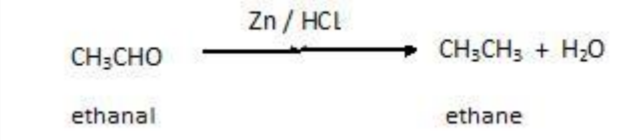
- Aldehyde gives primary alcohol.

- Ketones give secondary alcohol.

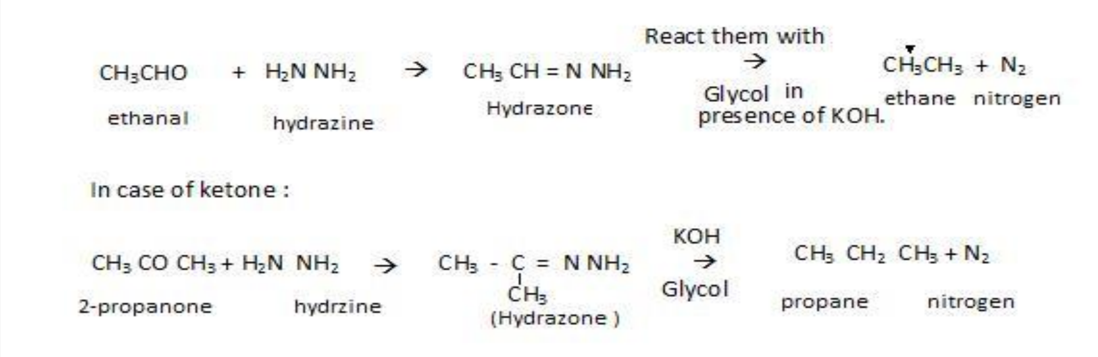
Major Oxidising agents can be used like Ni , Pt , $LiALH_4$, $NaBH_4$ etc. Out of them , $LiALH_4$is the strongest one .The reaction that occurs is given below:



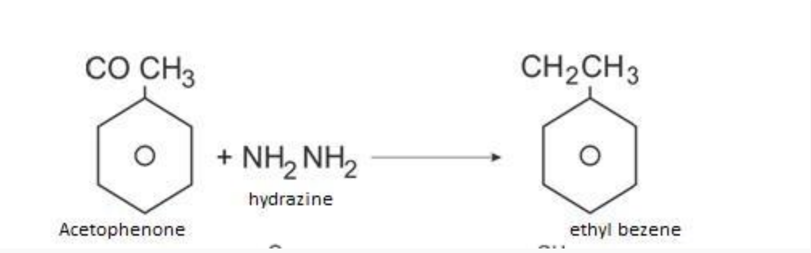
- **Reduction to HC's**
- **Clemenson reduction** – In this ,we take aldehyde and use Zinc in presence of HCl or Zn / Hg amalgam in HCl. The reaction involved is:



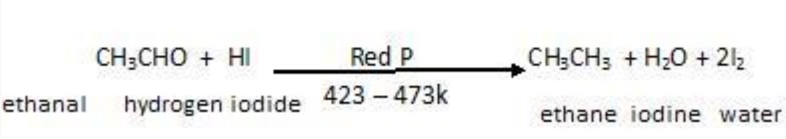
- **Wolf kishner reduction**: In this aldehyde is reacted with hydrazine as shown below :



- **For aromatic ketones**

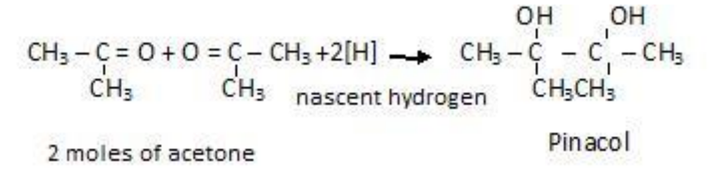


- By action of red phosphorous on HI we get, hydrocarbons [temperature 423 – 473k] as shown below:



$$CH_3CHO + HI \xrightarrow[423-473k]{Red\ P} CH_3CH_3 + H_2O + 2I_2$$

- **Reduction to Pinacol** – For this ,we take 2 moles of acetone and reduce them as shown:



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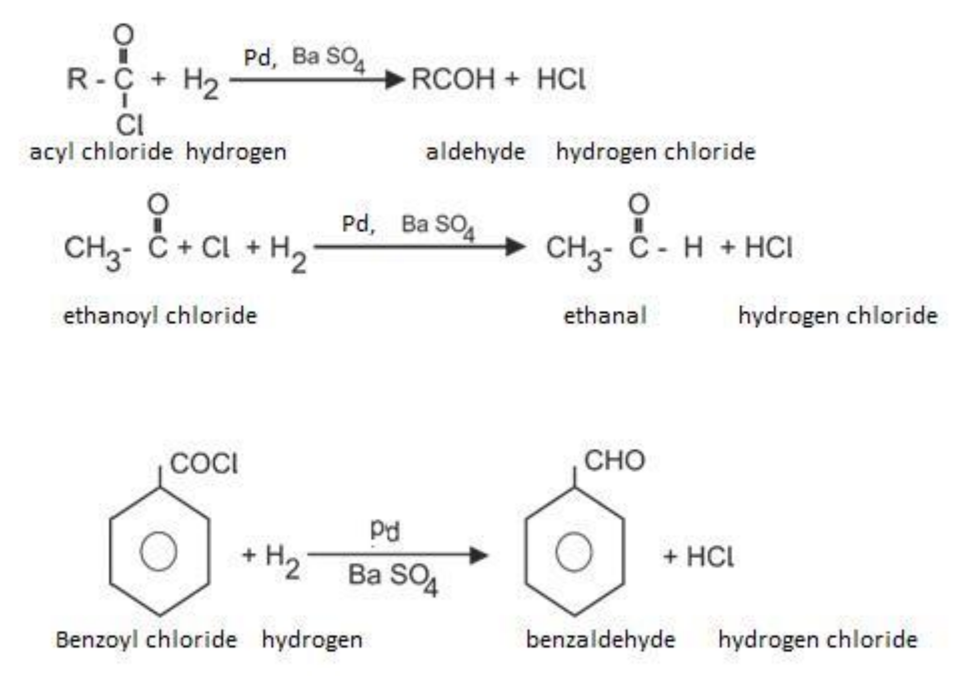
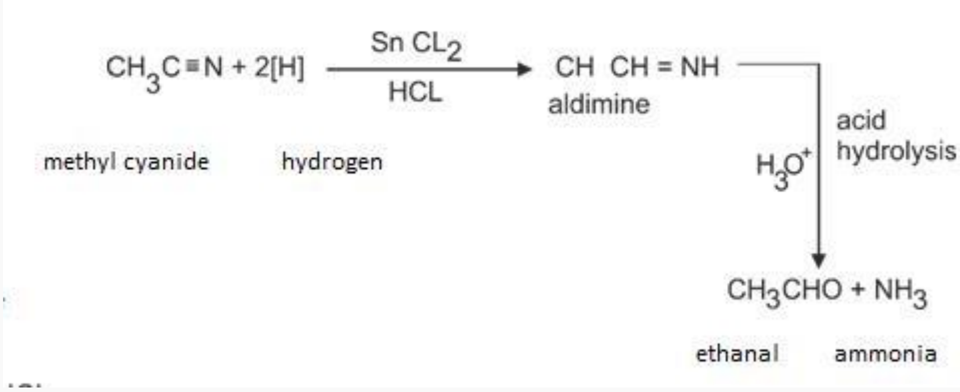
Methods for preparing only aldehydes

From acid chlorides - Rosenmund reaction

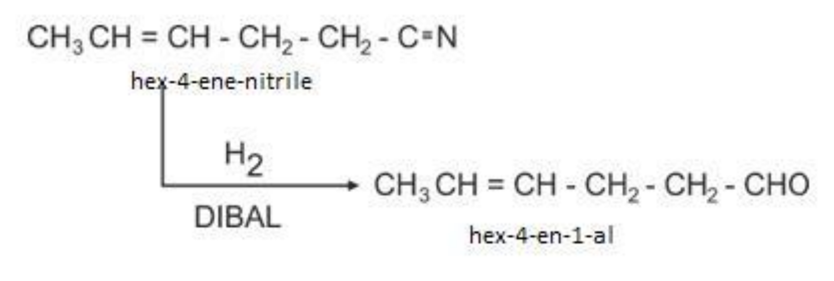


Drawback – Formaldehyde can’t be prepard by this method : formyl chloride H – COCl is unstable .Aldehydes can be further reduced to alcohol. So, in order to stop it at aldehyde stage we have to poison it.

2.**From reduction of alkyl cyanides – known as Stephen’s reduction (use of $SnCl_2$)**

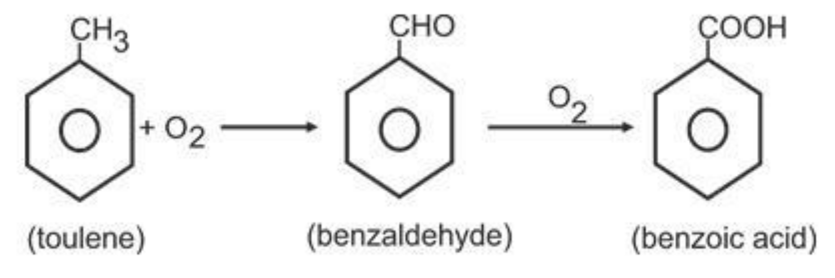


This can also be occur in presence of other reducing agent like – DIBAL. (Disobutyl aluminiun hydride).It is used for long chain nitrils.

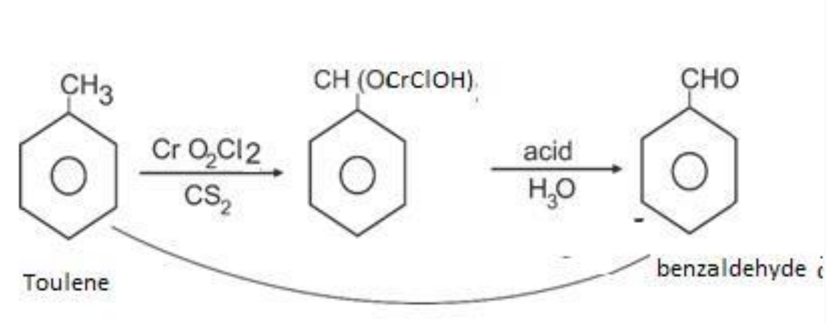


2.**Oxidation reaction – from hydrocarbons**

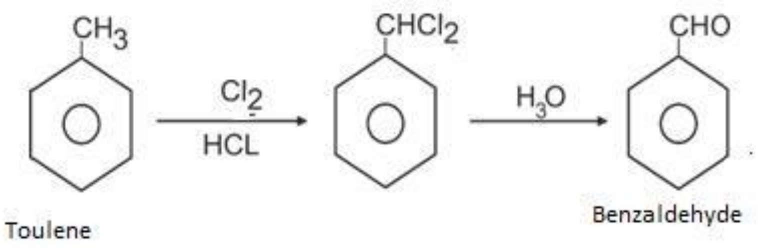
- Oxidation of methyl benzene



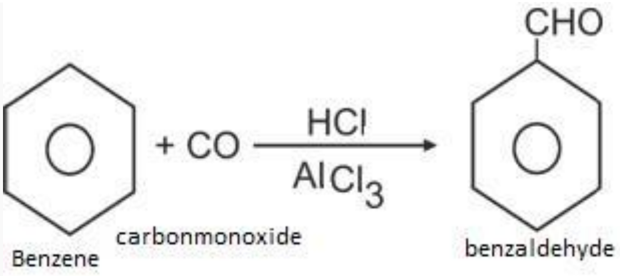
- **Use of chromyl chloride - Etard reaction**



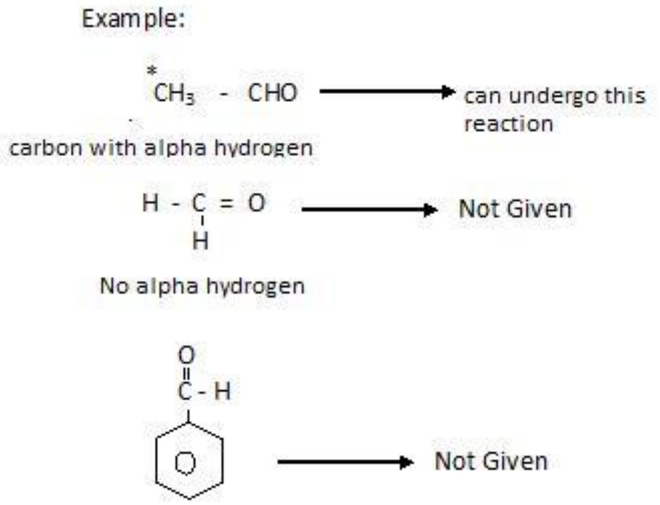
- **Side chain chlorination followed by hydrolysis**



- **Gatterman kosh reaction**



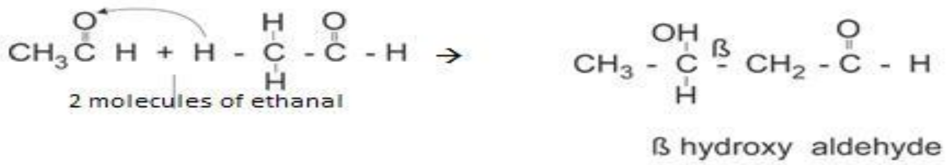
- **Miscellaneous reactions: Aldehyde / ketone**



- **Aldol condensation:** If we take two molecules of aldehyde and they are condensed .The product obtained is a compound with aldehyde and alcoholic group. These reactions are given by compounds that have – alpha C atom.

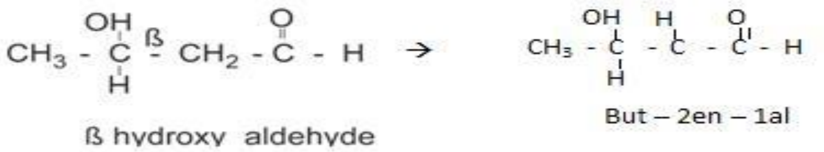
Example:

- **Self-aldol condensation :** In these 2 molecules of same aldehyde are taken:



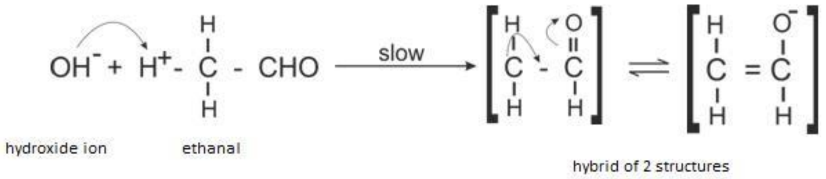
Change reaction in the following

The rxn doesn't stop here so,

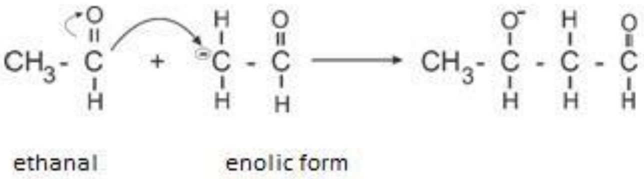


Mechanism of this reaction

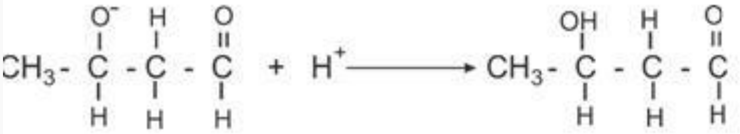
1. First step is slow and is rate determining step. In this OH^- act on aldehyde.



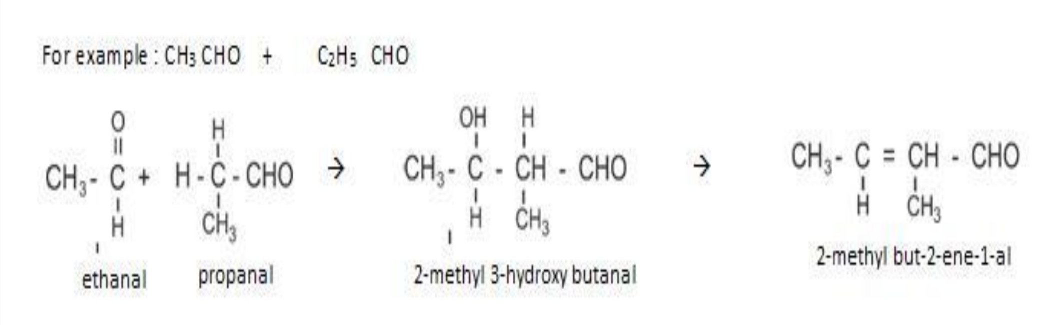
1. Second step – The enolic form react with another molecule.



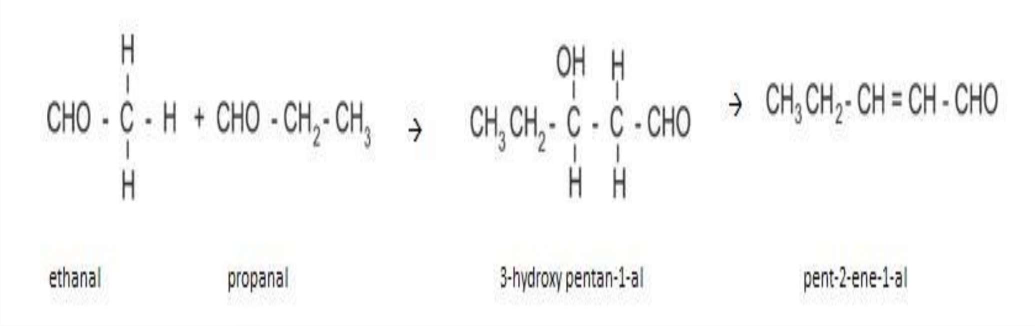
1. Addition of hydrogen ion



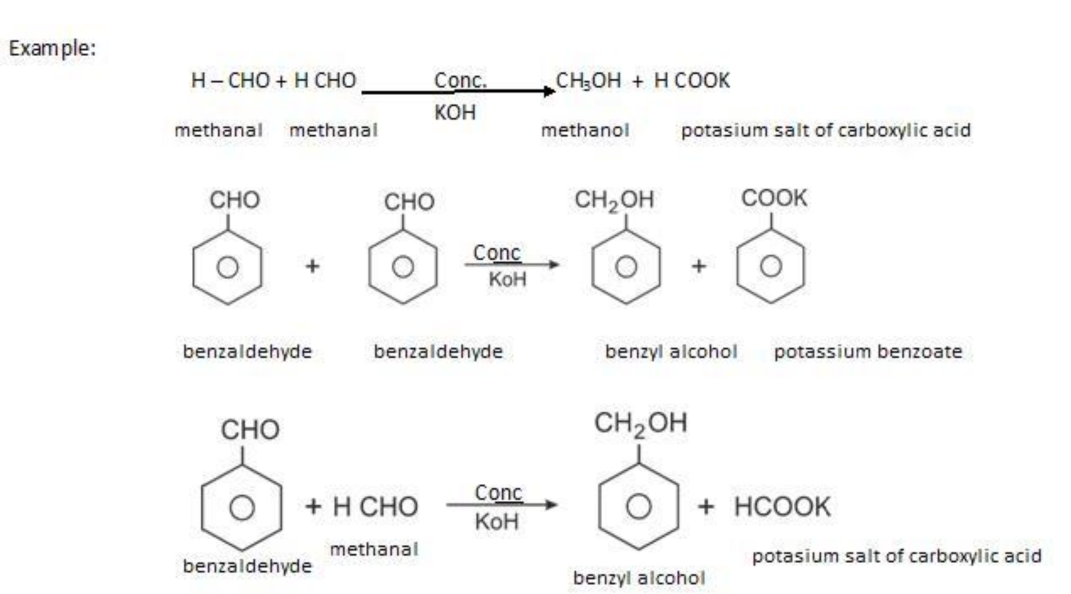
- **Cross- aldol condensation :** In this we take molecules that are different:



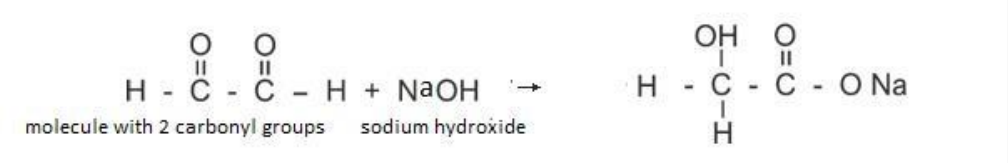
We can take other ways also in which We take alpha Hydrogen of CH_3HO(ethanal).



- **Cannizzaro Reaction**– It is shown by those that do not have alpha Hydrogen. In these two products are formed – alcohol and acid.



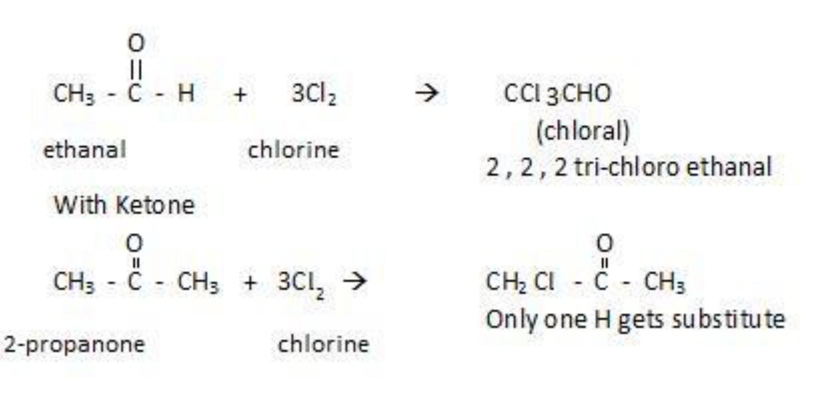
Intermolecular Cannizzaro reaction– The reaction occurs within same molecule, which has more than 2 or more carbonyl groups present.



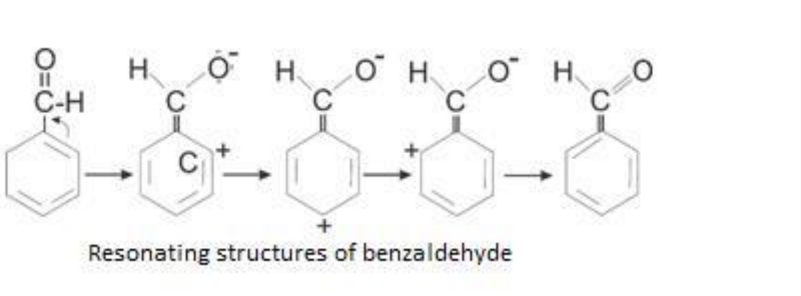
One "O" gets connected to OH and other to acid.

Halogenation Reaction -

In this alpha hydrogen is substituted by a halogen and we get product accordingly.



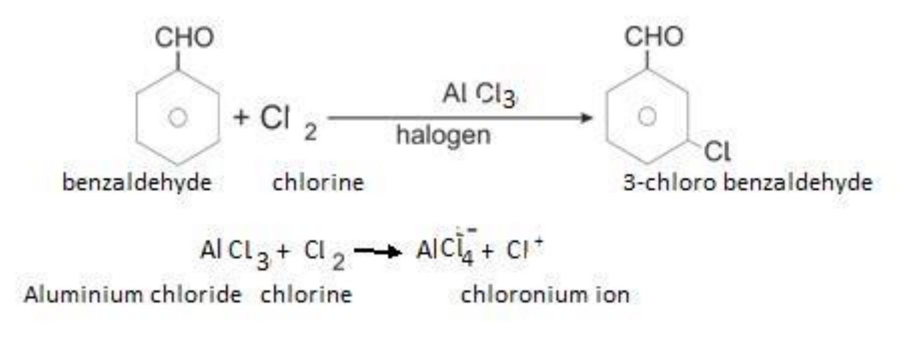
Ring substitution reaction: It is meta directing



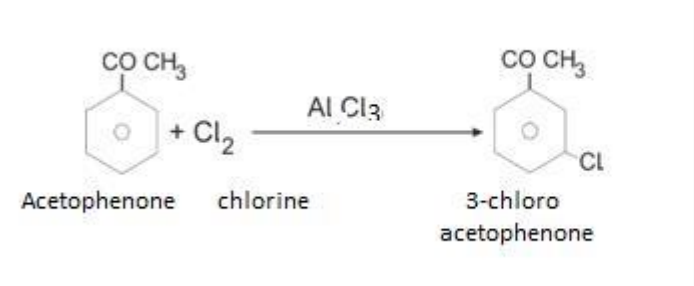
Resonating structures of benzaldehyde

The electrophile can't attack at ortho and para position. As they are meta directing compounds. So, all substitution occurs on Meta position.

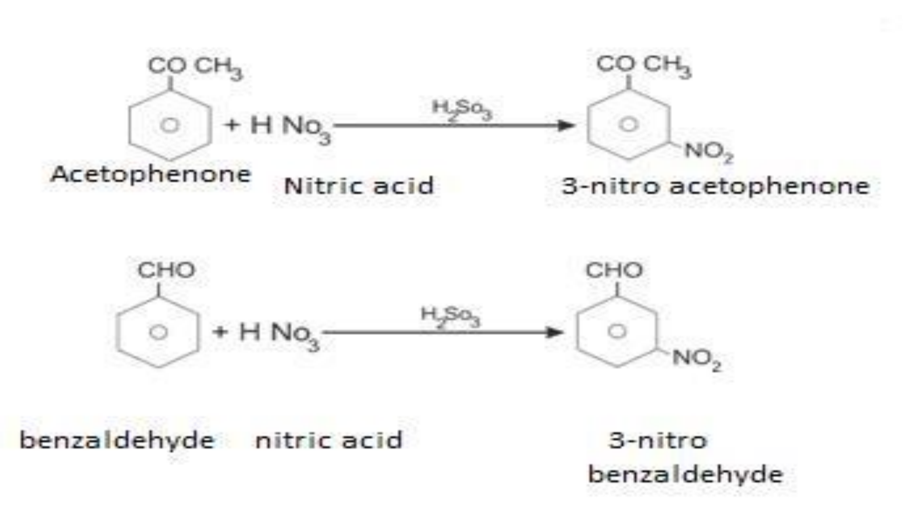
Halogenations



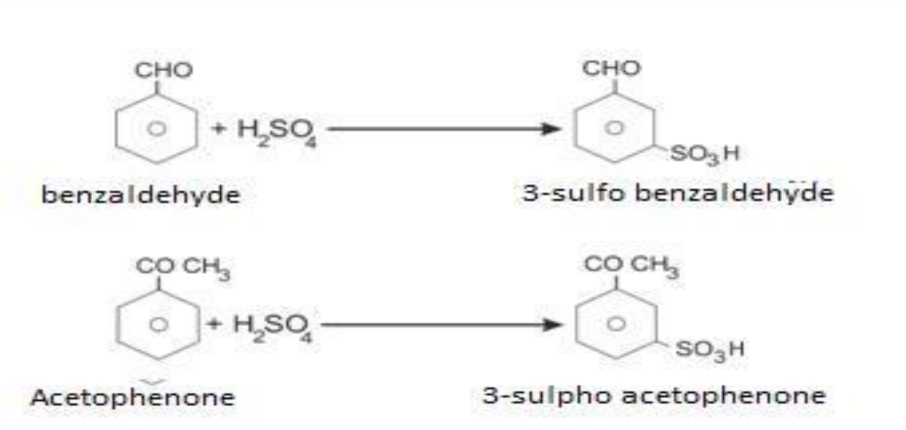
With Ketone



Nitration

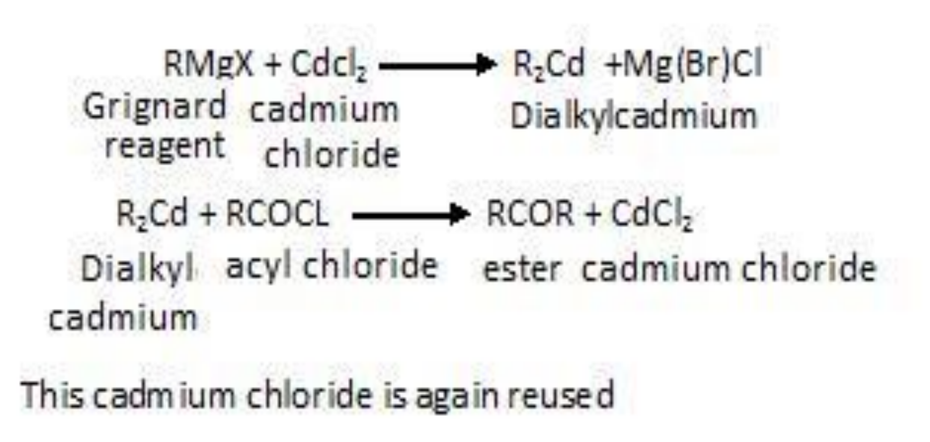


Sulphonation



Preparation of only ketones

1.From acyl chloride : In this we make use of dialkyl cadmium ,then we react with RCOCL. For preparation we take grignard reagent :



$RMgX + Cdcl_2 \longrightarrow R_2Cd + Mg(Br)Cl$

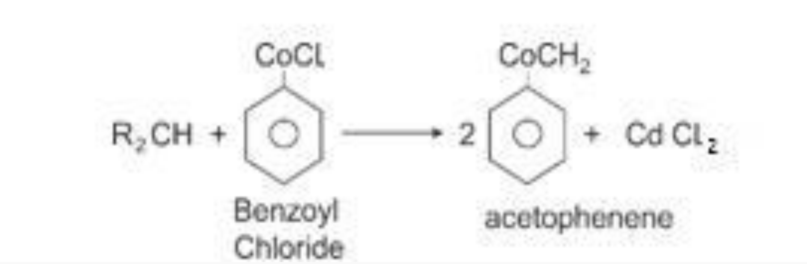
Grignard reagent cadmium chloride Dialkylcadmium

$R_2Cd + RCOCL \longrightarrow RCOR + CdCl_2$

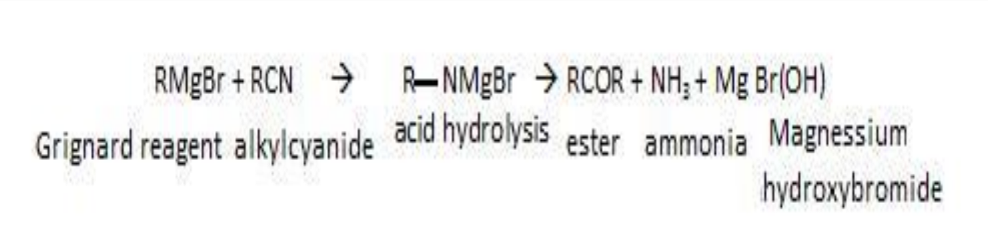
Dialkyl cadmium acyl chloride ester cadmium chloride

This cadmium chloride is again reused

Lets prepare acetophenone by this method :



2.From nitriles : In this we make use of grignard reagent and nitriles as shown in reaction :



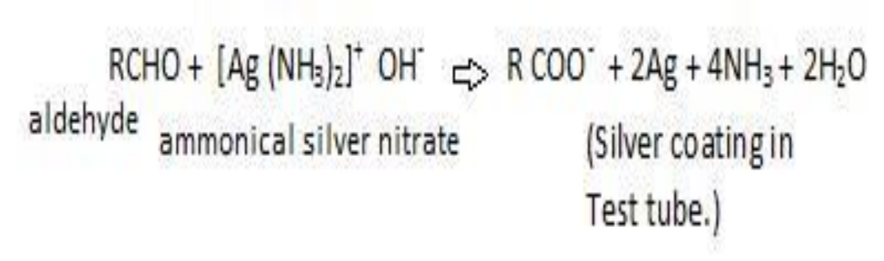
$$RMgBr + RCN \rightarrow R{-}NMgBr \rightarrow RCOR + NH_3 + Mg\,Br(OH)$$

In a similar manner, we can prepare acetophenone by taking grignard reagent as phenyl magnesium bromide and methyl cyanide.

Test for aldehydes and ketones

1. **For aldehydes**

- **Tollen's reagent** – It is a solution of Ammonical silver nitrate and it has formula [Ag $(NH_3)_2$ $]^+$ OH^-] .Now ,Let's take any aldehyde like :Formaldehyde and react with it as shown below .



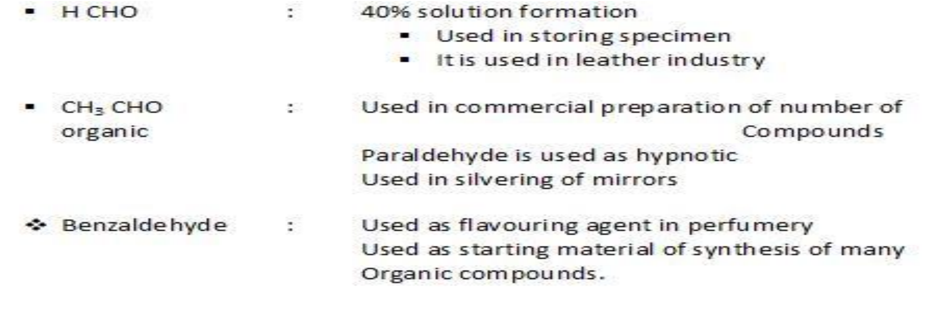
$$RCHO + [Ag(NH_3)_2]^+ OH^- \Rightarrow RCOO^- + 2Ag + 4NH_3 + 2H_2O$$

Therefore, called as "Silver mirror test". This test of oxidation that is Silver mirror test is not given by ketones.

- **Fehling solution test**
- It is prepared by missing equal amount of Fehling solution A and Fehling solution B.(Fehling A has Aq. $CuSO_4$ and Fehling B has Rochelle salt) .
- We take test tube and add both solutions A & B equally and resulting solution is blue due to $CuSO_4$).
- Now, when we add aldehyde this blue solution turns red. The medium is

alkaline due to Fehling solution B.

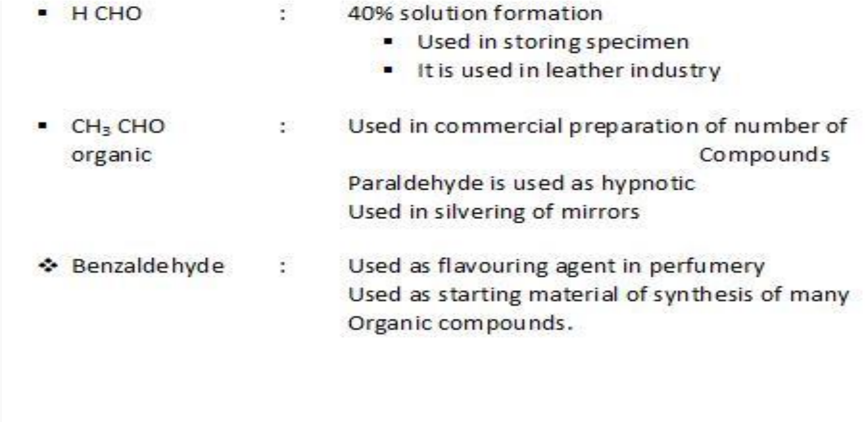
- The following reaction occurs.



- H CHO : 40% solution formation
  - Used in storing specimen
  - It is used in leather industry
- CH_3 CHO organic : Used in commercial preparation of number of Compounds
  Paraldehyde is used as hypnotic
  Used in silvering of mirrors
- Benzaldehyde : Used as flavouring agent in perfumery
  Used as starting material of synthesis of many Organic compounds.

<u>Identification</u>: The Colour changes from blue to red .This test is not given by ketones.

- **Benedict's solution test**- It is alkaline solution of cupric ion complied with citrate ions. When we react with aldehyde the following reaction occur:

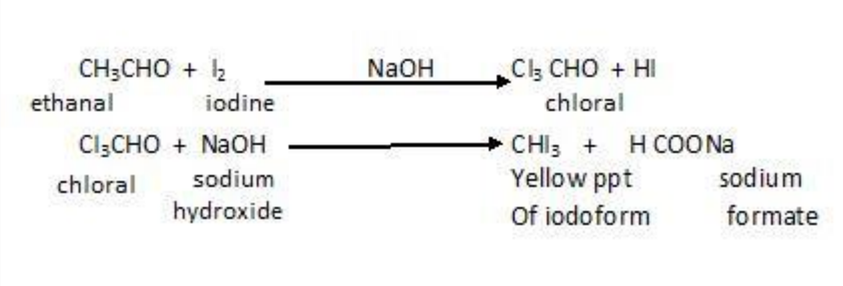


- H CHO : 40% solution formation
  - Used in storing specimen
  - It is used in leather industry
- CH_3 CHO organic : Used in commercial preparation of number of Compounds
  Paraldehyde is used as hypnotic
  Used in silvering of mirrors
- Benzaldehyde : Used as flavouring agent in perfumery
  Used as starting material of synthesis of many Organic compounds.

<u>Identification</u>: The Colour change from blue to red .This test is not given by ketones.

Test for Ketones

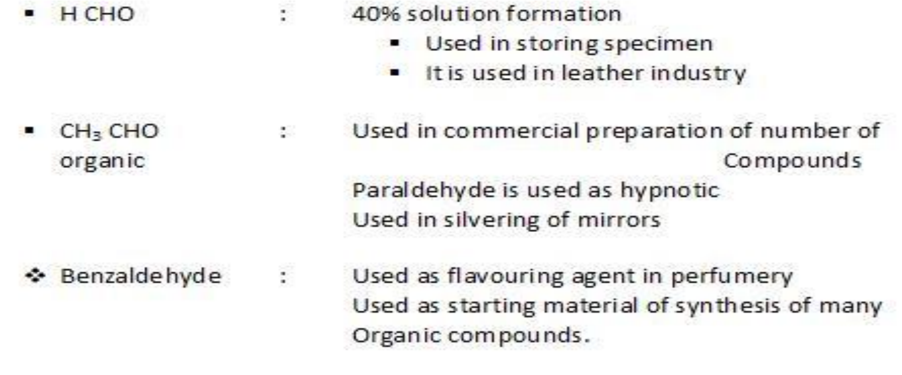
- **Iodoform test**
- By performing this test, we get yellow precipitate due to Formation of Iodoform.
- In this, we react aldehyde with Iodine in presence of NaOH. In this 3H are substitute by Iodine as shown below:



$$\underset{\text{ethanal}}{CH_3CHO} + \underset{\text{iodine}}{I_2} \xrightarrow{NaOH} \underset{\text{chloral}}{Cl_3CHO} + HI$$

$$\underset{\text{chloral}}{Cl_3CHO} + \underset{\text{sodium hydroxide}}{NaOH} \longrightarrow \underset{\text{Yellow ppt Of iodoform}}{CHI_3} + \underset{\text{sodium formate}}{HCOONa}$$

Uses of Aldehydes & Ketones:-



- H CHO : 40% solution formation
    - Used in storing specimen
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- CH_3 CHO : Used in commercial preparation of number of organic Compounds
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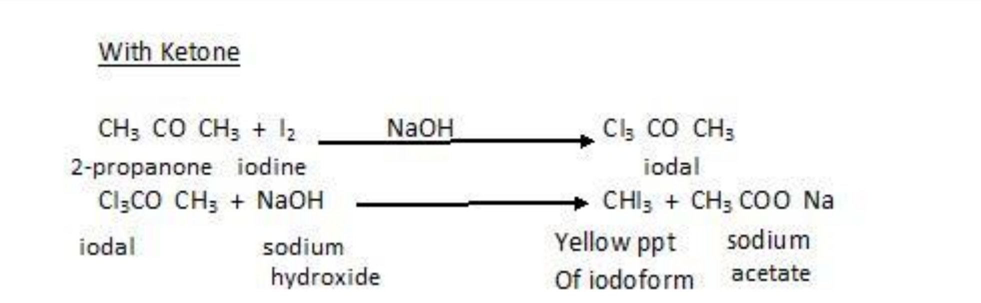
  Used as starting material of synthesis of many Organic compounds.

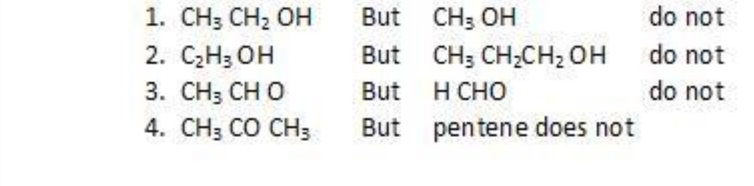


With Ketone

$$\underset{\text{2-propanone}}{CH_3\ CO\ CH_3} + \underset{\text{iodine}}{I_2} \xrightarrow{NaOH} \underset{\text{iodal}}{Cl_3\ CO\ CH_3}$$

$$\underset{\text{iodal}}{Cl_3CO\ CH_3} + \underset{\text{sodium hydroxide}}{NaOH} \longrightarrow \underset{\text{Yellow ppt Of iodoform}}{CHI_3} + \underset{\text{sodium acetate}}{CH_3\,COO\ Na}$$

- Limitation of this test: This is given only by methyl ketones i.e. one of the R in ketone should be CH_3 ,and also by ethanol as it also contains methyl group.
- See we have few examples Which will give and which will not give this test –



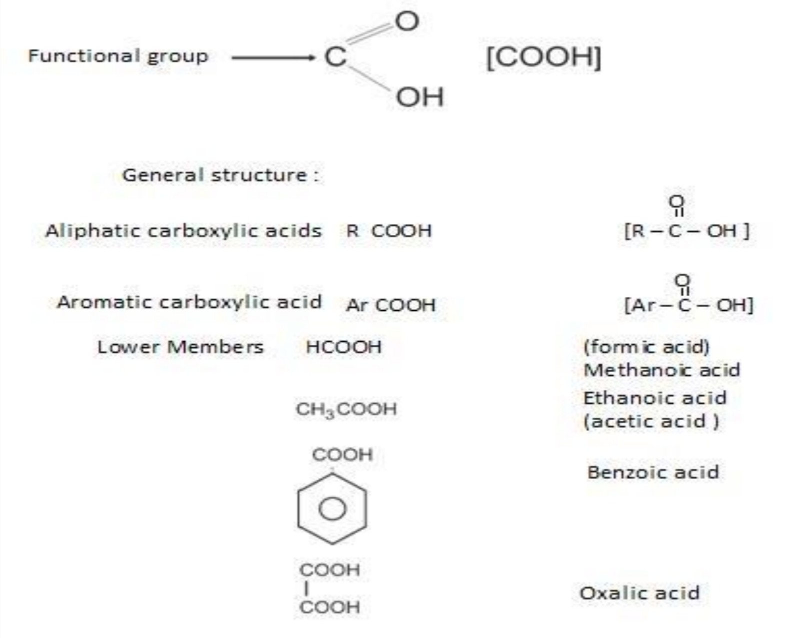
1. $CH_3\,CH_2\,OH$ But $CH_3\,OH$ do not
2. $C_2H_5\,OH$ But $CH_3\,CH_2CH_2\,OH$ do not
3. $CH_3\,CH\,O$ But H CHO do not
4. $CH_3\,CO\,CH_3$ But pentene does not

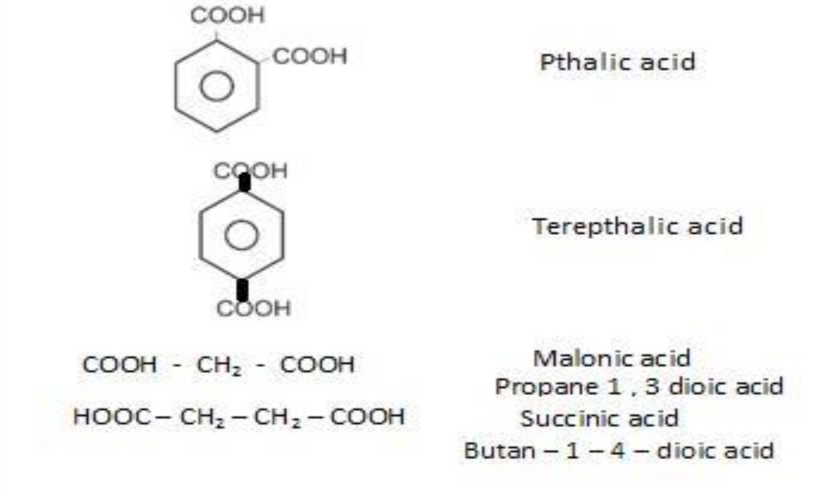
Physical properties of aldehydes and ketones :

- **Lower members** have unpleasent smell and up to 11 members they are liquids.
- **Solubility** : Aldehydes are more polar in nature.As we know, in ketones two alkyl groups are present. So, if electron density on carbon increases, the polarity of bond decreases, due to +I effect .

Therefore, solubililty of aldehyde is more as they have more tendency to form hydrogen bonds .As number of carbon atoms increase, the solubility decrease because of non polar nature .

- **Boiling points** : Boiling point is always more for polar compounds .
- ketones have higher boiling points than aldehyde because of more polarity .
- Their boiling point is always lower than alcohols and carboxylic acids because they are less polar then them .
- In aldehydes and ketones, dipole dipole interactions are comparitively less .
- **CARBOXYLIC ACID**

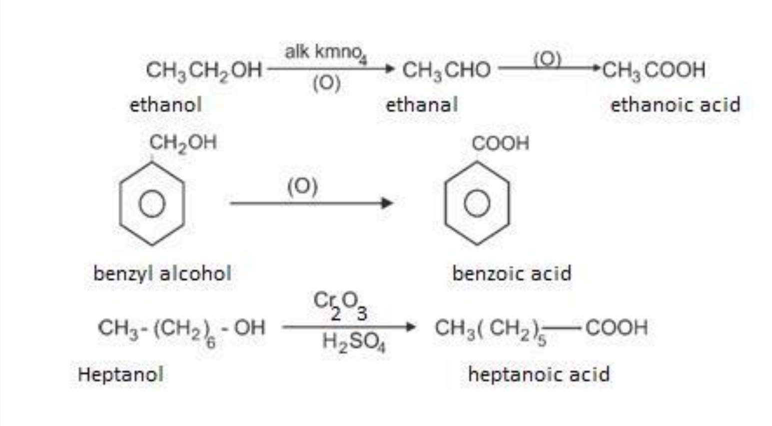
- 

- 

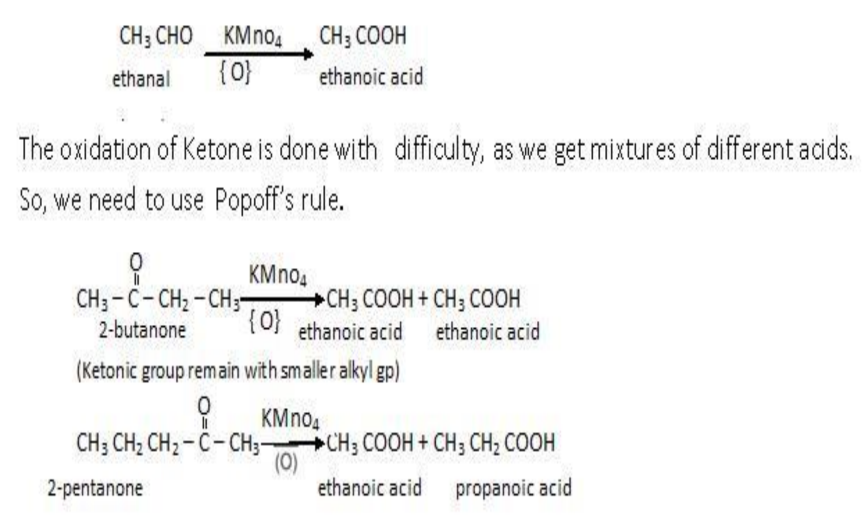
Method of preparation

It is prepared basically from oxidation and hydrolysis method.

1. **From alcohols by oxidation:** For this alkaline $kMnO_4$, CrO_3 in $H_2 SO_4$,acidified $K_2 Cr_2 O_7$ like oxidising agents are used.The reaction occurs as shown below :



2. **Oxidation of Aldehyde and Ketones:** In this aldehyde and ketones can be oxidised in presence of oxidising agents like alkaline potassium permagnante as shown below .



$CH_3CHO \xrightarrow[\{O\}]{KMno_4} CH_3COOH$

ethanal ethanoic acid

The oxidation of Ketone is done with difficulty, as we get mixtures of different acids. So, we need to use Popoff's rule.

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow[\{O\}]{KMno_4} CH_3COOH + CH_3COOH$

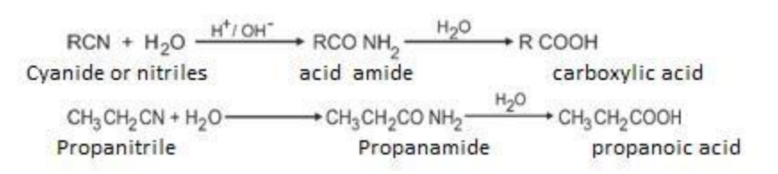
2-butanone ethanoic acid ethanoic acid

(Ketonic group remain with smaller alkyl gp)

$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[(O)]{KMno_4} CH_3COOH + CH_3CH_2COOH$

2-pentanone ethanoic acid propanoic acid

3.Hydrolysis of nitriles: In this cyanides are hydrolysed to form amides which further on hydrolysis yields carboxylic acid .



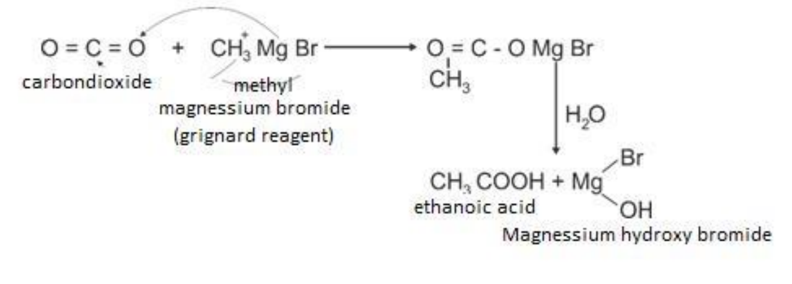
$RCN + H_2O \xrightarrow{H^+/OH^-} RCONH_2 \xrightarrow{H_2O} RCOOH$

Cyanide or nitriles acid amide carboxylic acid

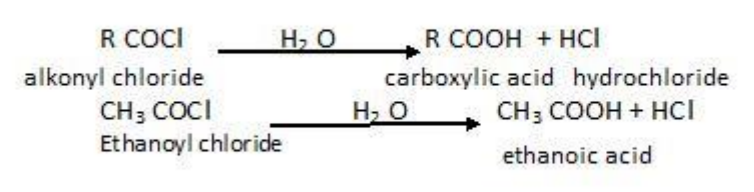
$CH_3CH_2CN + H_2O \longrightarrow CH_3CH_2CONH_2 \xrightarrow{H_2O} CH_3CH_2COOH$

Propanitrile Propanamide propanoic acid

4.From Grignard reagent : In this grignard reagent is made to react with carbondioxide .



5.From acyl halide: In this hydrolysis of acyl halide is hydrolysed to form respective carboxylic acid .



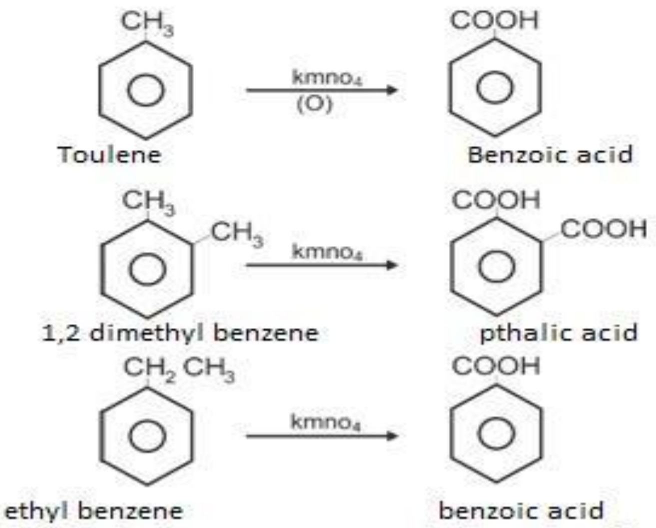
$RCOCl \xrightarrow{H_2O} RCOOH + HCl$

alkonyl chloride carboxylic acid hydrochloride

$CH_3COCl \xrightarrow{H_2O} CH_3COOH + HCl$

Ethanoyl chloride ethanoic acid

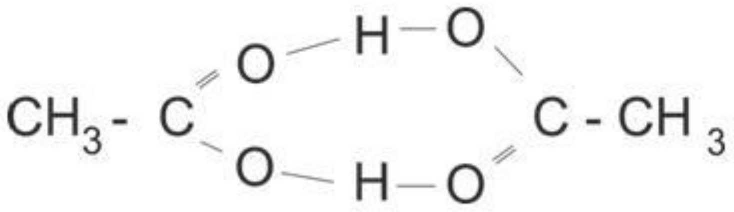
6.From alkyl benzene : In this alkyl benzene is oxidised in presence of oxidising agent like alkaline potassium permagnate to form respectice carboxylic acid .



(In this last one you can see only the carbon directly attached to benzene ring gets oxidised to carboxylic acid .

Physical properties

1. **Existence**: They are Colourless liquids with pungent smell. The higher members are oily liquids and still higher members are waxy solids.
2. **Solubility** : First four members are soluble in H_2O that is- HCOOH , CH_3 , COOH , C_2H_5 COOH , C_3H_7 But as number of Carbon atoms increase , solubility decrease because size of non-polar group increases. Solubility of smaller members is due to formation of Hydrogen bonds.
3. **Boiling points**:Boiling points are higher due to formation of hydrogen bonds . As number of Carbon atoms increases , boiling point also increases.

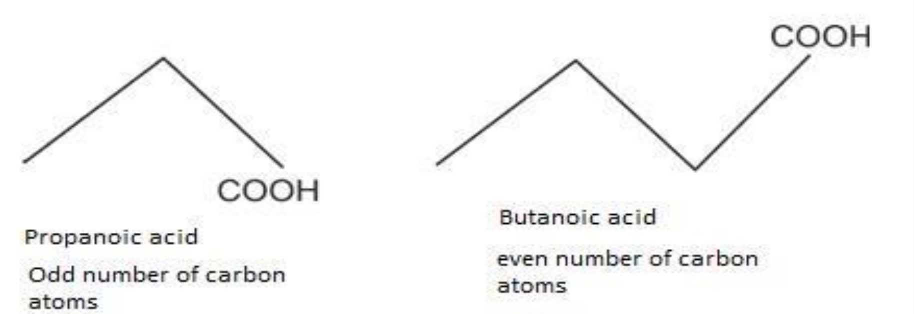


(exist as dimer)

Acetic acid

1. **Melting point** : Show un-usual behaviour.

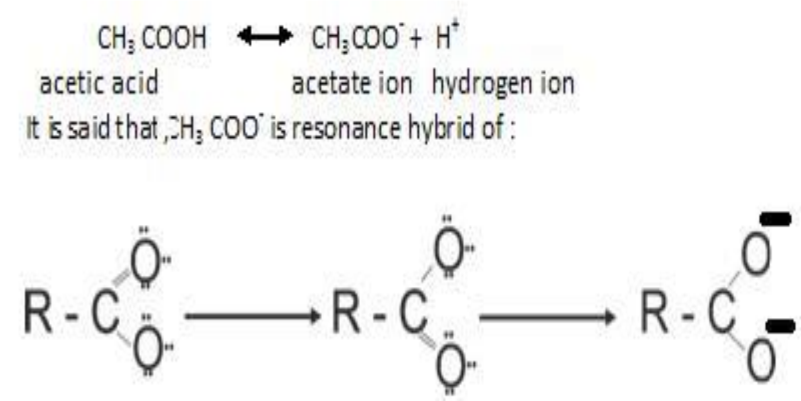
- Those having odd number of carbon atoms possess low Melting point -
- $\underline{CH_3\ CH_2\ COOH}$ = 251k
- High Melting point of members with even number of Carbon atoms –
- $\underline{CH_3\ CH_2\ CH_2\ COOH}$ = 367k
- It is due to symmetrical structure.



Chemical properties of carboxylic acid

Main four types of reactions shown by them:

1. **Reaction due to Hydrogen atom of carboxylic acid:** This property actually shows acidic character of carboxylic acid acids that is :



$CH_3COOH \leftrightarrow CH_3COO^- + H^+$

acetic acid acetate ion hydrogen ion

It is said that ,CH_3COO^- is resonance hybrid of :

If we talk about Strength of acidic character of CH_3 COOH,then we have :

$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$

According to Arhenius acid and Bronstedconcept: Carboxylic acid is regarded as an acid.We can write its expression for dissociation constant as written below.

$$Ka = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

It is seen that :

- Higher the value of ka, stronger is the acid.
- Pka = -log ka
- Higher the value of Pka, weaker is the acid.

Effect of substituents on strength of acid

We can have subsituents of two types :

- Electron withdrawing

- Electron Releasing groups

Electron withdrawing subsituents: They will neutralize the intensity of -ve charge and hence, $RCOO^-$ ion gets stablized. Therefore , the acid srength increases. Eg:Halogens

Electron releasing subsituents : They will increase the intensity of negative charge and hence ,$RCOO^-$ ion gets less stablized. Therefore, acidic strength due to this decreases.

<u>The acidic strength also depends upon other factors such as :</u>

1. Type of halogen attached :

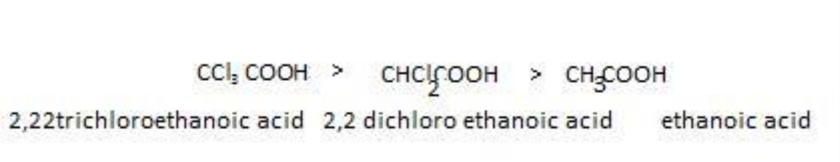
F>Cl>Br

Fluroine is much more electronegative

Acidic Strength CH_3COOF more stronger acid > CH_3COCl

$BrCH_3COOH$ > CH_3COOI

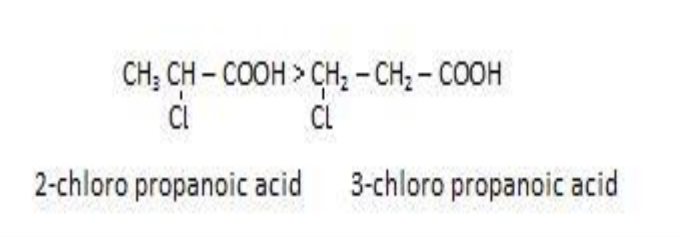
1. Acidic strength depending upon number of halogen atoms attached :



CCl_3COOH > $CHCl_2COOH$ > CH_3COOH

2,22trichloroethanoic acid 2,2 dichloro ethanoic acid ethanoic acid

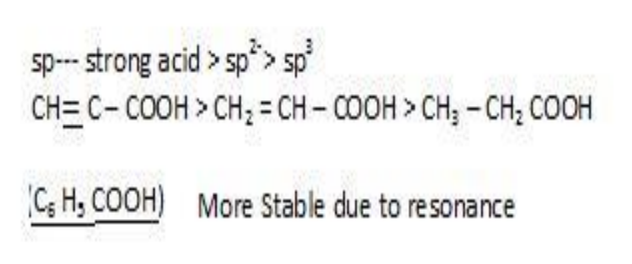
1. Depending upon the position, where X is attached



$$\underset{\displaystyle Cl}{CH_3\,CH} - COOH > \underset{\displaystyle Cl}{CH_2} - CH_2 - COOH$$

2-chloro propanoic acid 3-chloro propanoic acid

4. Depending upon hybridisation:



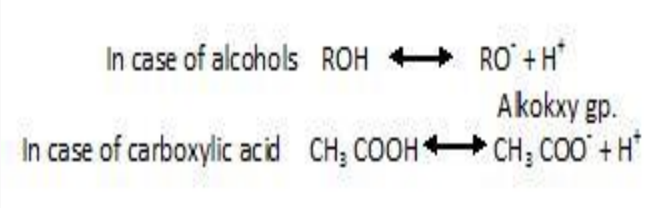
sp--- strong acid > sp^2 > sp^3

$CH\equiv C-COOH > CH_2=CH-COOH > CH_3-CH_2\,COOH$

(C_6H_5COOH) More Stable due to resonance

Comparison of acidic strength of alcohol , phenols and carboxylic acid

- If we compare Alcohol and carboxylic acid, we see that :

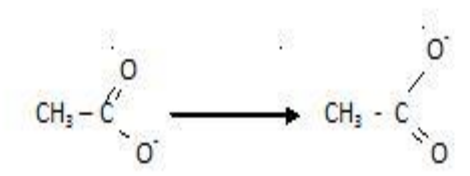


In case of alcohols $ROH \longleftrightarrow RO^- + H^+$

Alkokxy gp.

In case of carboxylic acid $CH_3COOH \longleftrightarrow CH_3COO^- + H^+$

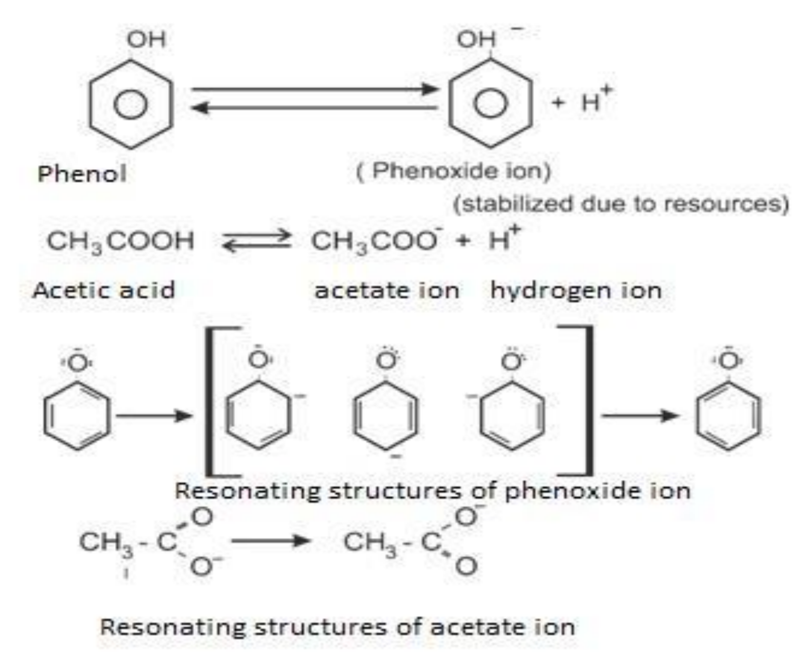
It’s seen that more the ion is stablized , more the reaction will be favoured in found direction.Below you can see carboxylic acid is resonance stabilized. So, it is more stable and on the other hand the R group attached to O^- in alcohol intensifies its charge. Hence, the stability is lowered in mparison to carboxylic acid.



Therefore, COOH is stronger acid than alcohol.

Phenols and carboxylic acid : Acidic character

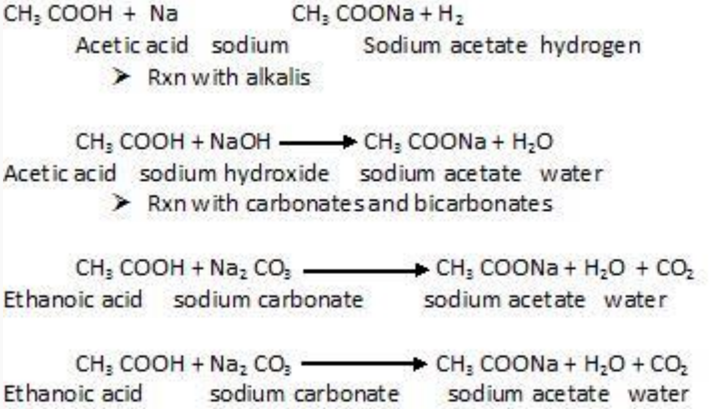
Similarly, if we look for phenoxide ion and carboxylate ion that is formed by phenol and carboxylic acid after loosing hydrogen ion, we can easily make out that carboxylate ion is more stabilized. In it negative charge resides on electronegative ion (resonating structure) whereas in case of phenoxide ion the negative charge is on carbon.let’s see. the structures below :



That is the reason ,carboxylic acid is stronger than phenols .

Reactions to prove acidic character of carboxylic acid

- Reaction with metal



$CH_3COOH + Na \qquad CH_3COONa + H_2$

Acetic acid sodium Sodium acetate hydrogen

- ➢ Rxn with alkalis

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Acetic acid sodium hydroxide sodium acetate water

- ➢ Rxn with carbonates and bicarbonates

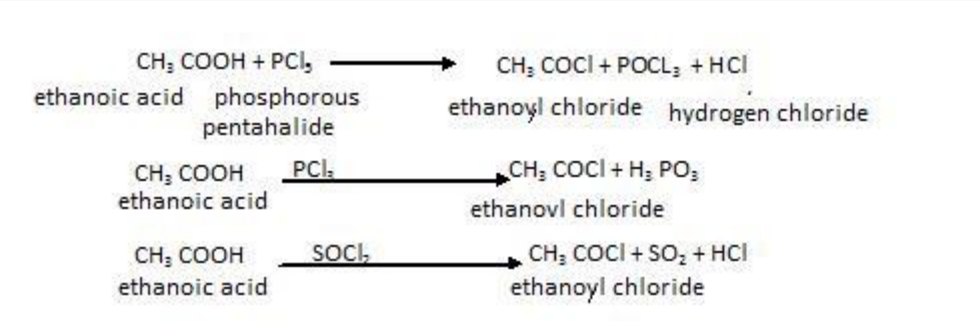
$CH_3COOH + Na_2CO_3 \longrightarrow CH_3COONa + H_2O + CO_2$

Ethanoic acid sodium carbonate sodium acetate water

$CH_3COOH + Na_2CO_3 \longrightarrow CH_3COONa + H_2O + CO_2$

Ethanoic acid sodium carbonate sodium acetate water

Reaction involving OH group: In this we react carboxylic acid with compounds like With PCl_5 , PCl_3 , $SOCl_2$.



$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCL_3 + HCl$

ethanoic acid phosphorous pentahalide ethanoyl chloride hydrogen chloride

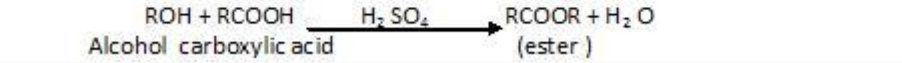
$CH_3COOH \xrightarrow{PCl_3} CH_3COCl + H_3PO_3$

ethanoic acid ethanovl chloride

$CH_3COOH \xrightarrow{SOCl_2} CH_3COCl + SO_2 + HCl$

ethanoic acid ethanoyl chloride

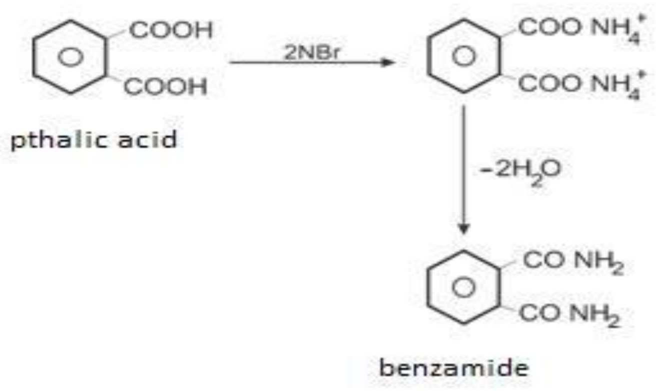
- Reaction with alcohol : Esterification



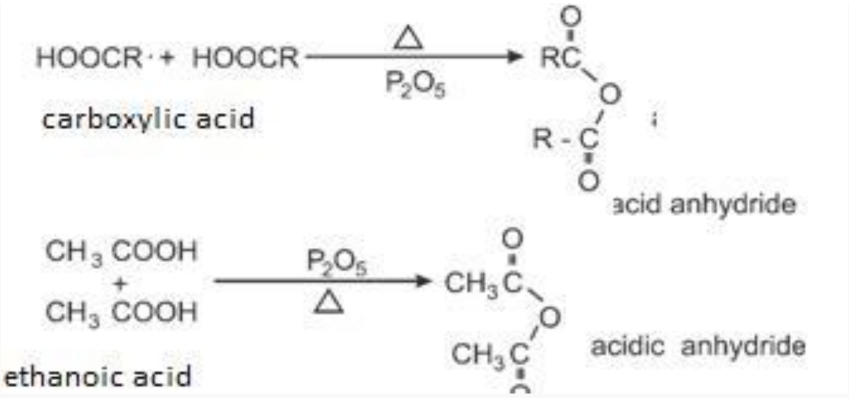
$ROH + RCOOH \xrightarrow{H_2SO_4} RCOOR + H_2O$

Alcohol carboxylic acid (ester)

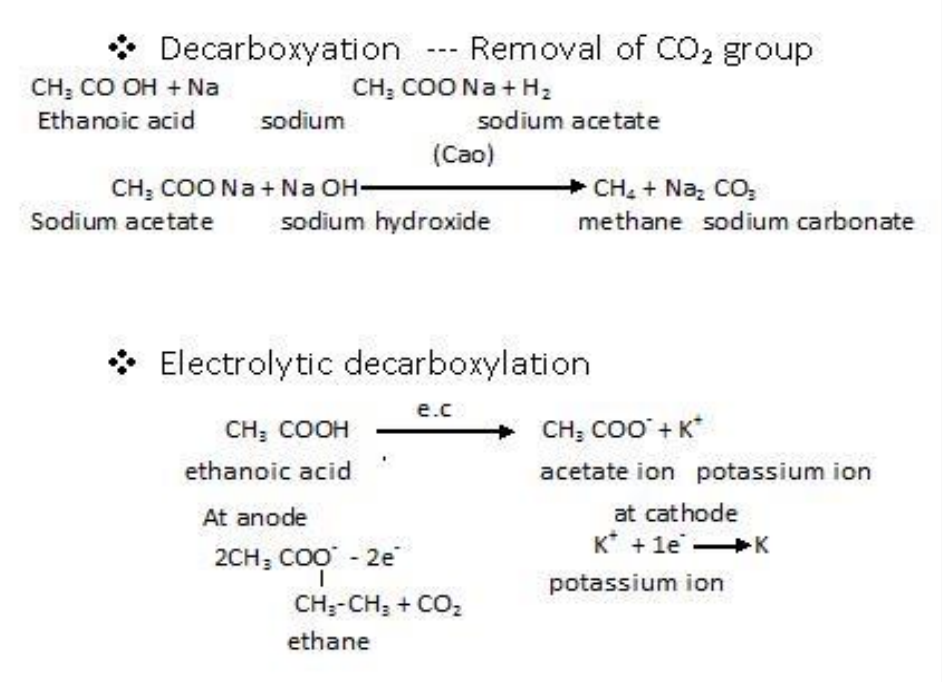
- Reaction with NH_3



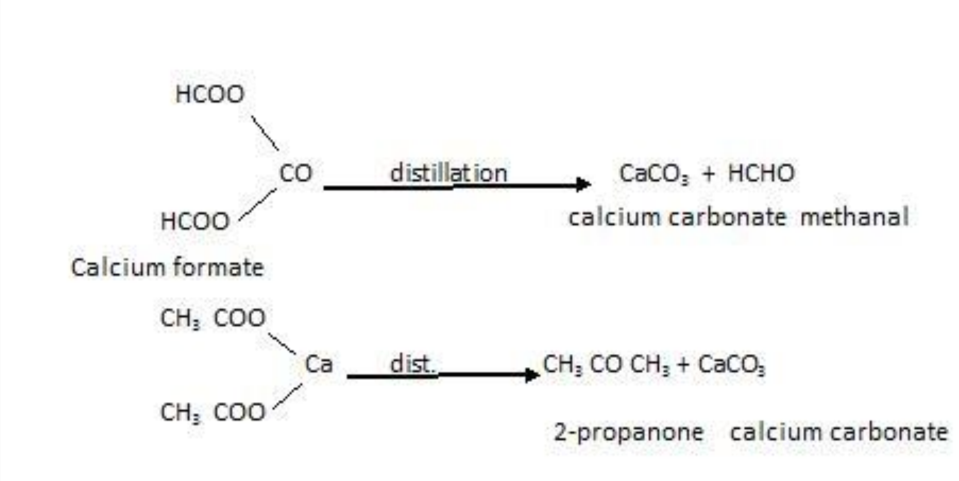
- Formation of acid anhydride



3.Reaction involving COOH group



- Reaction of carboxylic salt of Calcium



4.Reduction reaction

- Partial Reduction

The acids on reduction in presence of reducing agents like are Li AlH_4 etc forms alcohols that is :

$$\underset{\text{carboxylic acid}}{RCOOH} \xrightarrow[H_2]{Li\ ALH_4} \underset{\text{alcohol}}{RCOH}$$

$$\underset{\text{ethanoic acid}}{CH_3COOH} \xrightarrow[H_2]{LiALH_4} \underset{\text{ethanol}}{CH_3CH_2OH}$$

- Complete reduction : When complete reduction is carried out, it forms alkane in presence of red Phosphorous that is :

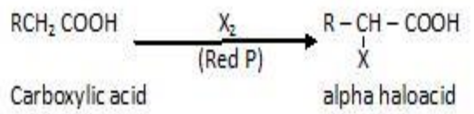
$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{hydrogen iodide}}{HI} \xrightarrow{Red\ P} \underset{\text{alkane}}{RCH_3} + \underset{\text{iodine}}{I_2}$$

Special name reactions

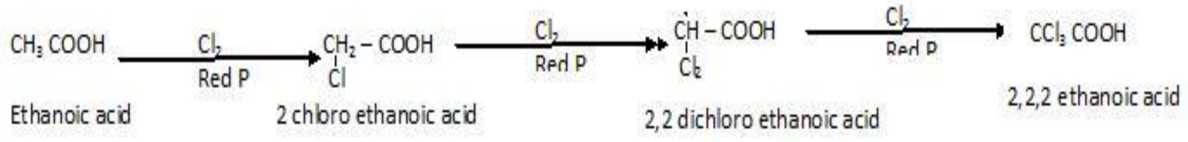
❖ Borodine Hunsdicker Reaction

$$\underset{\text{Silveracetate}}{CH_3COOAg} + \underset{\text{bromine}}{Br_2} \xrightarrow{CCl_4} \underset{\text{methyl bromide}}{CH_3Br} + \underset{\text{silverbromide}}{AgBr} + CO_2$$

❖ Hellvolhart - Zelincky Reaction



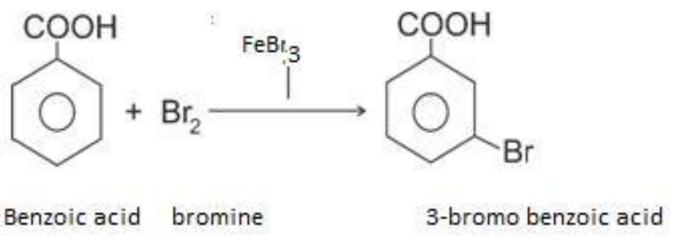
$$\underset{\text{Carboxylic acid}}{RCH_2COOH} \xrightarrow[(Red\ P)]{X_2} \underset{\text{alpha haloacid}}{R-\underset{X}{\underset{|}{CH}}-COOH}$$



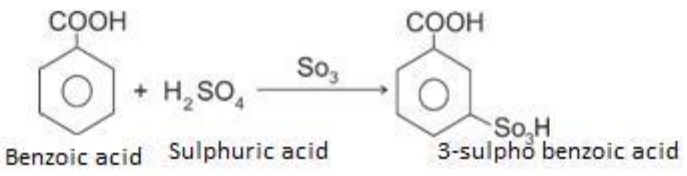
$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[Red\ P]{Cl_2} \underset{\text{2 chloro ethanoic acid}}{\underset{Cl}{\underset{|}{CH_2}}-COOH} \xrightarrow[Red\ P]{Cl_2} \underset{\text{2,2 dichloro ethanoic acid}}{\underset{Cl_2}{\underset{|}{CH}}-COOH} \xrightarrow[Red\ P]{Cl_2} \underset{\text{2,2,2 ethanoic acid}}{CCl_3COOH}$$

__Ring subsitution reactions :__

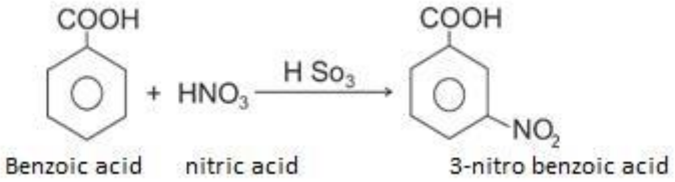
- Bromination



- Sulphonation



- Nitration



Uses of carboxylic acid

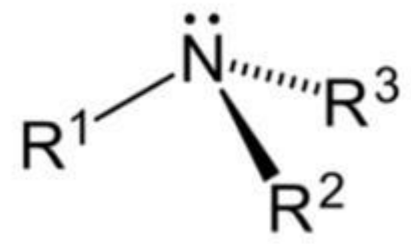
1. Methanoic acid is used as coagulating agent in rubber industry.
2. Benzoic acid is used as antiseptic and also in perfumery.
3. Ethanoic acid is used as solvent and also in cooking as vinegar and much more.

Introduction

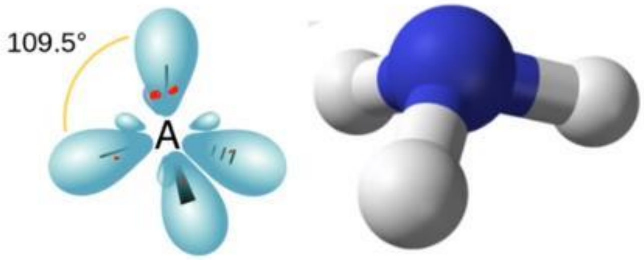
- Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl group(s).
- In nature, they occur among proteins, vitamins, alkaloids and hormones.
- Amines have lot of importance in our day to day life.
- For example:-
  - Polymers, dyestuffs and drugs contain amines.
  - Two biologically active compounds, namely adrenaline and ephedrine, both containing secondary amino group, are used to increase blood pressure.
  - Novocain, a synthetic amino compound, is used as an anaesthetic in dentistry.
  - Benadryl, a well-known antihistaminic drug also contains tertiary amino group.
  - Quaternary ammonium salts are used as surfactants. Diazonium salts are intermediates in the preparation of a variety of aromatic compounds including dyes.

Structure of Amines

- Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl and/or aryl groups.
- Nitrogen atom of amines is trivalent and carries an unshared pair of electrons.



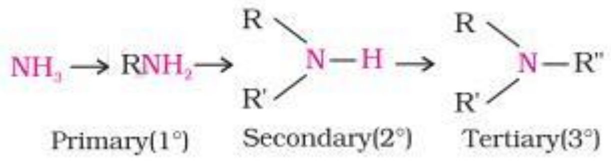
- Nitrogen orbitals of amines are sp^3 hybridized and the geometry of amines is pyramidal.
- Each of the three sp^3 hybridised orbitals of nitrogen overlap with orbitals of hydrogen or carbon depending upon the composition of the amines.
- The fourth orbital of nitrogen in all amines contains an unshared pair of electrons.
- Due to the presence of unshared pair of electrons, the angle C–N–E, (where E can be either C or H). is less than 109.5^0.

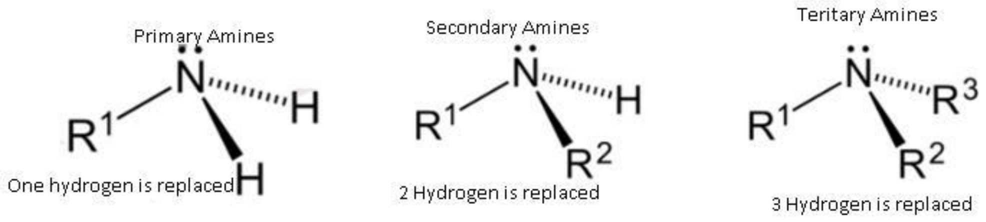


- In case of trimethylamine the bond angle is 108°.

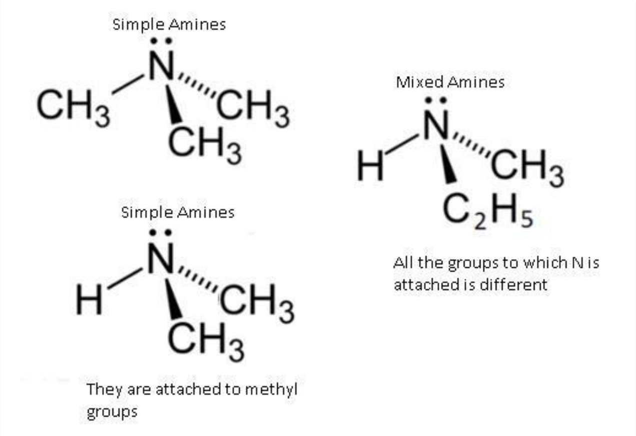
Classification of Amines as Primary, Secondary & Tertiary

- Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups in ammonia molecule.
- If one hydrogen atom of ammonia is replaced by R or Ar, we get RNH_2 or $ArNH_2$, a primary amine (1°).
- If two hydrogen atoms of ammonia or one hydrogen atom of $R\text{-}NH_2$ are replaced by another alkyl/aryl (R’) group then it is called as secondary amine.
- The second alkyl/aryl group may be same or different.
- Replacement of another hydrogen atom by alkyl/aryl group leads to the formation of tertiary amine.



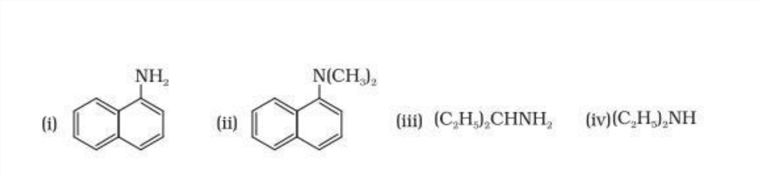


- Amines are said to be ‘simple’ when all the alkyl or aryl groups are the same, and ‘mixed’ when they are different.



Problem:-

Classify the following amines as primary, secondary or tertiary:



Answer:-

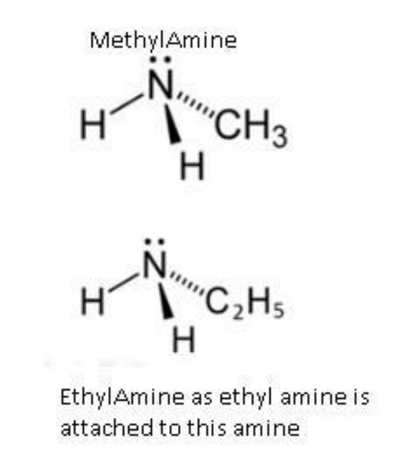
- It is a primary amine because only 1 hydrogen is replaced if we compare this structure with ammonia.
- It is a tertiary amine as all the 3 hydrogen is replaced.
- It is a primary amine as only 1 hydrogen is replaced.

It is a secondary amine as 2 hydrogens are

Nomenclature of Amines by IUPAC System

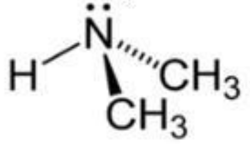
Common Names of Amines

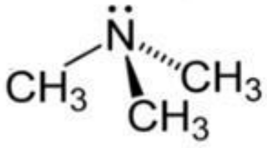
- An aliphatic amine is named by prefixing alkyl group to amine, i.e. alkylamine as 1 word.
- We are considering primary amines.



- In secondary and tertiary amines, when two or more groups are the same, the prefix di or tri is added to the before the name of alkyl group.

Dimethylamine

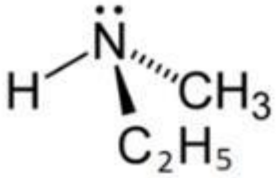




Trimethylamine

- In case of mixed amine, alkyl group are written in alphabetical order.

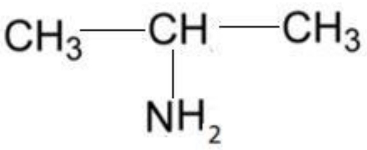
Ethyl Methyl Amine



IUPAC System

- In IUPAC system, amines are named as alkanamines, derived by replacement by ‘e’ of alkane by the word amine.
- For Example: - Methanamine (CH_3NH_2), Ethan amine ($C_2H_5NH_2$).
- For naming higher member hydrocarbon, longest chain containing amino group is selected. C atom to which amino group is attached is given to lower number.

Propan 2 Amine

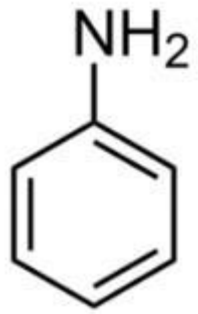


$CH_3-CH(NH_2)-CH_3$

- In case, more than one amino group is present at different positions in the parent chain, their positions are specified by giving numbers to carbon atoms bearing –NH_2 groups and suitable prefix such as di, tri etc. is attached to the amine. The letter ’e’ of the suffix of the hydrocarbon part is retained.
- For Example:- (Ethane 1,2 diamine) $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$
- Each alkyl group bonded to the N atom is named as N-alkyl group.

Aryl Amines

- In aryl amines, -NH_2 group is directly attached to the benzene ring.
- $C_6H_5NH_2$ is the simplest example of aryl amine. It is also known as aniline.



- Naming aryl amines according to IUPAC system, suffix ‘e’ of arene is replaced by ‘amine’.
- For Example: - C_6H_5-NH_2 is named as benzenamine.

Preparation of Amines

- Amines are prepared by the following methods:
- 1. Reduction of nitro compounds

2. Ammonolysis of alkyl halides
3. Reduction of nitriles
4. Reduction of amides
5. Gabriel phthalimide synthesis
6. Hoffmann bromamide degradation reaction

1. 1. Reduction of nitro compounds

- Nitro compounds are reduced to amines by passing hydrogen gas in the presence of finely divided nickel, palladium or platinum and also by reduction with metals in acidic medium.

R- NO_2 + $3H_2$ à R-NH_2 + $2H_2O$ {In the presence of Ni, Pt or Pd}

Ar- NO + $3H_2$à Ar- NH_2 + $2H_2O$

- Nitro alkanes can also be similarly reduced to the corresponding alkanamines.
- Reduction with iron scrap and hydrochloric acid is preferred because $FeCl_2$ formed gets hydrolysed to release hydrochloric acid during the reaction.
- Thus, only a small amount of hydrochloric acid is required to initiate the reaction.

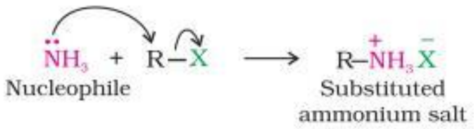
- Nitro compounds can also be reduced with active metals such as Fe, Sn, Zn etc. with conc. HCl

R- NO_2 + $3H_2$ à R- NH_2 + $2H_2O$ {In the presence of Sn/HCl}

Ar- NO_2 + $3H_2$ à Ar- NH_2 + $2H_2O$

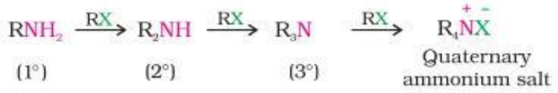
2. Ammonolysis of alkyl halides

- The carbon - halogen bond in alkyl or benzyl halides can be easily cleaved by a nucleophile.



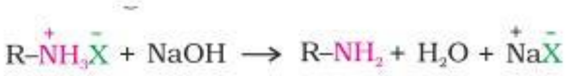
$$\ddot{N}H_3 + R-X \longrightarrow R-\overset{+}{N}H_3\overset{-}{X}$$

- Therefore, an alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino (–NH_2) group.
- This process of cleavage of the C–X bond by ammonia molecule is known as ammonolysis.



$$RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4\overset{+}{N}\overset{-}{X}$$

- The reaction is carried out in a sealed tube at 373 K. The primary amine thus obtained behaves as a nucleophile and can further react with alkyl halide to form secondary and tertiary amines, and finally quaternary ammonium salt.
- The free amine can be obtained from the ammonium salt by treatment with a strong base:



$$R-\overset{+}{N}H_3\overset{-}{X} + NaOH \longrightarrow R-NH_2 + H_2O + \overset{+}{N}a\overset{-}{X}$$

- Disadvantages:-
- When ammonia is taken in excess primary amine is formed as main Product
- When alkyl halide is used in excess quaternary ammonium salt is formed as main product
- Note: - This method is not suitable for preparation of aryl amines because aryl amines are relatively less reactive than alkyl halides towards nucleophilic substitution reactions.

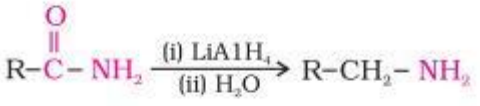
3. Reduction of nitriles

- Nitriles on reduction with lithium aluminium hydride ($LiAlH_4$) or catalytic hydrogenation produce primary amines.
- This reaction is used for ascent of amine series, i.e., for preparation of amines containing one carbon atom more than the starting amine.

$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$$

4. Reduction of amides

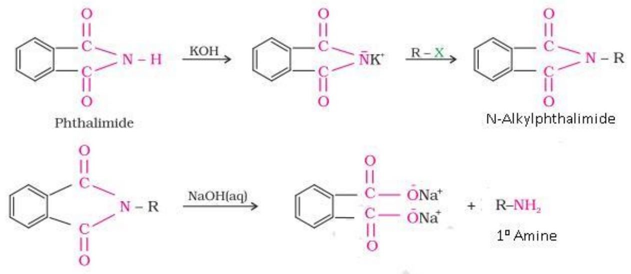
- The amides on reduction with lithium aluminium hydride yield amines.



$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-NH_2$$

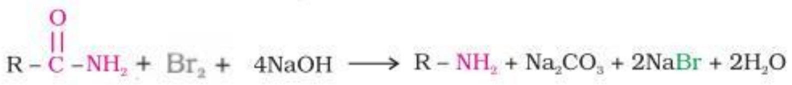
5. Gabriel phthalimide synthesis

- Gabriel synthesis is used for the preparation of primary amines.
- Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine.
- Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.



6. Hoffmann bromamide degradation reaction

- Hoffmann developed a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide.
- In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom.
- The amine so formed contains one carbon less than that present in the amide.



$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

Physical & Chemical Properties of Amines

General:-

- The lower aliphatic amines are gases with fishy odour.
- Primary amines with three or more carbon atoms are liquid and still higher ones are solid.

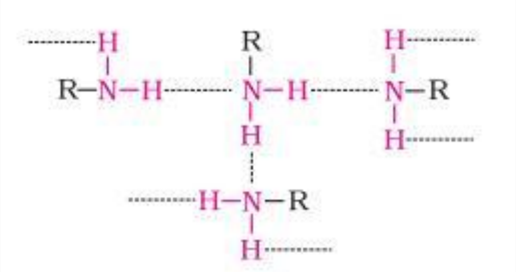
- Aniline and other arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.

1. Solubility:-
    1. Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules.
    2. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part. Higher amines are essentially insoluble in water.
    3. Amines are soluble in organic solvents like alcohol, ether and benzene.
2. Boiling Points:-

- Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule.
- This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it.
- Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation. Therefore, the order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary

- Intermolecular hydrogen bonding in primary amines is as:-

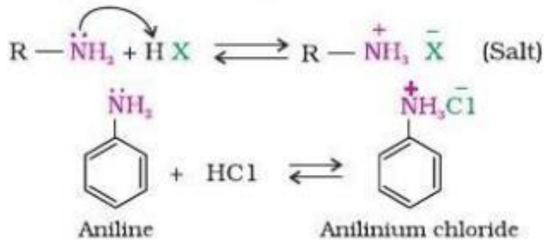


Chemical Properties of Amines

- Amines behave as nucleophiles due to the presence of unshared electron pair.
- Difference in electronegativity between nitrogen and hydrogen atoms and the presence of unshared pair of electrons over the nitrogen atom makes amines reactive.
- Primary, secondary and tertiary amines differ in reactions because of number of hydrogen attached to nitrogen.

Following are the chemical properties of Amines:-

1. Basicity of Amines
    1. They are basic in nature and form salts when react with acids.



1. Amine salts on treatment with a base like NaOH, regenerate the parent amine.

$$R\overset{+}{N}H_3\bar{X} + \bar{O}H \longrightarrow R\ddot{N}H_2 + H_2O + \bar{X}$$

1. Amine salts are soluble in water but insoluble in organic solvents like ether.
2. They form ammonium salts when react with mineral acids.
3. Amines have an unshared pair of electrons on nitrogen atom due to which they behave as Lewis base.

Why Amines are basic in nature in terms of K_b and pK_b values?

- Larger the value of K_b or smaller the value of pK_b, stronger is the base. The pK_b values of few amines are given in.

$$R - NH_2 + H_2O \rightleftharpoons R - \overset{+}{N}H_3 + \bar{O}H$$

$$K = \frac{[R-\overset{+}{N}H_3][\bar{O}H]}{[R-NH_2][H_2O]}$$

$$\text{or } K[H_2O] = \frac{[R-\overset{+}{N}H_3][\bar{O}H]}{[R-NH_2]}$$

$$\text{or} \quad K_b = \frac{[R-\overset{+}{N}H_3][\bar{O}H]}{[R-NH_2]}$$

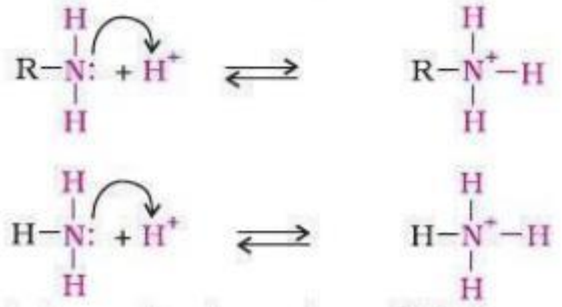
$$pK_b = -\log K_b$$

- pK_b value of ammonia is 4.75. Aliphatic amines are stronger bases than ammonia due to +I effect of alkyl groups leading to high electron density on the nitrogen atom.
- Their pK_b values lie in the range of 3 to 4.22. On the other hand, aromatic amines are weaker bases than ammonia due to the electron withdrawing nature of the aryl group.

Structure-basicity relationship of amines

- Basicity of amines to their structure.

1. Alkanamines versus ammonia
    1. Reaction of alkanamines and ammonia in order to compare their basicity.



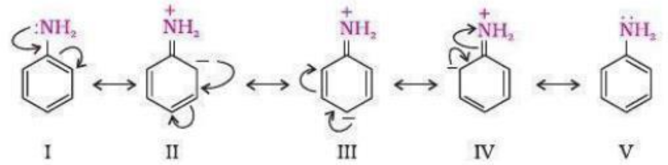
1. Due to the electron releasing nature of alkyl group, it (R) pushes electrons towards nitrogen and thus making them available for the unshared electron pair for the proton of the acid.
2. The substituted ammonium ion formed from the amine gets stabilised due to dispersal of the positive charge by the +I effect of the alkyl group.
3. Hence, alkylamines are stronger bases than ammonia. Thus, the basic nature of aliphatic amines should increase with increase in the number of alkyl groups.
4. The order of basicity of amines in the gaseous phase follows the expected order: tertiary amine > secondary amine > primary amine > NH_3.
5. But this not same in aqueous state, in that the substituted ammonium cations get stabilised not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules.
6. The greater the size of the ion, lesser will be the solvation and the less stabilised is the ion.
7. The order of stability of ions are as follows:

Decreasing order of extent of H-bonding in water and order of stability of ions by solvation.

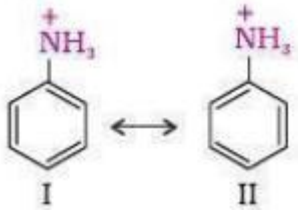
1. Thus, the order of basicity of aliphatic amines should be: primary > secondary > tertiary, which is opposite to the inductive effect based order.
2. When the alkyl group is small, like $–CH_3$ group, there is no steric hindrance to H-bonding.
3. In case the alkyl group is bigger than CH_3 group, there will be steric hindrance to H-bonding.
4. Therefore, the change of nature of the alkyl group, e.g., from $–CH_3$ to $–C_2H_5$ results in change of the order of basic strength.
5. Thus, there is a subtle interplay of the inductive effect, solvation effect and steric hindrance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state.
6. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:

- $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
- $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH3$

1. Arylamines versus ammonia
    1. pK_b value of aniline is quite high because in aniline or other arylamines, the -NH_2 group is attached directly to the benzene ring.
    2. As a result the unshared electron pair on nitrogen atom will be less available for protonation as it is in conjugation with the benzene ring.
    3. Aniline is resonance hybrid of 5 resonance structures.



    1. On the other hand, anilinium ion obtained by accepting a proton can have only two resonating structures (kekule).



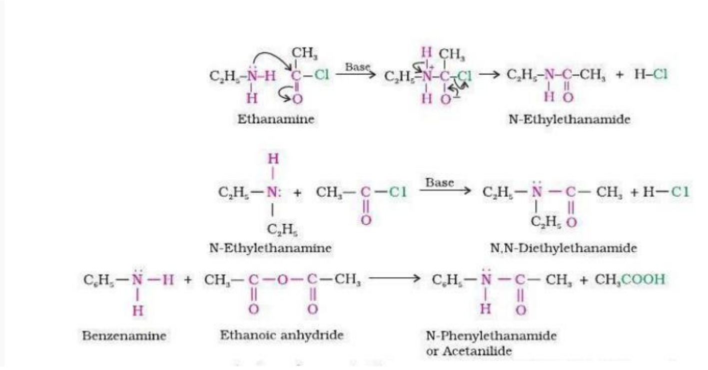
    1. Aniline is more stable than anilinium ion as it has greater number of resonating structure.
    2. Therefore, the proton acceptability or the basic nature of aniline or other aromatic amines would be less than that of ammonia.
    3. In case of substituted aniline, it is observed that electron releasing groups like $-OCH_3$, $-CH_3$ increase basic strength whereas electron withdrawing groups like $-NO_2$, $-SO_3H$, $-COOH$, $-X$ decrease it.

1. Alkylation

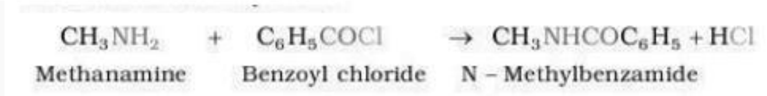
1. Amines undergo alkylation on reaction with alkyl halides.

1. Acylation

1. The reaction of aliphatic and aromatic primary and secondary amines with acid chlorides, anhydrides and esters by nucleophilic substitution reaction is known as Acylation.
2. In this reaction there will be replacement of hydrogen atom of $-NH_2$ or $>N-H$ group by the acyl group.
3. The products obtained by acylation reaction are known as amides. The reaction is carried out in the presence of a base stronger than the amine, like pyridine, which removes HCl so formed and shifts the equilibrium to the right hand side.



1. Amines also react with benzoyl chloride (C_6H_5 COCl). This reaction is known as benzoylation.



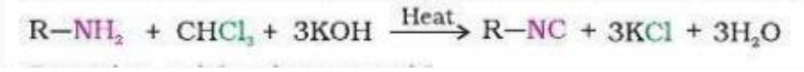
$$CH_3NH_2 + C_6H_5COCl \rightarrow CH_3NHCOC_6H_5 + HCl$$

Methanamine Benzoyl chloride N – Methylbenzamide

1. They form salts when they react with carboxylic acids at room temperature.

1. Carbylamine reaction

1. Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances.
2. Secondary and tertiary amines do not show this reaction. This reaction is known as carbylamines reaction or isocyanide test and is used as a test or primary amines.



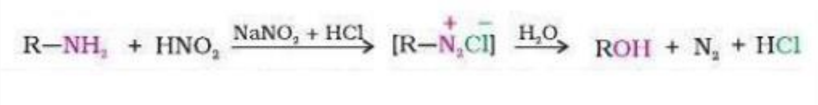
$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

1. Reaction with nitrous acid

1. Different types of amines react differently with nitrous acid which is prepared in situ from a mineral acid and sodium nitrite.

(i) Primary Amines:-

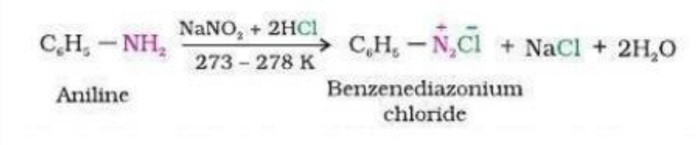
1. Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols.
2. Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.



$$R-NH_2 + HNO_2 \xrightarrow{NaNO_2 + HCl} [R-\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

(ii) Secondary Amines:-

1. Aromatic amines react with nitrous acid at low temperatures (273-278 K) to form diazonium salts, a very important class of compounds used for synthesis of a variety of aromatic compounds.

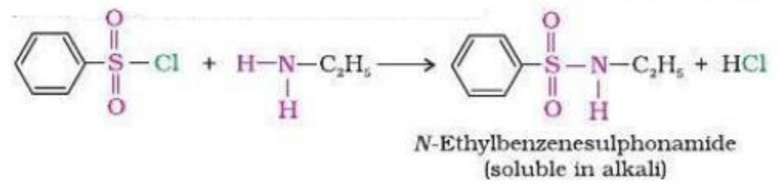


- Secondary and tertiary amines react with nitrous acid in a different manner.

1. Reaction with aryl sulphonyl chloride

- Reaction with Benzene sulphonyl Chloride: - Benzene sulphonyl chloride ($C_6H_5SO_2Cl$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

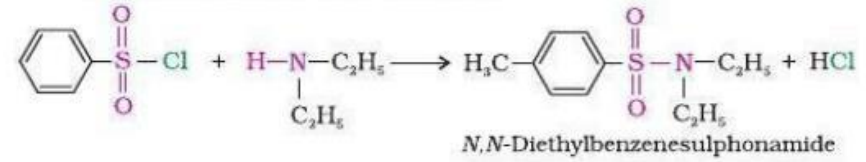
2. The reaction of benzenesulphonyl chloride with primary amine yields N-ethylbenzene sulphonyl amide.



2. The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group.
3. Hence, it is soluble in alkali.

- Reaction of secondary Amine benzenesulphonyl chloride: - In this reaction, N, N-diethylbenzenesulphonamide is formed.

5. Since N, N-diethyl benzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom; it is not acidic and hence insoluble in alkali.



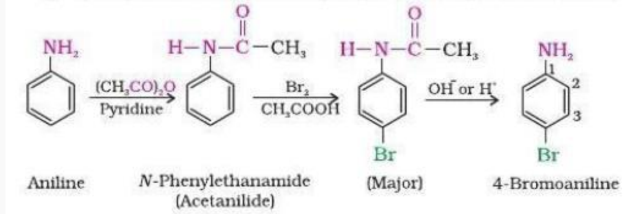
- Tertiary amines do not react with benzenesulphonyl chloride.
- Note:-
    1. Amine reacting with benzenesulphonyl chloride in a different manner is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines.
    2. These days benzenesulphonyl chloride is replaced by p-toluenesulphonyl chloride.

1. Electrophilic Substitution

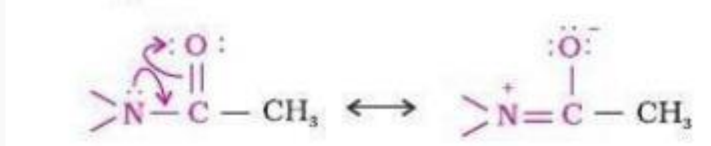
- **Bromination :-**

- Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline.
- Because of high reactivity of aromatic amines problems occur during electrophilic substitution because it occurs at ortho- and para-positions.

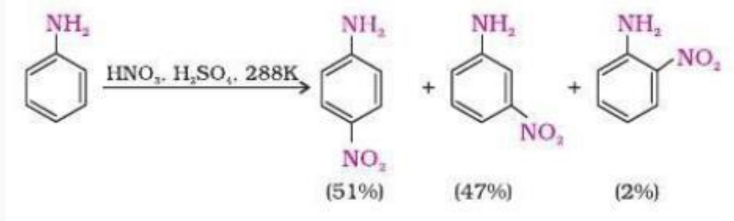
- In order to prepare monosubstituted aniline derivative activating effect of –NH_2 group be controlled done by protecting the -NH_2 group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.



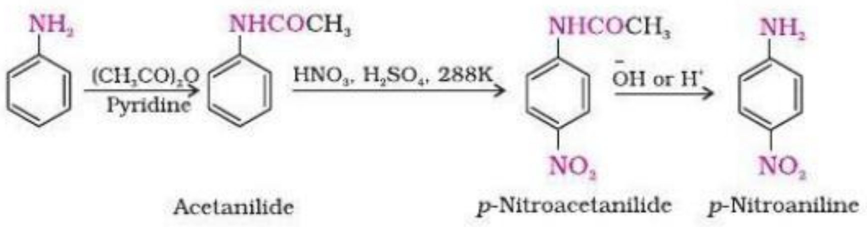
- The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:



- Hence, the lone pair of electrons on nitrogen is less available for donation to benzene ring by resonance.
- Therefore, activating effect of –$NHCOCH_3$ group is less than that of amino group.
- **Nitration:**-
- Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives.
- Moreover, in the strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing.
- That is why besides the ortho and para derivatives, significant amount of meta derivative is also formed.



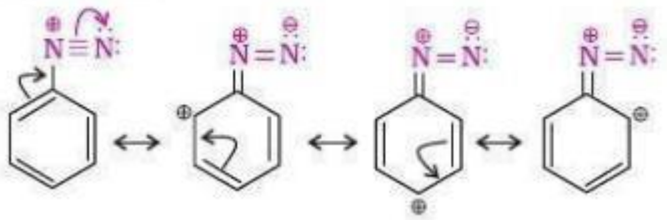
- In order to protect $-NH_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the p-nitro derivative can be obtained as the major product.



- **Sulphonation:**-
- Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate which on heating with sulphuric acid at 453-473K produces p-aminobenzene sulphonic acid, commonly known as sulphanilic acid, as the major product.
- Aniline does not undergo Friedel-Crafts reaction (alkylation and acetylation) due to salt formation with aluminium chloride, the Lewis acid, which is used as a catalyst.
- Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

Diazonium Salts

- General formula of diazonium salts is $RN_2^+X^-$ where R = aryl group and X- ion can be Cl^-, Br^-,HSO_4^- and BF_4^-.
- Diazonium salts are named by suffixing diazonium to the name of the parent hydrocarbon from which they are formed, followed by the name of anion such as chloride, hydrogensulphate, etc.
- The N_2^+ group is called diazonium salt.
  - For example, $C_6H_5N_2^+Cl^-$ is named as benzenediazonium chloride and $C_6H_5N_2^+HSO_4^-$ is known as benzenediazonium hydrogensulphate.
- Primary aliphatic amines form highly unstable alkyldiazonium salts. Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (273-278 K). The stability of arenediazonium ion is explained on the basis of resonance.



Preparation of Diazonium Salts

- Benzenediazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278K.
- Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid.

- The conversion of primary aromatic amines into diazonium salts is known as diazotisation. Due to its instability, the diazonium salt is not generally stored and is used immediately after its preparation.

$C_6H_5NH_2 + NaNO_2 + 2HCl$ à $C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

(273 – 278K)

Properties of Diazonium Salts

Physical Properties:-

- Benzenediazonium chloride is a colourless crystalline solid.
- It is readily soluble in water and is stable in cold but reacts with water when warmed.
- It decomposes easily in the dry state. Benzenediazonium fluoroborate is water insoluble and stable at room temperature.

Chemical Properties:-

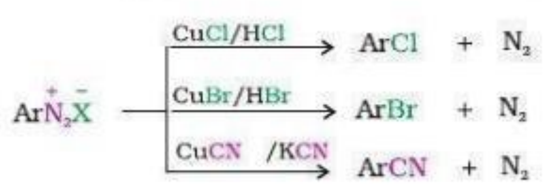
There are 2 reactions into with diazonium salts can be divided:-

- Reactions involving displacement of nitrogen
- Reactions involving retention of diazo group.

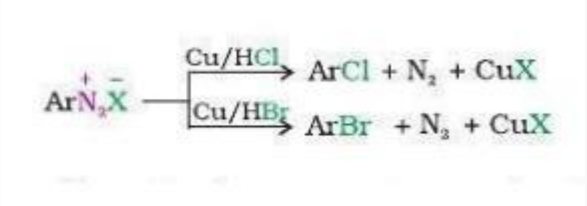
Reactions involving displacement of nitrogen

- Diazonium group being a very good leaving group is substituted by other groups such as Cl^-, Br^-, I^-, CN^- and OH^- which displace nitrogen from the aromatic ring. The nitrogen formed escapes from the reaction mixture as a gas.

- Replacement by halide or cyanide ion:
- The Cl^-, Br^- and CN^- nucleophiles can easily be introduced in the benzene ring in the presence of Cu (I) ion.
- This reaction is called Sandmeyer reaction.



- Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred as Gatterman reaction.



- The yield in Sandmeyer reaction is found to be better than Gatterman reaction.
- Replacement by iodide ion:
- Iodine is not easily introduced into the benzene ring directly, but, when the diazonium salt solution is treated with potassium iodide, iodobenzene is formed.

$ArN_2^+Cl^- + KI$ à $Ar\ I + KCl + N_2$

- Replacement by fluoride ion:
- When arenediazonium chloride is treated with fluoroboric acid, arene diazonium fluoroborate is precipitated which on heating decomposes to yield aryl fluoride.

$ArN_2^+Cl^- + HBF_4$ à $Ar – N_2^+BF_4^-$ à $Ar\text{-}F + BF_3 + N_2$

Δ

- Replacement by H:
- Certain mild reducing agents like hypophosphorous acid (phosphinic acid) or ethanol reduce diazonium salts to arenes and they get oxidised to phosphorous acid and ethanal, respectively.

$ArN_2^+Cl^- + H_3PO_4 + H_2O$ à $ArH + N_2 + H_3PO_3 + HCl$

$ArN_2^+Cl^- + CH_3CH_2OH$ à $ArH + N_2 + CH_3CHO + HCl$

- Replacement by hydroxyl group:
- If the temperature of the diazonium salt solution is allowed to raise upto 283 K, the salt gets hydrolysed to phenol.

$ArN_2Cl^- + H_2O$ à $ArOH + N_2 + HCl$

- Replacement by $–NO_2$ group:
- When diazonium fluoroborate is heated with aqueous sodium nitrite solution in the presence of copper, the diazonium group is replaced by $–NO_2$ group

(B)

Reactions involving retention of diazo group coupling reactions:-

- The azo products obtained have an extended conjugate system having both the aromatic rings joined through the –N=N– bond.
- These compounds are often coloured and are used as dyes. Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form

p-hydroxyazobenzene.

- This type of reaction is known as coupling reaction.
- Similarly the reaction of diazonium salt with aniline yields

p-aminoazobenzene. This is an example of electrophilic substitution reaction.

Introduction

The complex organic substances like carbohydrates, proteins etc which combine in a specific manner to produce living systems and maintain it are called biomolecules. The branch of chemistry that deals with the study of chemical reactions that occur in living organisms is called biomolecules.

Carbohydrates

- They are polyhydroxy-aldehydes or ketones or substances which give these substances on hydrolysis and contain at least one chiral atom.
- They have general formula of $C_x(H_2O)$
- Rhamnose, deoxyribose, rhamnohexose do not obey this formula but are carbohydrates.

Types of carbohydrates

- Monosaccharide
- Oligosaccharide
- Polysaccharide

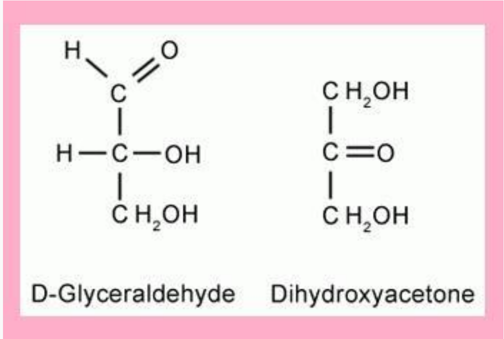
Monosaccharide

- These are simplest carbohydrate which can't be hydrolyzed further into smaller compounds.
- They are called as aldose or ketose depending upon whether they have aldehyde or ketone group.
- Depending upon the number of carbon atoms present they are called as triose, tetrose etc.
- All monosaccharide's are sweet smelling crystalline, water soluble and are also capable of diffusing through cell membranes.

For example: Glucose is aldohexose while fructose is a ketohexose. Both of them have 6 carbon atoms. The simplest monosaccharide is a triose (n=3).

Example: Glyceraldehyde and Dihydroxyacetone. They have one or more asymmetric carbon and are optically active.

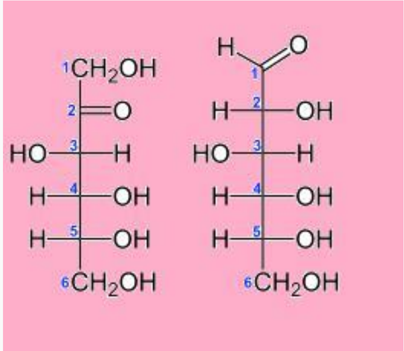
Their structures are:



Configuration

All naturally occuring monosaccharides belong to D—series that is OH group at their penultimate C-atom.

Open chain structures:



Glucose **fructose**

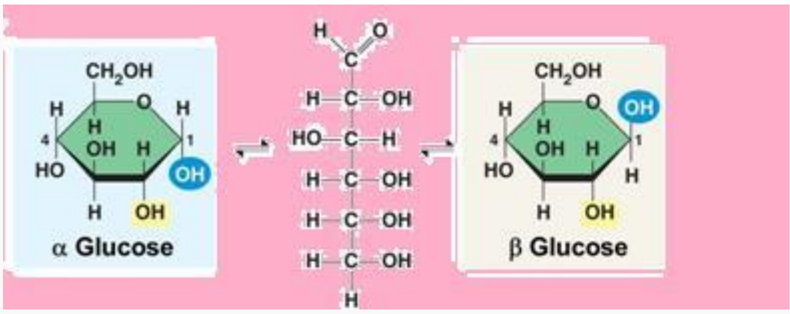
- D-glucose and D-mannose, differ only in configuration at C-2 and are known as epimers.
- Similarly D-glucose and D-galactose, differ in configuration around C-4 atom and are also known as epimers.
- Thus a pair of diastereomers, differing only in configuration around C-2 or any other chiral carbon except C-1 is called epimers.

Close chain structure

- All the pentose's and hexoses exist in cyclic hemiacetal structure.
- In free state, they have generally six membered cyclic structure known as pyranose form and in combined state, some of them have 5 membered cyclic structure called as furanose .

Due to cyclic hemiacetal or hemiketal structure all the pentoses and hexoses exist in two stereoisomeric forms

- Alpha form
- Beta form
- Both alpha and beta form are Anomers.
- Their structure is given below :



Oligosaccharides

These carbohydrates on hydrolysis give 2 to 9 molecules of monosaccharides.

They are further of few types:

- Disaccharides ($C_{12}H_{22}o_{11}$): On hydrolysis, they give 2 molecules of monosaccrides which are held together by Glycosidic linkage

Example: sucrose etc

- Trisaccharides ($C_{18}H_{32}o_{16}$): On hydrolysis, they form three molecules of monosaccharides.

Example: raffinose

- Tetra-saccharides: ($C_{24}H_{42}o_{21}$): Such as stachyose which gives four monosaccrides on hydrolysis.

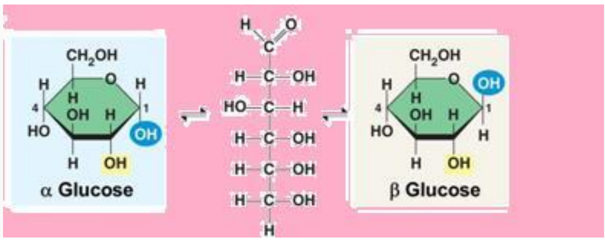
Polysaccharides

These are the carbohydrates which on hydrolysis, yield more than nine monosaccharides molecules.

Example: Starch etc

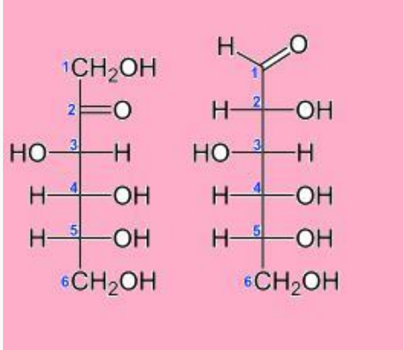
Mutarotation

- Glucose exist in two forms : i.e. alpha –D glucose with specific rotation of 112degree and beta D-glucose with specific rotation of +19 degree.
- However, when either of these two forms is dissolved in water and allowed to stand, it gets converted into same equilibrium mixture of both the alpha and beta forms with a small amount of open chain form having specific rotation of 52.7 degree.
- As a result of this, equilibrium the specific rotation of freshly prepared solution of alpha glucose decreases from +112 degree to 52.7 degree while that for beta glucose increases from +19 to 52.7 degrees.
- The phenomenon of change of change in specific rotation of optically active compounds with time to an equilibrium value is known as Mutarotation.



- The alpha D (+) glucose and beta (+) glucose, differ in configuration at C-1 carbon and the compounds differing in configuration at C-1 are called Anomers.

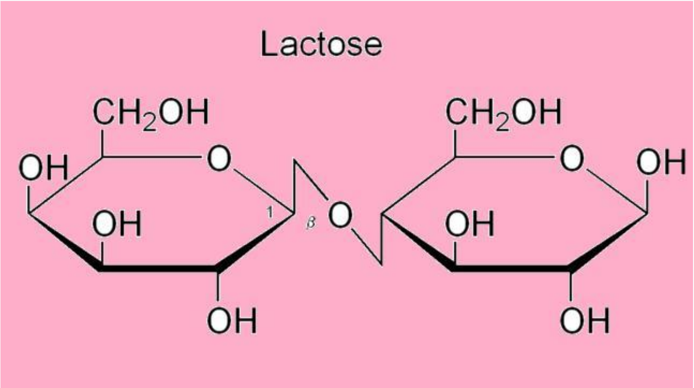
Fructose: It is represented by six membered ring as shown:



Beta –D+(fructose) **furanose structure**

Fructose is assigned furanose structure.

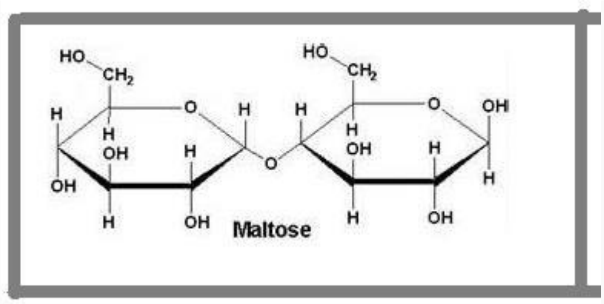
Lactose: It is made up of molecule and a molecule of galactose. The units are linked together.



Lactose

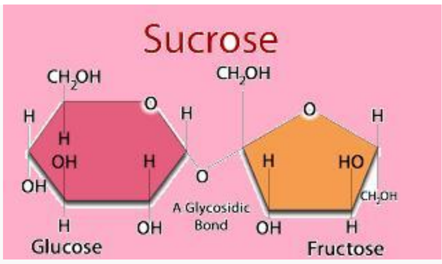
Maltose: It has the structure as shown below

- On treatment, with acid or with enzyme maltose gets hydrolysed to 2 molecules.
- That is alpha D-glucose.
- Since one of the glucose units exist in hemiacetal form it is a reducing sugar.



Sucrose: It has a structure shown below

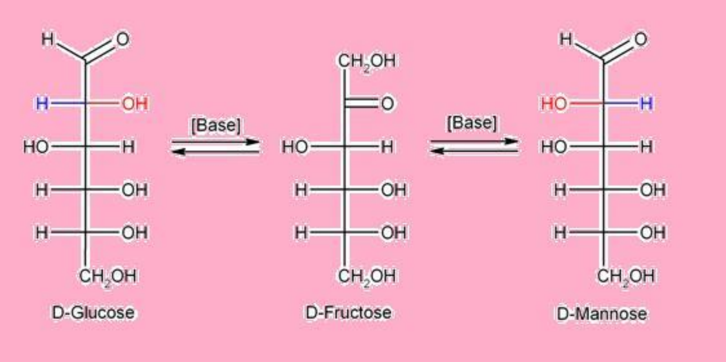
- On hydrolysis, with dilute mineral acid or enzyme invertase sucrose gives glucose and fructose in equal amounts.
- Sucrose and glucose are dextrorotatory while fructose is laevorotatory and has higher value of specific rotation.
- Thus the process is accompanied by inversion of optical activity. The mixture formed is invert sugar. That is sucrose àglucose + fructose



(water and invertase)

Sweetness of sugars

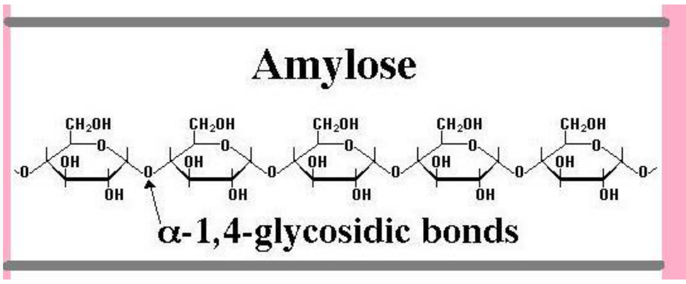
- All the monosaccharide and disaccharides are sweet in taste and hence also known as sugars.
- Sucrose is given sweetness value of 100. The sweetness of other sugars is compared with the value of sucrose.
- The sweetness of fructose -173, invert sugar 130, sucrose 100, glucose 74,glactose 32,maltose 32 and that of lactose is 16.
- All the monosaccharide and disaccharides are reducing agents due to hemiacetal and hemiketal forms which easily change in to aldehydic form in the alkaline medium.
- Although fructose doesn't contain any aldehydic group yet it gives Tollen's reagent test and Fehling's solution test because under the basic conditions of reagent the fructose gets converted into the mixture of glucose and mannose both of which contains aldehydic group.
- This is called Lobry De Bruyn Van Eikensten rearrangement.



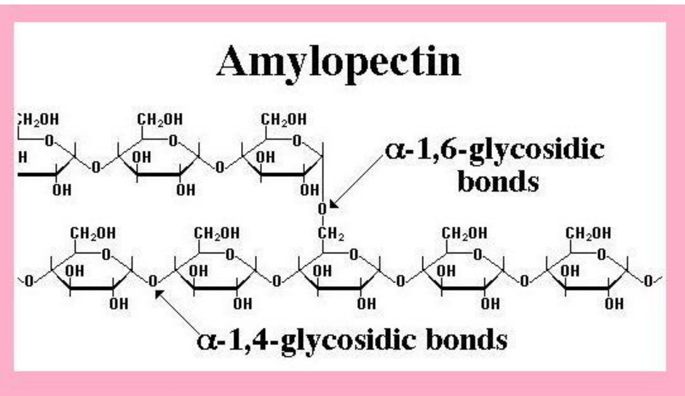
- The alpha and beta glucose reacts with one molecule of ethanol to form the corresponding methyl glucosides.
- When glucose is treated with methanol in presence of HCl the hemiacetal form changes to acetal form.

Starch: It serves as a storage polysaccharide in plants .It consist of two components of alpha glucose.

- **Amylase**
  - It is a linear polymer of glucose and is soluble in water.
  - Its percentage in starch is about 10-20 %.
  - These are linked together by alpha linkage involving C-1 of glucose unit to C-4 of the other.

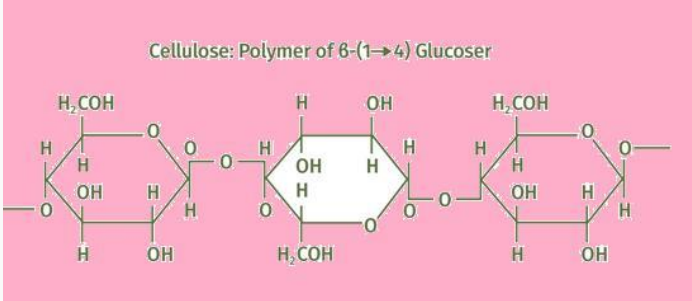


- **Amylopectin**
- It is branched chain polymer of alpha glucose and is insoluble in water.
- There are about 1000 units of glucose.



(c) Cellulose

- It is found in all plants
    - It constitutes 50% of total organic matter in the living beings.
    - Cotton is pure cellulose.
    - Cellulose is linear polymer of beta D-glucose.
    - The chains are arranged to form bundles and linked together by hydrogen bonds between glucose molecules of adjacent organic solvents.
    - When it is treated with concentrated sulphuric acid in cold it slowly passes into solution.
    - This solution when diluted with water gives starch like substance amyloid which is known as parchment paper.
    - On boiling with water it is hydrolyzed into D-glucose.
    - Cellulose gives many useful products when treated with different chemicals like rayon, gum, cotton etc.
    - Cellulose is directly used in making cloth and paper.



Glycogen

- In glycogen there are about 25 glucose units. Its structure is similar to amylopectin and is a condensation polymer of alpha glucose.
- Glycogen in short term food storage in animals.

Tests for carbohydrates

- For this Molisch test is performed.
- In it Molisch reagent is used which is 10%alcoholic solution of alpha naphthol and it is added to aqueous solution of carbohydrate followed by concentrated sulphuric along the sides of tube.
- As a result a violet ring is formed at the junction of two layers.

Proteins

Introduction of proteins

- They are high weight polymers.
- They are polyamides that contain C, H, N, O and S.
- Proteins are derived from alpha amino carboxylic acid monomers.
- A simple protein may contain hundred even thousands of amino acid units.
- In living organisms twenty alpha amino acids occur which combine to form different protein molecules.

Amino acids

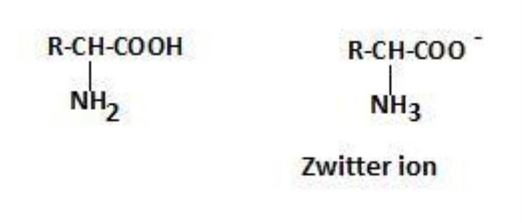
- A simple amino acid can be represented as $R\text{-}CH(NH)_2COOH$ (carboxy group and amino group is present in it).

Alpha amino acids

- The acid in which NH_2 group is present at carbon atom adjacent to the COOH group are called alpha amino acids.
- Alpha amino acids are the building blocks of proteins the alpha carbon of all amino acids is chiral, hence all amino acids exhibit stereoisomerism that is existence of D and L types of structures.
- All the naturally occurring amino acids, belong to L form category.
- In L amino acid NH_2 group lies left to the chiral carbon as shown :

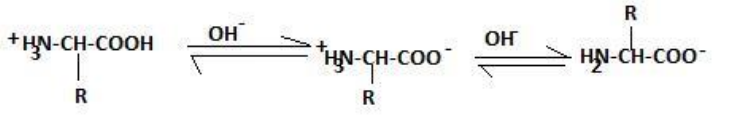
$H_2N\text{-}CH_2R$ (C0OH)   L –amino acid

- Due to transfer of proton from carboxy to amino group, alpha amino acid exists as dipolar ion or called **as Zwitter ion.**



Isoelectric point

- Due to the zwitter ion structure, alpha amino acids are high meting crystalline solids and moderately soluble in water.
- In acidic medium caboxylate ion group act as a base and accepts a proton. Thus alpha amino acids exist as cations (I) under the influence of electric field.



(zwitter ion)

- In alkaline medium, NH_3^+groups act as an acid and thus loses a proton.

- Due to this, alpha amino acids exist as anions (III) and thus migrate towards the anode in the electric field.
- However, at some intermediate value of ph, the concentration of cationic form (I) and the anionic form (III) become equal.
- Hence, there is no migration in electric field. This pH is known as isoelectric point.

Types of amino acids

The amino acids are of two types:

- Essential
- Non essential

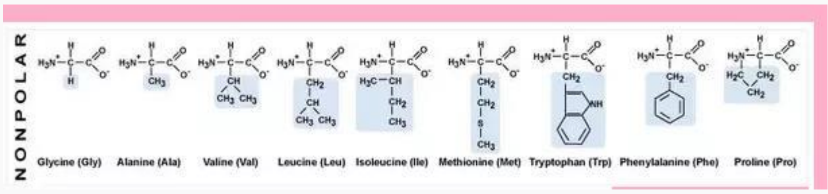
Essential amino acids

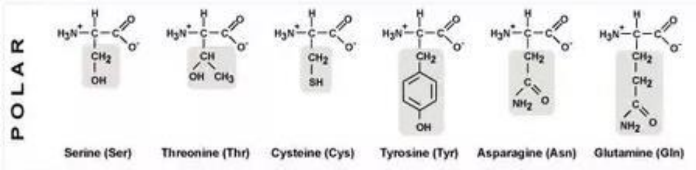
- The amino acids that can’t be made in our body and must be supplied from outside.
- The lack of these amino acids in diet can cause lot of diseases like kwashiorkor (the disease in which water balance in body is disturbed).
- The essential amino acids are 10 in number out of all.

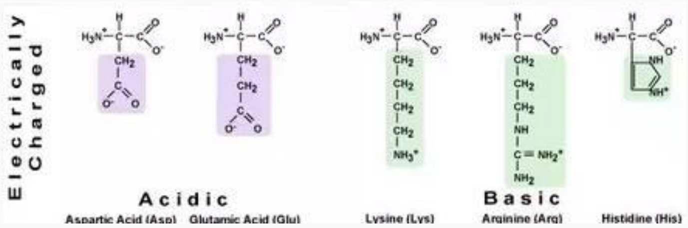
Non essential amino acids

- They are those that can be synthesized in our body.
- Out of total 20 amino acids the 10 can be synthesized in the body.

List of different types of amino acids:



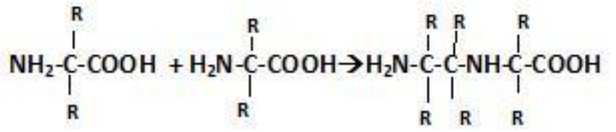




Polypeptide formation

- The interaction between amino group and carboxyl of amino group give compounds called peptides.
- The amide group –CONH in each such compound is called peptide linkage.
- Depending upon the number of amino acid, residues per molecule they are called as dipeptide, tripeptide etc.

- Peptides of molecular weight up to 10,000 are known as polypeptides and those with higher than 10,000 are called as proteins.
- Each polypeptide chain has a free amino group at one end and a free carboxyl group at other end.
- They are collectively called as end groups.
- The amino acid unit having –NH_2group is called **N-terminal end** and the amino acid unit having free –COOH group is called **C-terminal end.**



$$NH_2\text{-}\overset{R}{\underset{R}{C}}\text{-}COOH + H_2N\text{-}\overset{R}{\underset{R}{C}}\text{-}COOH \rightarrow H_2N\text{-}\overset{R}{\underset{R}{C}}\text{-}\overset{R}{\underset{R}{C}}\text{-}NH\text{-}\overset{R}{\underset{R}{C}}\text{-}COOH$$

- In this NH-CH-CO is the repeating unit in polypeptide.

Structure of proteins

Proteins have three structures:

- Primary structure
- Secondary structure
- Tertiary structure

Primary structure: The sequence in which amino acids are arranged in protein is called primary structure. The sequence determines the function of a protein.

Secondary structure: The fixed configuration of polypeptide skeleton is known as secondary structure.

- There are two types of secondary structure :
- Alpha helix
- Beta pleated sheet

Alpha helix: If the size of group R is large, intermolecular hydrogen bonds are formed between CO of one amino acid residue and NH of the fourth amino acid residue in polypeptide chain which gives right handed alpha helix structure to the protein molecule.

Example: Alpha keratin in hair etc it is also elastic.

Beta pleated sheet: If the size of group R is small, intermolecular hydrogen bonds are formed between CO of one polypeptide chain with NH of the other chain. Thus the chains are bonded together forming a sheet which can slide over each other to form a three dimensional structure called beta pleated sheet.

Example: silk

Tertiary structure: It implies the three dimensional structure of proteins.

There are two types tertiary structure:

- Fibrous and globular.
- Proteins contain one or more polypeptide chains.
- A protein having one polypeptide chain is known as monomeric while that having more than one polypeptide chains is called oligomeric.

- The constituent peptide chains of an oligomeric protein are called protomers which are held together by weak forces.
- Native state: At normal pH and temperature each protein takes a shape which is energetically most stable.
- In amino acid the shape is specific and is known as native state.
- Globular proteins are tightly folded and give rise to spherical form.

Forces that stabilize protein structures

The forces that are present are as follows:

- Hydrogen bonding
- Anionic bonding
- Hydrophobic bonding
- Covalent bonding

Hydrogen bonding: These forces operate between a partially positive hydrogen and partially negative atom like O or N on the same or on another molecule.

Anionic bonding: A bonding between cation and anion of side chains resulting in side linkage.

Hydrophobic bonding: Some side chains in same amino acid are hydrophobic. In aqueous solutions proteins fold in such a way that these chains get clustered inside the folds .The polar side chains which are hydrophilic lie on the outside or surface of proteins.

Covalent bonding: The bond occurs between S atoms of two residues between two adjacent chains.

- Insulin which contains 51 amino acids is arranged in two polypeptide chains containing 21 and 30 amino acid residues connected by S-S cross links.

Denaturation of proteins

- The globular proteins, which are soluble in water on heating or on treatment of mineral acids or bases undergo coagulation or precipitation to give fibrous proteins which are insoluble in water.
- After coagulation, proteins lose their biological activity this is called denaturation.
- It can be reversible or irreversible.
- Coagulation of lactalbumin to form cheese and coagulation of albumins are examples of denaturation.

Classification of proteins

On the basis of composition, proteins are of following types :

- Simple proteins
- Conjugated proteins
- Derived proteins
- Fibrous proteins
- Globular proteins

Simple proteins: On hydrolysis they give only amino acids.

Example: Globulins and albumin

Conjugated proteins: They contain non protein group attached to the protein part. These non protein groups are called prosthetic groups.

Example: Nucleo-protein contains nucleic acid, phosphor-protein contains phosphoric acid contains phosphoric acid, glycol-proteins contains carbohydrates etc.

Derived proteins: These are the degradation products obtained by the hydrolysis of simple and conjugated proteins.

Example: Peptides, peptones etc

Fibrous proteins: They are long and thread like and tend to lie side by side to form fibers .In some cases, they are held together by hydrogen bonds at many points .these proteins serves as a chief structural material of animal tissues .

Globular proteins: The molecules of these proteins are folded into compact units and form spheroid shapes .Intermolecular forces are weak. These proteins are soluble in water or aqueous solution of acids, bases or salts .Globular proteins make up all enzymes, hormones ,fibrinogen etc.

Role of proteins

- They act as enzymes and transport agents.
- They are structural materials for nails, hair etc.
- Antibodies formed in body are globular proteins.
- They are metabolic regulators like insulin etc.

Hydrolysis of proteins

- Proteins are hydrolyses when boiled with acids or alkalis or when treated with enzymes .the hydrolysis takes place as:

Proteins àproteasesàpeptones àpolypeptides àsimple peptides àamino acids

- Every protein has an isoelectric point at which their ionization is minimum. Proteins have charged groups i.e. NH_3 and COO^- at the ends of peptide chain.
- They are amphoteric in nature.
- Protein accepts a proton in strong basic solution.
- The pH at which the protein molecule has no net charge is known as isoelectric point.

Enzymes

They are biological catalysts .Chemically all enzymes are globular proteins

Some important enzymes with their function:

1. **Lactase : convert lactose àglucose + glactose**
2. **Invertase : convert sucrose à glucose and fructose**
3. **Maltase : convert maltose à2glucose**
4. **Emulsion: convert cellulose àn glucose**
5. **Urease : convert urea àcarbon dioxide and water**
6. **And many more.**

Some industrial enzymes invertase and zymase are present in yeast .Enzyme diastase is used as converting starch to maltose , a sugar .the names of all enzymes end with the suffix “ase”.

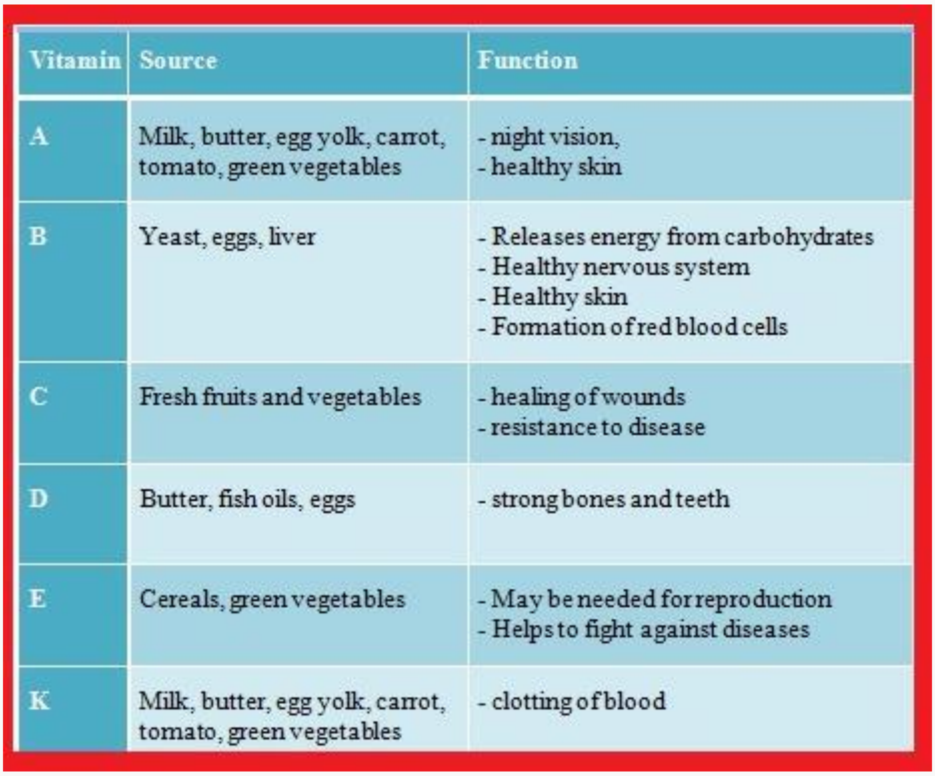
Properties of enzymes

- Enzymes are required only in small amounts.
- They are highly specific.
- Enzymes are efficient catalyst: they speed up reaction.
- They work at optimum pH, at optimum temperature.
- Their mechanism is controlled by various mechanisms and stopped by various organic and inorganic compounds.
- The action of enzymes follows lock and key mechanism .however enzyme action is inhibited by certain organic molecules called inhibitors.

Vitamins

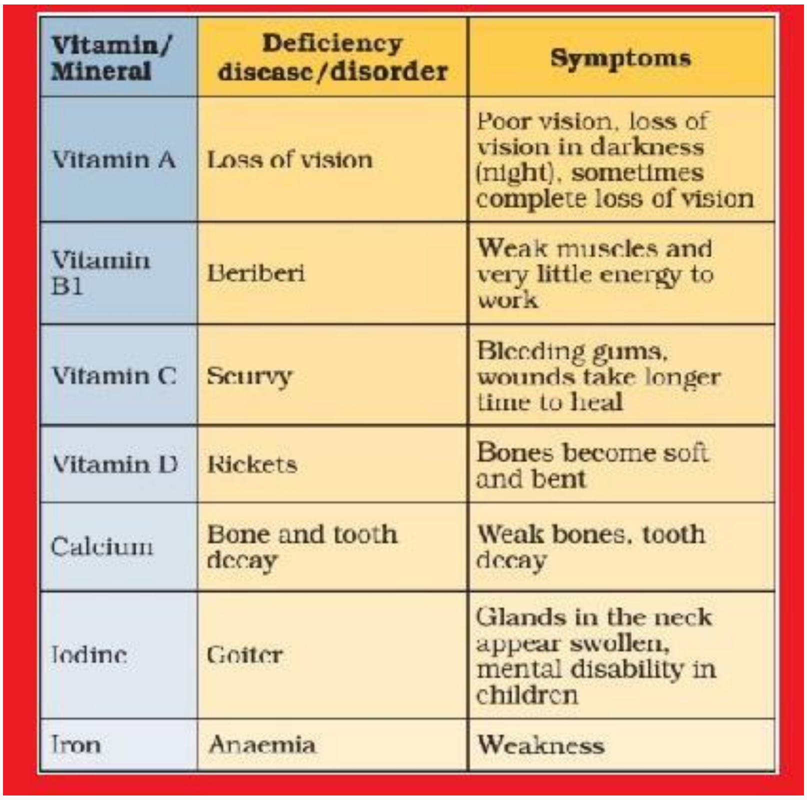
- They are the chemical substances which are needed in small amounts for the growth of human beings.
- They can’t be synthesized in our body therefore need to taken from outsource.
- Their deficiency can cause one or other type of disease.

The following vitamins with their function and deficiency disease are listed below:

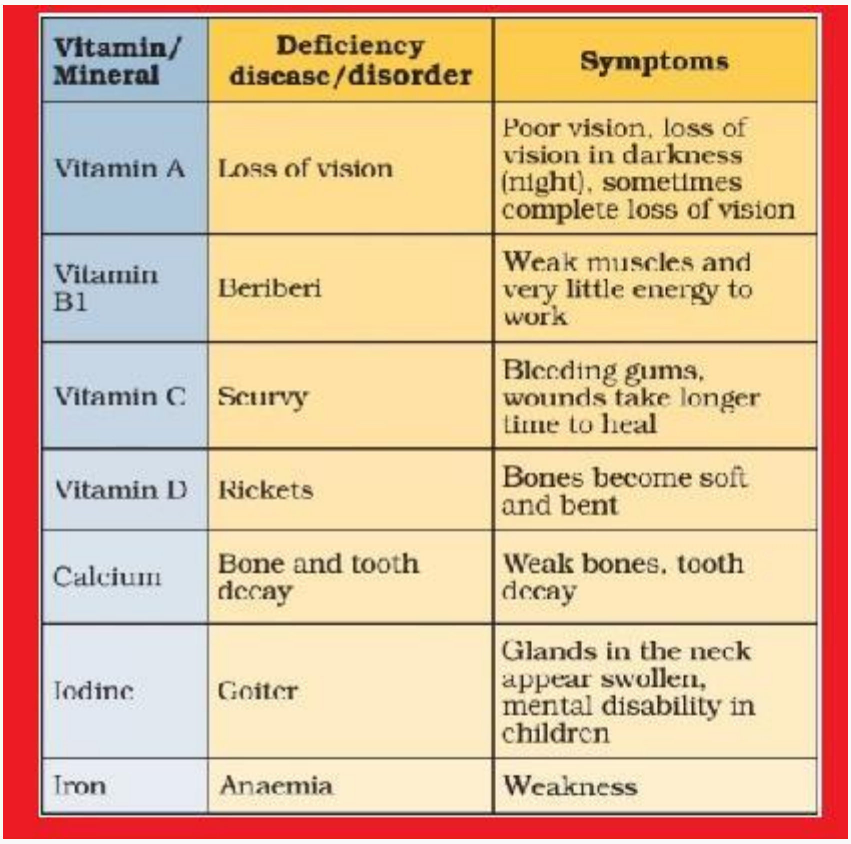


Vitamin	Source	Function
A	Milk, butter, egg yolk, carrot, tomato, green vegetables	- night vision, - healthy skin
B	Yeast, eggs, liver	- Releases energy from carbohydrates - Healthy nervous system - Healthy skin - Formation of red blood cells
C	Fresh fruits and vegetables	- healing of wounds - resistance to disease
D	Butter, fish oils, eggs	- strong bones and teeth
E	Cereals, green vegetables	- May be needed for reproduction - Helps to fight against diseases
K	Milk, butter, egg yolk, carrot, tomato, green vegetables	- clotting of blood

The diseases caused by them with their symptoms:



Vitamin/ Mineral	Deficiency disease/disorder	Symptoms
Vitamin A	Loss of vision	Poor vision, loss of vision in darkness (night), sometimes complete loss of vision
Vitamin B1	Beriberi	Weak muscles and very little energy to work
Vitamin C	Scurvy	Bleeding gums, wounds take longer time to heal
Vitamin D	Rickets	Bones become soft and bent
Calcium	Bone and tooth decay	Weak bones, tooth decay
Iodine	Goiter	Glands in the neck appear swollen, mental disability in children
Iron	Anaemia	Weakness



Vitamin/ Mineral	Deficiency disease/disorder	Symptoms
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Vitamin D	Rickets	Bones become soft and bent
Calcium	Bone and tooth decay	Weak bones, tooth decay
Iodine	Goiter	Glands in the neck appear swollen, mental disability in children
Iron	Anaemia	Weakness

Nucleic acids

- Nucleic acids are the polymers in which nucleotides are monomers. These are biomolecules present in nuclei of all living cells in the form of nucleoproteins .They are also called as polynucleotides .

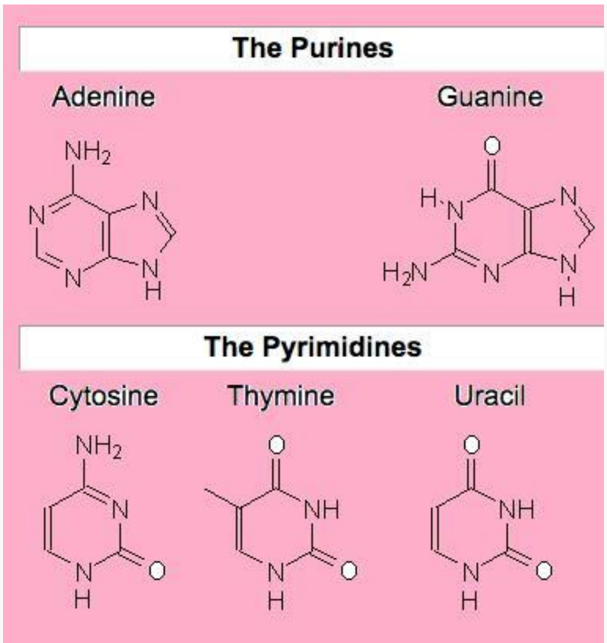
They help in the role of transmission of hereditary characters and synthesis of proteins.

Each nucleotide consists of 3 parts:

- A pentose sugar
- A nitrogenous base
- A phosphate group
- The nitrogenous base and a pentose sugar are called as nucleoside.

Nitrogenous bases are of two types: Purines and Pyrimidines

- Purines: adenine and guanine
- Pyrimidines: cytosine , thiamine and uracil



Please note that Purines and Pyrimidines are linked together by hydrogen bonds

- Adenine always bond with thiamine by double bond or vice versa.
- Cytosine always pairs with guanine by triple bond or vice versa.

Types of nucleic acids

- Deoxyribonucleic acid (DNA)
- Ribonucleic acid (RNA)

DNA

- It occurs in nucleus of cell. It has double stranded helical structure

DNA contains:

- Deoxyribose sugar
- Nitrogenous bases :
- Purines (adenine and guanine), Pyrimidines (thiamine and cytosine)
- A phosphate group
- It can undergo replication
- It helps in transfer of genetic information from parents to offspring

RNA

- It occurs in cytoplasm of cell

It consist of:

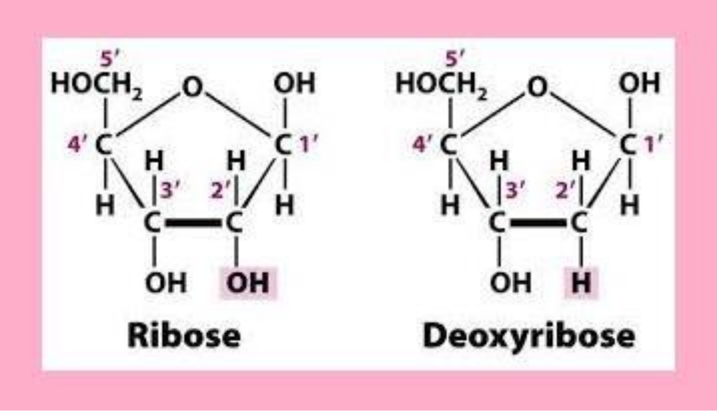
- Ribose sugar
- Nitrogenous base
- Purines: adenine and guanine
- Pyrimidines: cytosine and uracil
- A phosphate group
- It has a single strand helical structure
- It doesn't undergo replication
- It controls synthesis of proteins

The structure of deoxyribose and ribose sugar is given:

Structure of nucleic acids

1. **Primary structure**

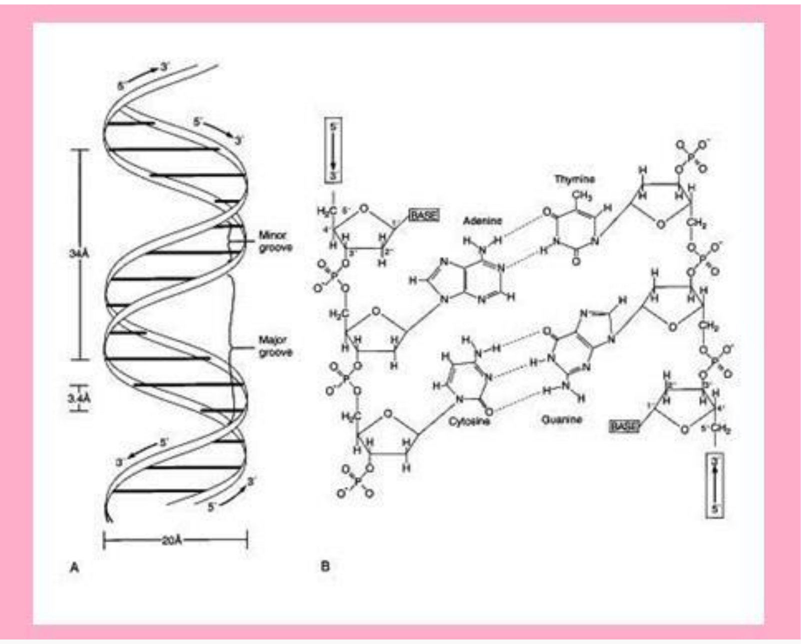
- The nucleic acids are formed by the condensation of thousands of molecules of nucleotides.
- On hydrolysis the nucleotides produces phosphoric acid and nucleoside .it means nucleosides on hydrolyses form Purine and Pyrimidines base and sugar moiety.
- A nucleic acid $\xrightarrow{NH_3}$ nucleotides $\xrightarrow{aq\ NH_3}$ nucleosides + phosphoric acid $\xrightarrow{dilute\ HCL}$ Purines + Pyrimidines + sugar.
- Nucleotides are building blocks of nucleic acids.
- These nucleotides are linked together with one another in a particular sequence, phosphate groups forming bridges between C-5 of the sugar residue of the one nucleoside and C-3 of the sugar residue of the other nucleoside.
- The manner in which the sugar, phosphate and bases are linked with one another in nucleic acids is known as primary structure of nucleic acids.



2. **Secondary structure:**

- Watson and Crick explained the double helix structure of DNA. The nucleotides in each strand are connected by phosphate ester bond and bases of one strand by hydrogen bonds.

- Adenine pairs with thiamine through two double hydrogen bonds whereas cytosine pairs with guanine by triple hydrogen bonds.
- The two strands of DNA are complementary to each other that is if one side there is Purine then on other side at same position Pyrimidine is present. For example if base sequence on strand is ACTCGCCA, then on the other strand the sequence will be complementary that is: TGAGCGGT
- **The primary and secondary structure is shown below:**



Watson and Crick model of DNA

Functions of nucleic acids

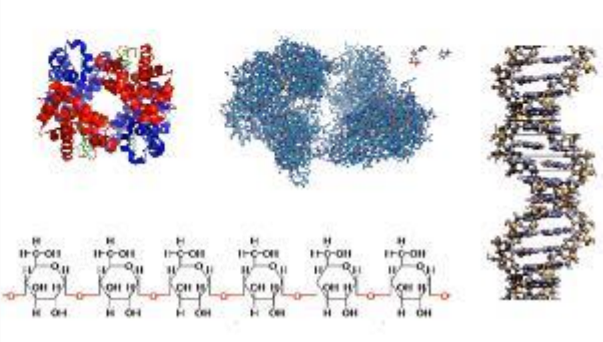
- **Replication**: The genetic information of cell is contained in the sequence of bases A, T, C and G in DNA molecule .In the division of cell, DNA molecules replicate and makes exact copies of themselves so that each daughter cell will have DNA identical to that of the parent cell.
- **Protein synthesis: The** specific information coded on DNA has to be translated and expressed in the form of synthesis of specific proteins which performs various functions in the cell. This synthesis is done in two steps:
- Transcription and translation.
- **Gene and genetic code**: Each segment of DNA molecule that codes for specific protein or a polypeptide is known as The relationship between nucleotides triplets and the amino acids are called the genetic code .This is gene and genetic code.
- **Mutation**: It is a chemical change in DNA molecule, which leads to the synthesis of proteins with a changed amino acid sequence.
    - These changes are caused by radiation, viruses or chemical agents.
    - The majority of changes in DNA are replicated by special enzymes in the cell, but if there is failure to repair by the enzymes then it can cause mutation.

Introduction

- The word ‘polymer’ is coined from two Greek words: poly means many and mer means unit or part.
- Plastics or polymers are integral part of our daily life.
- Polymers have huge applications everywhere.
- For example: - Hot water bag, tooth brush, switches, ropes etc. are all made of polymers.

Define the terms: Monomers, Polymers & Polymerization

- The term polymer is defined as a chemical substance of a very high molecular mass (10^3-10^7u) formed by combination of a simple molecule, called <u>monomers</u>.
- Polymers are also known as <u>macromolecules</u>, which are formed by repeating structural units on large scale.



- This process of formation of polymers from respective monomers is called polymerisation.
- For example:- $n\ CH_2 = nCH_2 \rightarrow n[-CH_2-CH_2-] \rightarrow [-CH_2-CH_2-]_n$

Ethene Repeating Unit Polythene polymer

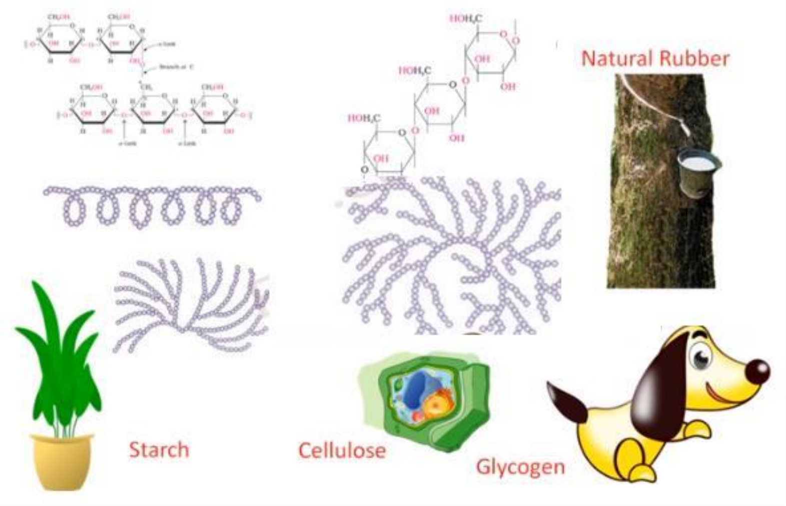
Classification of Polymers

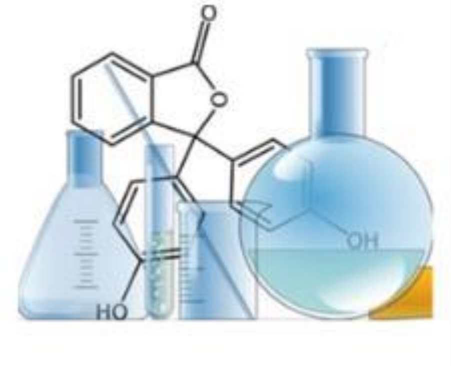
There are several ways of classification of polymers based on some special considerations.

The following are some of the common classifications of polymers:

1. Source
2. Structure
3. Mode of polymerization
4. Molecular Force

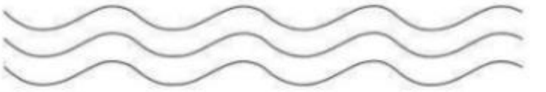
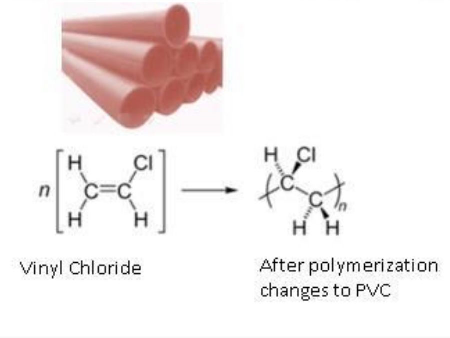
Source

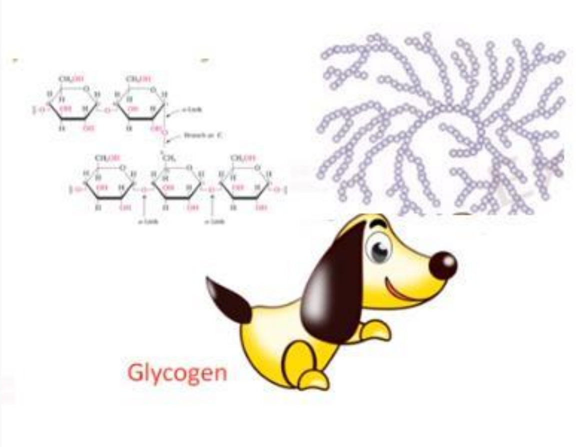
- Under this type of classification, there are three sub categories.
    1. Natural polymers
        1. These polymers are found in plants and animals. Examples are proteins, cellulose, starch, some resins and rubber.
- 

    1. Semi-synthetic polymers
    2. b) Cellulose derivatives as cellulose acetate (rayon) and cellulose nitrate, etc. are the some examples.
- 

    1. Synthetic Polymers
- A variety of synthetic polymers as plastic (polythene), synthetic fibres. Examples: - (nylon 6, 6) and synthetic rubbers (Buna - S) are polymers extensively used in daily life as well as in industry.

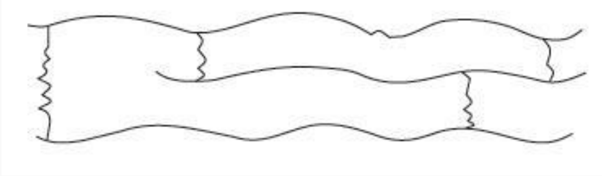
1. **Structure**

- There are three different types based on the structure of the polymers.
  1. Linear Polymers: -
     1. These polymers consist of long and straight chains. The examples are high density polythene, polyvinyl chloride, etc. These are represented as:
     2. 
     3. 

1. Branched chain polymers:-
2. b) These polymers contain linear chains having some branches, e.g. low density polythene. These are depicted as follows:
3. 

4. 

1. Cross linked or Network polymers:-
2. c) These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains, e.g. Bakelite, melamine, etc. These polymers are depicted as follows:

5. 
6. 

1. **Mode of Polymerization**

Polymers can also be classified on the basis of mode of polymerisation into two sub groups.

1. Addition polymers: -

- The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds.
    - For example: - The formation of polythene from Ethene and polypropene from propene.
- However, the addition polymers formed by the polymerisation of a single monomeric species are known as homopolymers.
    - For example: - polythene.

n $CH_2=CH_2$ --> $(CH_2-CH_2-)_n$ Homopolymer

Ethene Polythene

- The polymers made by addition polymerisation from two different monomers are termed as copolymers, e.g., Buna-S, Buna-N, etc.

nCH_2 = CH- CH =CH_2 + n $C_6H_5CH=CH_2$ à $(-CH_2-CH=CH-C_6H_5-CH_2-CH-CH_2-)_n$

1,3 – Butadiene Styrene Butadiene-styrene copolymer

(Buna-S)

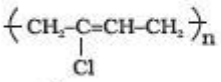
2. Condensation polymers

- The condensation polymers are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units.
- In these polymerisation reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place.
    - The examples are Terylene (Dacron), nylon 6, 6, nylon 6, etc.
    - For example, nylon 6, 6 is formed by the condensation of hexamethylene diamine with adipic acid.

1. **D. Molecular Forces**

1. A large number of polymers can be used in different fields because of their mechanical properties like tensile strength, elasticity, toughness etc.
2. These mechanical properties are governed by intermolecular forces, e.g., van der Waals forces and hydrogen bonds, present in the polymer. These forces also bind the polymer chains.
3. The polymers are classified into the following four sub groups on the basis of magnitude of intermolecular forces present in them.
4. a) Elastomers: -

1. These are rubber – like solids with elastic properties.
2. The polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched.
3. A few 'crosslinks' are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanised rubber. The examples are Buna-S, Buna-N, neoprene, etc.

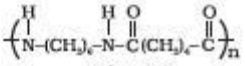


$$\left(CH_2-\underset{\displaystyle Cl}{\underset{|}{C}}=CH-CH_2 \right)_n$$

Neoprene

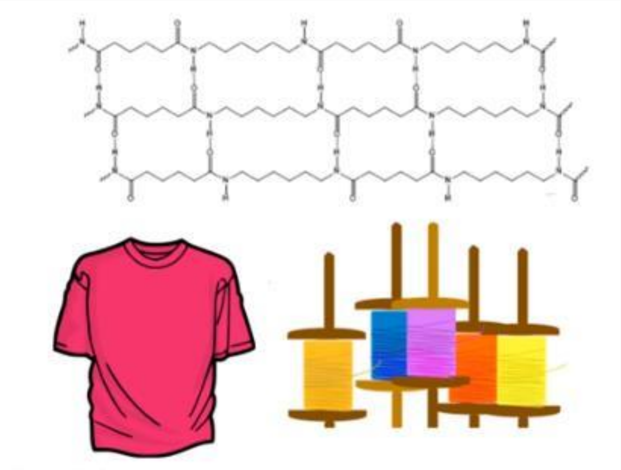
1. b) Fibres:-

1. Fibres are the thread forming solids which possess high tensile strength and high modulus.
2. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding.
3. These strong forces also lead to close packing of chains and thus impart crystalline nature. The examples are polyamides (nylon 6, 6), polyesters (terylene), etc.



$$\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{||}{C}}(CH_2)_4-\overset{O}{\overset{||}{C}} \right]_n$$

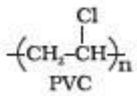
Nylon 6,6



1. c) Thermoplastic Polymers:-

1. These are the linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling.
2. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibres.

- Some common thermoplastics are polythene, polystyrene, polyvinyl, etc.



$$\left(CH_2-\overset{Cl}{\overset{|}{CH}} \right)_n$$

PVC

1. d) Thermosetting Polymers:-
2. These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible.
3. These cannot be reused. Some common examples are Bakelite, urea-formaldehyde resins, etc.

ypes of Polymerization Reactions

- There are broadly 2 types of polymerization reactions:-

1. Addition or chain growth polymerization
2. Condensation or step growth polymerization

Addition or chain growth polymerization

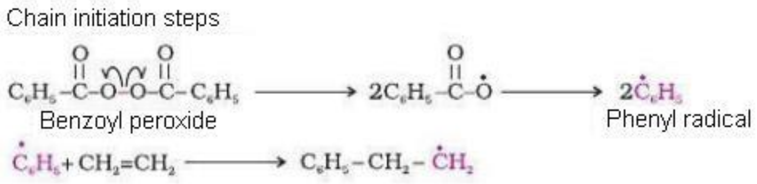
- The molecules of the same monomer or different monomers add together on a large scale to form a polymer.
- The monomers used are unsaturated compounds, e.g., alkenes, alkadienes and their derivatives.
- This mode of polymerisation leading to an increase in chain length or chain growth can take place through the formation of either free radicals or ionic species.
- However, the free radical governed addition or chain growth polymerisation is the most common mode.

1. Free Radical Mechanism:-

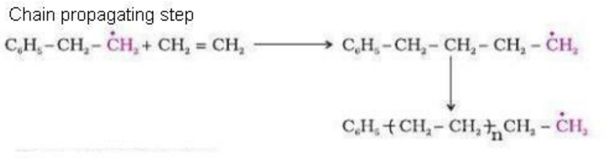
- Many of alkenes or dienes and their derivatives are polymerized in the presence of a free radical (catalyst) like benzoyl peroxide.
- The sequence of steps may be depicted as follows:
- Chain initiation steps
- Chain propagating step
- Chain terminating step

For example:-

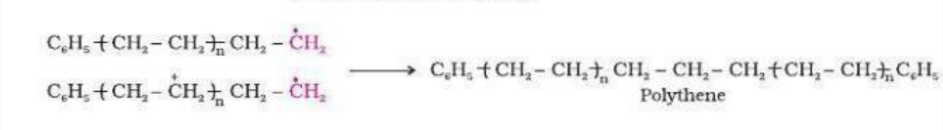
- The polymerisation of Ethene to polythene consists of heating or exposing to light a mixture of Ethene with a small amount of benzoyl peroxide initiator.
- The process starts with the addition of phenyl free radical formed by the peroxide to the Ethene double bond thus generating a new and larger free radical. This step is called chain initiating step.



- As this radical reacts with another molecule of Ethene, another bigger sized radical is formed. The repetition of this sequence with new and bigger radicals carries the reaction forward and the step is termed as chain propagating step.



- Ultimately, at some stage the product radical thus formed reacts with another radical to form the polymerised product. This step is called the chain terminating step.



Chain terminating step

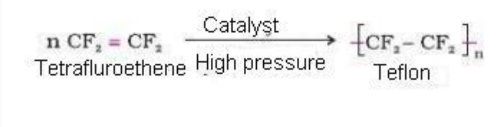
Preparation of Important Addition Reaction

Polythene: - There are two types of polythene-

- Low density polythene:
    - It is obtained by the polymerisation of Ethene under high pressure of 1000 to 2000 atmospheres at a temperature of 350 K to 570 K in the presence of traces of dioxygen or a peroxide initiator (catalyst).
    - The low density polythene (LDP) obtained through the free radical addition and H-atom abstraction has highly branched structure.
    - Low density polythene is chemically inert and tough but flexible and a poor conductor of electricity.
    - Hence, it is used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes.

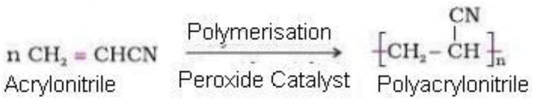
- High density polythene:
    - It is formed when addition polymerisation of Ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6-7 atmospheres.
    - High density polythene (HDP) thus produced, consists of linear molecules and has a high density due to close packing.
    - It is also chemically inert and more tough and hard. It is used for manufacturing buckets, dustbins, bottles, pipes, etc.

- **Polytetrafluroethene (Teflon)**
    - Teflon is manufactured by heating tetrafluoroethene with a free radical or per sulphate catalyst at high pressures.
    - It is chemically inert and resistant to attack by corrosive reagents. It is used in making oil seals and gaskets and also used for non – stick surface coated utensils.



- **Polyacrylonitrile**

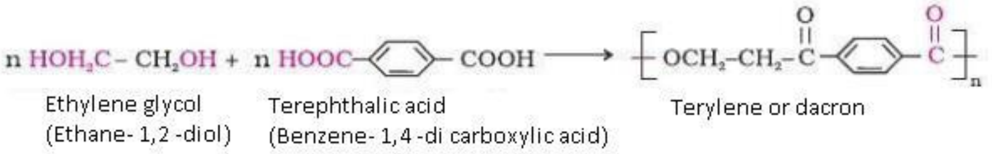
- The addition polymerisation of acrylonitrile in presence of a peroxide catalyst leads to the formation of polyacrylonitrile.
- Polyacrylonitrile is used as a substitute for wool in making commercial fibres as Orlon or acrilan.



$$n\,CH_2=CHCN \xrightarrow[\text{Peroxide Catalyst}]{\text{Polymerisation}} \left[CH_2-\overset{\overset{CN}{|}}{CH} \right]_n$$

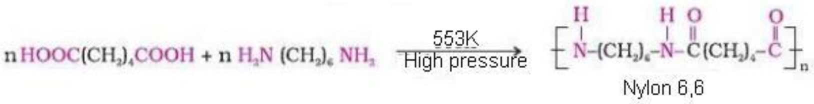
Condensation Polymerization or step growth polymerization

- This type of polymerisation involves a repetitive condensation reaction between two bi-functional monomers.
- These poly condensation reactions results in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers.
- In these reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on.
- Since, each step produces a distinct functionalised species and is independent of each other; this process is also called as step growth polymerisation.
- The formation of Terylene or Dacron by the interaction of ethylene glycol and terephthalic acid is an example of this type of polymerisation.



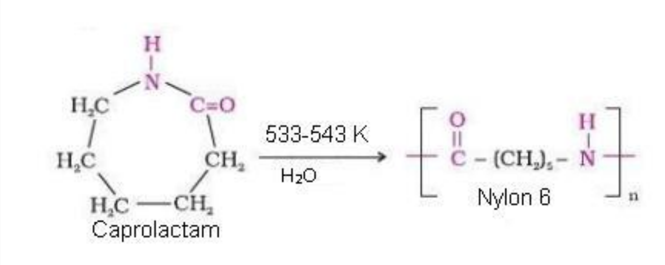
Preparation of Important Addition Reaction

1. **Polyamides**:-
   1. These polymers possessing amide linkages are important examples of synthetic fibres and are termed as nylons. The general method of preparation consists of the condensation polymerisation of diamines with dicarboxylic acids and also of amino acids and their lactams.
   2. Preparation of Nylons
      1. Nylon 6, 6:-
         1. It is prepared by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.
         2. Nylon 6, 6 is used in making sheets, bristles for brushes and in textile industry.

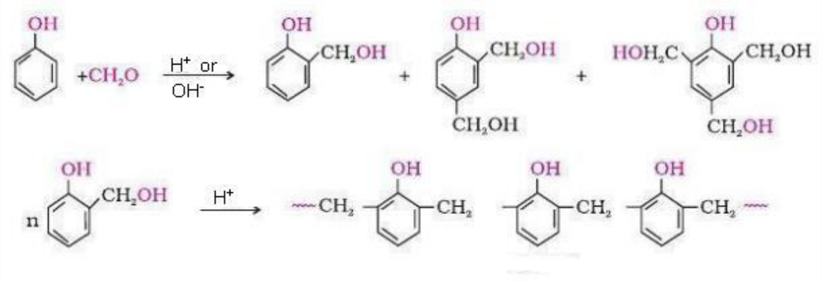


$$n\,HOOC(CH_2)_4COOH + n\,H_2N(CH_2)_6NH_2 \xrightarrow[\text{High pressure}]{553K} \left[\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}(CH_2)_4-\overset{\overset{O}{\|}}{C} \right]_n$$

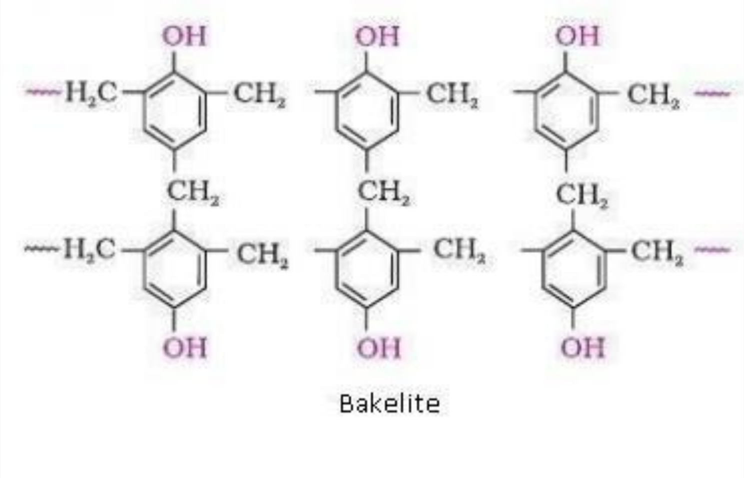
   3.
      1. Nylon 6:-
         1. It is obtained by heating Caprolactum with water at a high temperature.
         2. Nylon 6 is used for the manufacture of tyre cords, fabrics and ropes.

4. 

1. **Polyesters**: - These are the poly condensation products of dicarboxylic acids and diols.
    1. Dacron or Terylene is the best known example of polyesters. It is manufactured by heating a mixture of ethylene glycol and terephthalic acid at 420 to 460 K in the presence of Zinc acetate antimony trioxide catalyst.
    2. Dacron fibre (Terylene) is crease resistant and is used in blending with cotton and wool fibres and also as glass reinforcing materials in safety helmets, etc.
2. **Phenol – formaldehyde polymer (Bakelite and related polymers)**:-
    1. Phenol - formaldehyde polymers are the oldest synthetic polymers.
    2. These are obtained by the condensation reaction of phenol with formaldehyde in the presence of either an acid or a base catalyst.
    3. The reaction starts with the initial formation of o-and/or p-hydroxymethylphenol derivatives, which further react with phenol to form compounds having rings joined to each other through $–CH_2$
    4. The initial product could be a linear product – Novolac used in paints.
    5. Novolac on heating with formaldehyde undergoes cross linking to form infusible solid mass called Bakelite. It is used for making combs, phonograph records, electrical switches and handles of various utensils.
3. Melamine- formaldehyde Polymer:-
    1. Melamine formaldehyde polymer is formed by the condensation polymerisation of melamine and formaldehyde.
    2. It is used in the manufacture of unbreakable crockery.

5. 

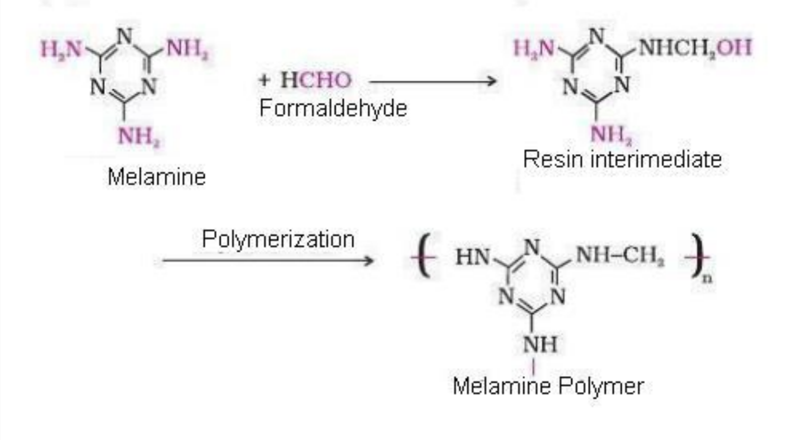
Novolac on heating with formaldehyde undergoes cross linking to form infusible solid mass called Bakelite. It is used for making combs, phonograph records, electrical switches and handles of various utensils.



Bakelite

2.

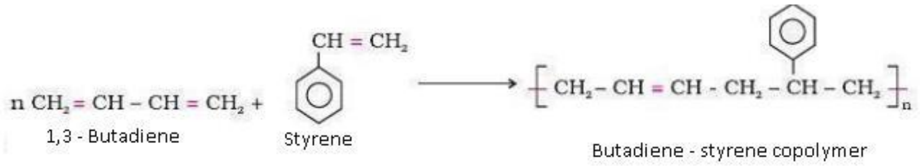
1. Melamine- formaldehyde Polymer:-
    1. Melamine formaldehyde polymer is formed by the condensation polymerisation of melamine and formaldehyde.
    2. It is used in the manufacture of unbreakable crockery.



3.

Co Polymerization

1. Copolymerisation is a polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerise and form a copolymer.
2. The copolymer can be made not only by chain growth polymerisation but by step growth polymerisation also.
3. It contains multiple units of each monomer used in the same polymeric chain.
4. For example:-a mixture of 1, 3 – butadiene and styrene can form a copolymer.
5. Copolymers have properties quite different from homopolymers.
6. For example: - butadiene - styrene copolymer is quite tough and is a good substitute for natural rubber.
7. It is used for the manufacture of auto tyres, floor tiles, footwear components, cable insulation, etc.



Rubber

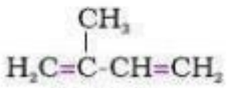
- Rubber is a natural polymer and possesses elastic properties.

- It is also termed as elastomer and has a variety of uses.
- It is manufactured from rubber latex which is a colloidal dispersion of rubber in water. This latex is obtained from the bark of rubber tree and is found in India, Sri Lanka, Indonesia, Malaysia and South America.

1. **Natural Rubber**

- Natural rubber may be considered as a linear polymer of isoprene (2-methyl-1, 3-butadiene) and is also called as cis - 1, 4 -polyisoprene.
- The cis-polyisoprene molecule consists of various chains held together by weak van der Waals interactions and has a coiled structure.

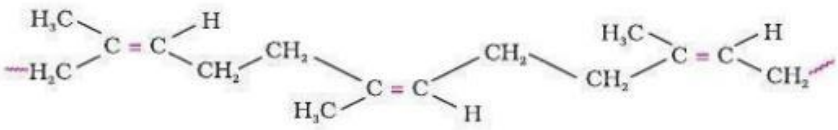
- Thus, it can be stretched like a spring and exhibits elastic properties.


$H_2C=C(CH_3)-CH=CH_2$

Isoprene

Vulcanization of Rubber:-

- Natural rubber becomes soft at high temperature (>335 K) and brittle at low temperatures (<283 K) and shows high water absorption capacity.
- It is soluble in non-polar solvents and is non-resistant to attack by oxidising agents. To improve upon these physical properties, a process of vulcanisation is carried out. This process consists of heating a mixture of raw rubber with sulphur and an appropriate additive at a temperature range 373 K to 415K.
- On vulcanisation, sulphur forms cross links at the reactive sites of double bonds and thus the rubber gets stiffened.
- In the manufacture of tyre rubber, 5% of sulphur is used as a crosslinking agent.
- The probable structures of vulcanised rubber molecules are depicted below:



Natural Rubber

2. **Synthetic Rubber**

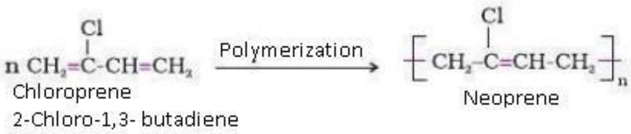
- Synthetic rubber is any vulcanisable rubber like polymer, which is capable of getting stretched to twice its length.

- However, it returns to its original shape and size as soon as the external stretching force is released.
- Thus, synthetic rubbers are either homopolymers of 1, 3 - butadiene derivatives or copolymers of 1, 3 - butadiene or its derivatives with another unsaturated monomer.

Preparation of Synthetic Rubbers

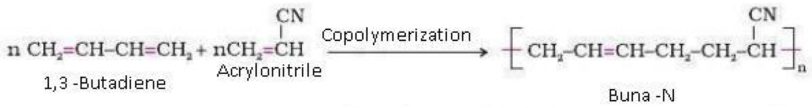
1. Neoprene:-

- Neoprene or poly chloroprene is formed by the free radical polymerisation of chloroprene.
- It has superior resistance to vegetable and mineral oils.
- It is used for manufacturing conveyor belts, gaskets and hoses.



2. Buna –N:-

- Buna –N is obtained by the copolymerisation of 1, 3 – butadiene and acrylonitrile in the presence of a peroxide catalyst.
- It is resistant to the action of petrol, lubricating oil and organic solvents. It is used in making oil seals, tank lining, etc.



Biodegradable Polymers

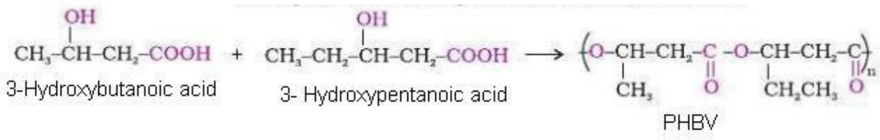
- A large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric solid waste materials.
- Aliphatic polyesters are one of the important classes of biodegradable polymers.
- Some important examples are given below:

1. Poly β-hydroxybutyrate – co-β-hydroxy valerate (PHBV)

- It is obtained by the copolymerisation of 3-hydroxybutanoic acid and

3 - Hydroxypentanoic acid.

- PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.



16.Chemistry In Everyday Life

Introduction

- Chemistry is essentially the study of materials and the development of new materials for the betterment of humanity.

- In our daily life we use so many substances like toothpaste, soaps, sugar etc. which are made up of chemicals compounds.
- In this lesson we will try to learn the uses and applications of chemistry in our day-to day life.
- For Example: - The basic common salt, baking soda, fruits; vegetables all are made up of carbon compounds.
- There are 3 important areas where we use chemistry in our life is:-
  - Medicines
  - Food materials
  - Cleaning agents

Importance of Chemistry in our daily life: Medicines

- A drug is a chemical agent, which affects human metabolism and provides cure from ailment.
- Or Drugs are chemicals which interact with macromolecular targets and produce a biological response.
- Drugs will interact with macromolecules targets (where these targets are chemical compounds like proteins, lipids etc.) in order to maintain balance in the body.

- When the biological response is therapeutic and useful, these chemicals are called medicines and are used in diagnosis, prevention and treatment of diseases.
- Medicines are sub classification of the drugs. They produce good response and they are useful in order to diagnosis, prevention and treatment of diseases.
- If taken in doses higher than those recommended, most of the drugs used as medicines are potential poisons.
- Use of chemicals for treatment and cure of disease is called chemotherapy.
  - The treatment of disease by chemical compound which destroy the microorganisms without attacking the tissue of the human body is known as chemotherapy.
  - The compounds used are called chemotherapeutic agents.

Classification of drugs

- On the basis of pharmacological effect
- On the basis of drug action
- On the basis of chemical structure
- On the basis of molecular targets

Pharmacological effect

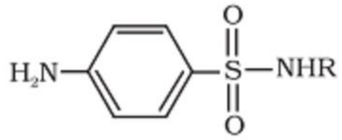
- This classification is based on pharmacological effect of the drugs.
- It is useful for doctors because it provides them the whole range of drugs available for the treatment of a particular type of problem.
  - For example, analgesics have pain killing effect; antiseptics kill or arrest the growth of microorganisms.

Drug Action

- It is based on the action of a drug on a particular biochemical process.
- For example, all antihistamines inhibit the action of the compound, histamine which causes inflammation in the body. There are various ways in which action of histamines can be blocked.
- Aspirin controls the synthesis of chemicals known as prostaglandins

Chemical Structure

- It is based on the chemical structure of the drug.
- Drugs classified in this way share common structural features and often have similar pharmacological activity.
- For example, sulphonamides have common structural feature, given below.



Structural features of sulphonamides

Molecular targets

- Drugs usually interact with biomolecules such as carbohydrates, lipids, proteins and nucleic acids.
- These are called target molecules or drug targets.
- Drugs possessing some common structural features may have the same mechanism of action on targets.

Drug- Target Interaction as Enzymes

- Macromolecules of biological origin perform various functions in the body.
    - For example, proteins which perform the role of biological catalysts in the body are called enzymes.
    - They are crucial to communication system in the body are called receptors.
- Carrier proteins carry polar molecules across the cell membrane.
- Nucleic acids have coded genetic information for the cell. Lipids and carbohydrates are structural parts of the cell membrane.

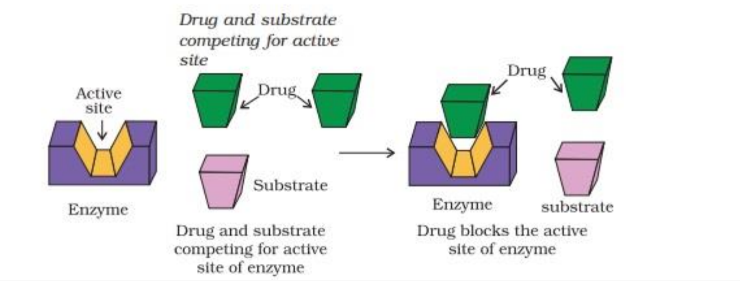
- **Catalytic Action of Enzymes**
- In order to carry catalytic activity enzymes perform 2 major functions:

1. The first function of an enzyme is to hold the substrate for a chemical reaction. Active sites of enzymes hold the substrate molecule in a suitable position, so that it can be attacked by the reagent effectively.

Substrates bind to the active site of the enzyme through a variety of interactions such as ionic bonding, hydrogen bonding, van der Waals interaction or dipole-dipole interaction.

2. The second function of an enzyme is to provide functional groups that will attack the substrate and carry out chemical reaction.

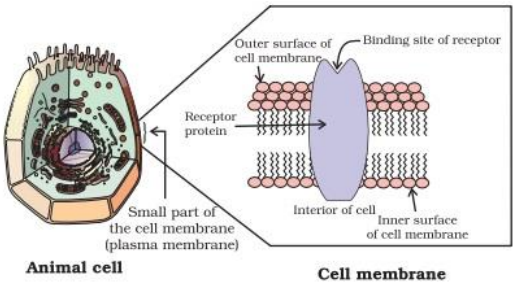
- **Drug-Enzyme Interaction**
- These drugs can block the binding site of the enzyme and prevent the binding of substrate, or can inhibit the catalytic activity of the enzyme. Such drugs are called enzyme inhibitors.
- Drugs inhibit the attachment of substrate on active site of enzymes in two different ways;
- Drugs compete with the natural substrate for their attachment on the active sites of enzymes. Such drugs are called competitive inhibitors.
- Some drugs do not bind to the enzyme's active site. These bind to a different site of enzyme which is called allosteric site. This binding of inhibitor at allosteric site changes the shape of the active site in such a way that substrate cannot recognise it.



- Note:-
- If the bond formed between an enzyme and an inhibitor is a strong covalent bond and cannot be broken easily, then the enzyme is blocked permanently.
- The body then degrades the enzyme-inhibitor complex and synthesises the new enzyme.

Drug- Target Interaction as Receptors

- Receptors are proteins that are crucial to body's communication process.
- Receptor proteins are embedded in the cell membrane in such a way that their small part possessing active site projects out of the surface of the membrane and opens on the outside region of the cell membrane.



- In the body, message between two neurons and that between neurons of muscles is communicated through certain chemicals.
- These chemicals are known as chemical messengers and are received at the binding sites of receptor proteins.
- To accommodate a messenger, shape of the receptor site changes, as a result transfer of message happens into the cell.
- Thus, chemical messenger gives message to the cell without entering the cell.

Note:-

- There are a large number of different receptors in the body that interact with different chemical messengers.

- These receptors show selectivity for one chemical messenger over the other because their binding sites have different shape, structure and amino acid composition.

Antagonists

- Drugs that bind to the receptor site and inhibit its natural function are called antagonists.
- These are useful when blocking of message is required.
- There are other types of drugs that mimic the natural messenger by switching on the receptor, these are called agonists. These are useful when there is lack of natural chemical messenger.

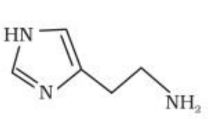
Therapeutic Action of Different Classes of Drugs

Antacids

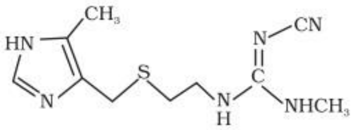
- The chemical substances which neutralises the excess acid in gastric juice and raise pH to an appropriate level in stomach are called antacids.

- For example: - Baking soda, mixture of Al and Mg hydroxide are commonly used antacids.

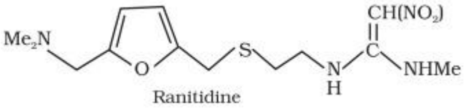
- Generally liquids antacids are more effective than tablets because of more of surface area available for interaction and neutralisation acids.
- Milk is a weak antacid.
- By using excess hydrogen carbonate stomach will become more of alkaline and as a result more of
-
- acid production happens.
- So Metal hydroxides are used instead of them which are insoluble and don't increase the pH value also.
- But they will only treat the symptoms not the cause.
- A major breakthrough in the treatment of hyperacidity happened by the discovery of chemical known as **histamine** which stimulates the secretion of pepsin and hydrochloric acid in the stomach.
- The drug cimetidine (Tegamet) was designed to prevent the interaction of histamine with the receptors present in the stomach wall.
- This resulted in release of lesser amount of acid.
- The importance of the drug was so much that it remained the largest selling drug in the world until another drug, ranitidine (Zantac), was discovered.



Histamine



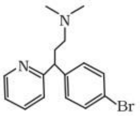
Cimetidine



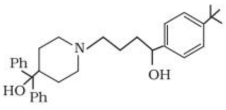
Ranitidine

Antihistamines

- Histamine is a potent vasodilator.
- It has various functions. It contracts the smooth muscles in the bronchi and gut and relaxes other muscles, such as those in the walls of fine blood vessels.
- Histamine is also responsible for the nasal congestion associated with common cold and allergic response to pollen.
- Synthetic drugs, brompheniramine (Dimetapp) and terfenadine (Seldane) act as antihistamines.
- They interfere with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect.
- The antihistamines don’t affect the secretion of acid in the stomach because antiallergic and antacid drugs work on different receptors.



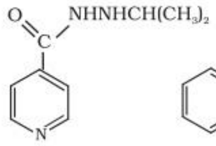
Brompheniramine
(Dimetapp, Dimetane)



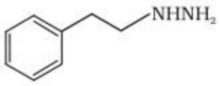
Terfenadine (Seldane)

Neurologically Active Drugs

- Tranquilizers and analgesics are neurologically active drugs. These affect the message transfer mechanism from nerve to receptor.
- **Tranquilizers**
- Tranquilizers are a class of chemical compounds used for the treatment of stress, and mild or even severe mental diseases.
- These relieve anxiety, stress, irritability or excitement by inducing a sense of well-being. They form an essential component of sleeping pills.
- There are various types of tranquilizers.
- They function by different mechanisms.
- For example, noradrenaline is one of the neurotransmitters that play a role in mood changes.
- If the level of noradrenaline is low for some reason, then the signal-sending activity becomes low, and the person suffers from depression.
- In such situations, antidepressant drugs are required.
- These drugs inhibit the enzymes which catalyse the degradation of noradrenaline.

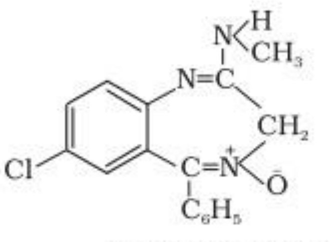


Iproniazid

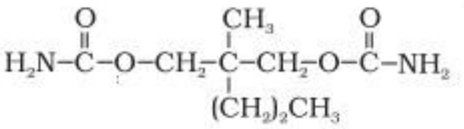


Phenelzine (Nardil)

- If the enzyme is inhibited, this important neurotransmitter is slowly metabolised and can activate its receptor for longer periods of time, thus counteracting the effect of depression.
- Iproniazid and phenelzine are two such drugs.
- Some tranquilizers namely, chlordiazepoxide and meprobamate, are relatively mild tranquilizers suitable for relieving tension.
- Equanil is used in controlling depression and hypertension.

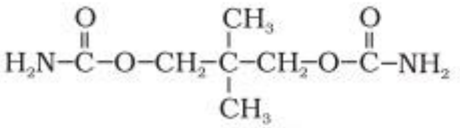


Chlordiazepoxide



$$H_2N-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{(CH_2)_2CH_3}{\overset{CH_3}{\overset{|}{C}}}-CH_2-O-\overset{O}{\overset{\|}{C}}-NH_2$$

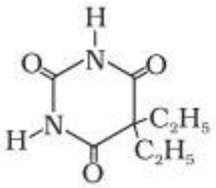
Meprobamate



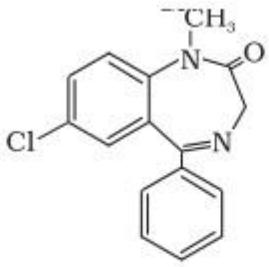
$$H_2N-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}-CH_2-O-\overset{O}{\overset{\|}{C}}-NH_2$$

Equanil

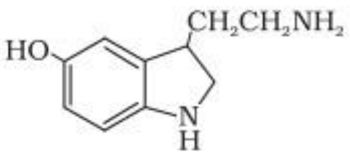
- Some important class of tranquilizers are as :
    - Derivatives of barbituric acid viz., veronal, amytal, nembutal, luminal and seconal.
    - These derivatives are called barbiturates. Barbiturates are hypnotic, i.e., sleep producing agents. Some other substances used as tranquilizers are valium and serotonin.



Veronal



Valium



Serotonin

- **Analgesics**
- Analgesics reduce or finish the pain without causing impairment of consciousness, mental confusion, incoordination or paralysis or some other disturbances of nervous system.
- These are classified as follows:

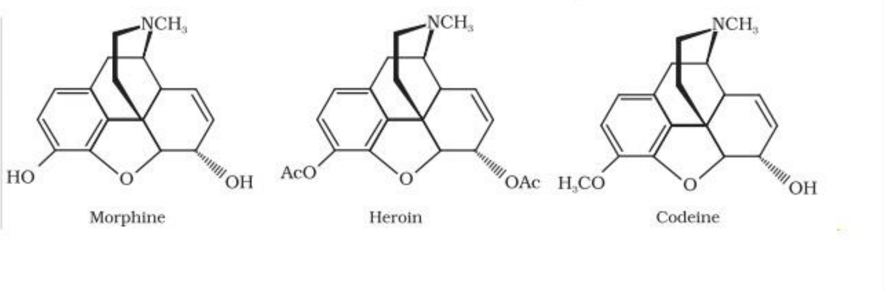
(i) Non-narcotic (non-addictive) analgesics

(ii) Narcotic drugs

Non-narcotic (non-addictive) analgesics

- Aspirin and paracetamol belong to the class of non-narcotic analgesics.
- Aspirin is the most common example. It inhibits the synthesis of chemicals known as prostaglandins which stimulate inflammation in the tissue and cause pain.
- These drugs are effective in relieving skeletal pain such as that due to arthritis. These drugs have many other effects such as reducing fever (antipyretic). and preventing platelet coagulation.
- They prevent platelet coagulation because of this anti-blood clotting action; aspirin finds use in prevention of heart attacks.
- Aspirin is toxic for liver and sometimes causes bleeding from stomach. So naproxen, ibuprofen, paracetamol are widely used analgesics.

- **Narcotic Analgesics**
- Morphine and many of its homologues, when administered in medicinal doses, relieve pain and produce sleep.
- In poisonous doses, these produce stupor, coma, convulsions and ultimately death.
- Morphine narcotics are sometimes referred to as opiates, since they are obtained from the opium poppy.
- These analgesics are chiefly used for the relief of postoperative pain, cardiac pain and pains of terminal cancer, and in child birth.



Antimicrobials

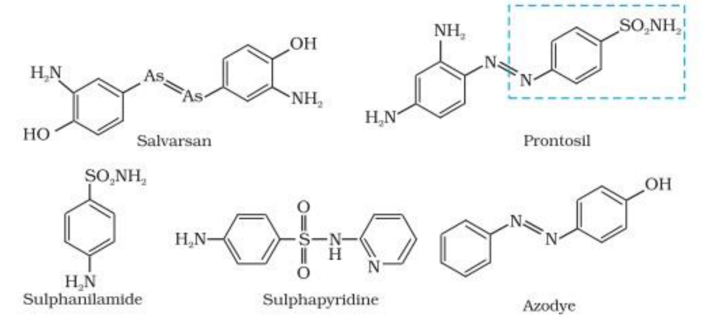
- Diseases in human beings and animals may be caused by a variety of microorganisms such as bacteria, virus, fungi and other pathogens.
- An antimicrobial tends to destroy/prevent development or inhibit the pathogenic action of microbes such as bacteria (antibacterial drugs), fungi (antifungal agents), virus (antiviral agents), or other parasites (antiparasitic drugs) selectively.
- Antibiotics, antiseptics and disinfectants are antimicrobial drugs.

Antibiotics

- Antibiotics are used as drugs to treat infections because of their low toxicity for humans and animals.
- An antibiotic is a substance produced wholly or partly by chemical synthesis, which in low concentrations inhibits the growth or destroys microorganisms by intervening in their metabolic processes.
- In order to find chemicals this will affect the invading bacteria and not the host.
- Paul Ehrlich, a German bacteriologist, conceived this idea. He investigated arsenic based structures in order to produce less toxic substances for the treatment of syphilis.
- He developed the medicine, arsphenamine, known as salvarsan.
- Although salvarsan is toxic to human beings, its effect on the bacteria, spirochete, which causes syphilis, is much greater than on human beings.
- He noted that there is similarity in structures of salvarsan and azodyes. The $–As = As–$ linkage present in arsphenamine resembles the $–N = N –$ linkage present in azodyes in the sense that arsenic atom is present in place of nitrogen.
- In 1932, he succeeded in preparing the first effective antibacterial agent, prontosil, which resembles in structure to the compound, salvarsan. Soon it was discovered that in the body prontosil is converted to a compound called sulphanilamide, which is the real active compound. Thus the sulpha drugs were discovered.
- A large range of sulphonamide analogues was synthesised. One of the most effective is sulphapyridine.
- Despite the success of sulphonamides, the real revolution in antibacterial therapy began with the discovery of Alexander Fleming in 1929, of the antibacterial properties of a Penicillium fungus.
- Antibiotics have either cidal (killing) effect or a static (inhibitory) effect on microbes.
- A few examples of the two types of antibiotics are as follows:

Bactericidal	Bacteriostatic
Penicillin	Erythromycin
Aminoglycosides	Tetracycline
Ofloxacin	Chloramphenicol

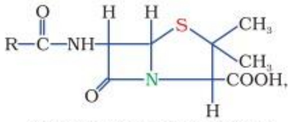
- Antibiotics which kill or inhibit a wide range of Gram-positive and Gram-negative bacteria are said to be broad spectrum antibiotics.
- Those are effective mainly against Gram-positive or Gram-negative bacteria are narrow spectrum antibiotics.
- If effective against a single organism or disease, they are referred to as limited spectrum antibiotics.
- Penicillin G has a narrow spectrum. Ampicillin and Amoxicillin are synthetic modifications of penicillin's. These have broad spectrum.
- It is absolutely essential to test the patients for sensitivity (allergy) to penicillin before it is administered.
- In India, penicillin is manufactured at the Hindustan Antibiotics in Pimpri and in private sector industry.



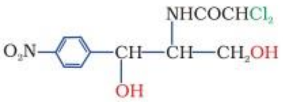
The structures of salvarsan, prontosil azodye and sulphapyridine showing structural similarity.

Chloramphenicol

- Chloramphenicol, isolated in 1947, is a broad spectrum antibiotic.
- It is rapidly absorbed from the gastrointestinal tract and hence can be given orally in case of typhoid, dysentery, and acute fever, certain form of urinary infections, meningitis and pneumonia.
- Vancomycin and ofloxacin are the other important broad spectrum antibiotics.
- The antibiotic dysidazirine is supposed to be toxic towards certain strains of cancer cells.



General Sturcture of Pencillin

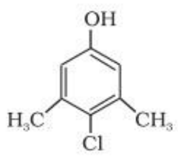


Chloramphenicol

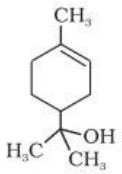
Antiseptics & disinfectants

- Antiseptics are applied to the living tissues such as wounds, cuts, ulcers and diseased skin surfaces.
- Examples are furacine, soframicine, etc. These are not ingested like antibiotics.
- Commonly used antiseptic, Dettol is a mixture of chloroxylenol and terpineol.

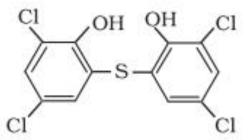
- Bithionol (the compound is also called bithionol) is added to soaps to impart antiseptic properties.
- Iodine is a powerful antiseptic. Its 2-3 per cent solution in alcohol water mixture is known as tincture of iodine.
- It is applied on wounds.
- Iodoform (CHI_3) is also used as an antiseptic for wounds.
- Boric acid in dilute aqueous solution is weak antiseptic for eyes.



Chloroxylenol



Terpineol



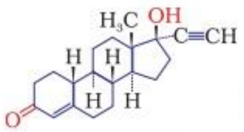
Bithionol

Disinfectants

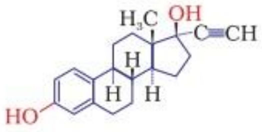
- They are applied to inanimate objects such as floors, drainage system, instruments, etc. Same substances can act as an antiseptic as well as disinfectant by varying the concentration.
- For example, 0.2 per cent solution of phenol is an antiseptic while its one percent solution is disinfectant.
- Chlorine in the concentration of 0.2 to 0.4 ppm in aqueous solution and sulphur dioxide in very low concentrations, are disinfectants.

Antifertility Drugs

- These are the chemical substances which are used to control pregnancy.
- They are also called as oral contraceptives.
- Birth control pills essentially contain a mixture of synthetic estrogen and progesterone derivatives. Both of these compounds are hormones.
- It is known that progesterone suppresses ovulation.
- Synthetic progesterone derivatives are more potent than progesterone.
- Norethindrone is an example of synthetic progesterone derivative most widely used as antifertility drug. The estrogen derivative which is used in combination with progesterone derivative is ethynylestradiol (novestrol).



Norethindrone



Ethynylestradiol (novestrol)

Chemicals in Food

- Chemicals are added to the food for the following reasons:-

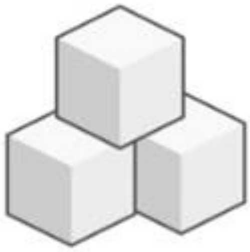
1. Their preservation
2. Enhancing their appeal
3. Adding nutritive value in them.

- Main categories of food additives are as follows:-

1. Food colours

1. Flavours and sweeteners

Sucrose (Natural sugar)



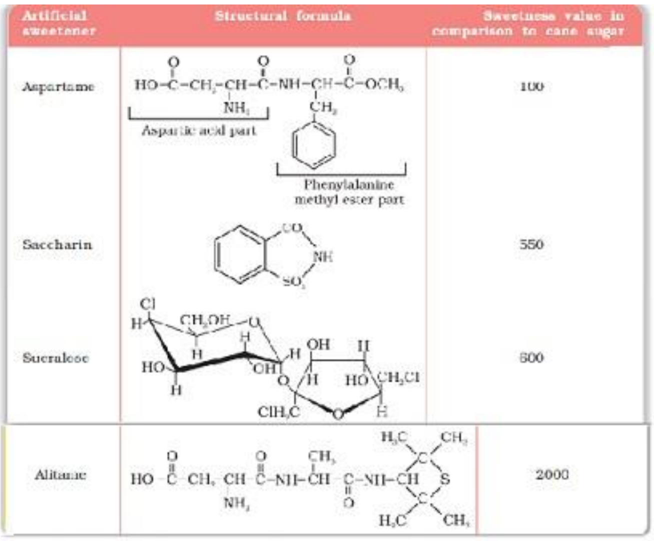
1. Fat emulsifiers and stabilising agents
2. Flour improvers - antistaling agents and bleaches
3. Antioxidants
    1. Antioxidants prevent damage to the cells, cell proteins and lipids. They neutralize the free radicals which causes aging and degeneration of body.
    2. For example: - Vitamin E and Vitamin C etc. They are electron rich substances so they can denote electrons to free radicals which are causing age degeneration.
    3. They stabilize the age causing radicals.
4. Preservatives
5. Nutritional supplements such as minerals, vitamins and amino acids.

Artificial Sweetening Agents

- Sucrose and fructose are the most widely used natural sweeteners.
- But their intake increases calories in the diet and excess of them can cause tooth decay.
- Ortho-sulphobenzimide, also called saccharin, is the first popular artificial sweetening agent. It is about 550 times as sweet as cane sugar. It appears to be entirely inert and harmless when taken.
- Its use is of great value to diabetic persons and people who need to control intake of calories.

Aspartame

- Aspartame is the most successful and widely used artificial sweetener. It is roughly 100 times as sweet as cane sugar.
- It is methyl ester of dipeptide formed from aspartic acid and phenylalanine.
- Use of aspartame is limited to cold foods and soft drinks because it is unstable at cooking temperature.
- Sucralose is trichloro derivative of sucrose. Its appearance and taste are like sugar. It is stable at cooking temperature. It does not provide calories.



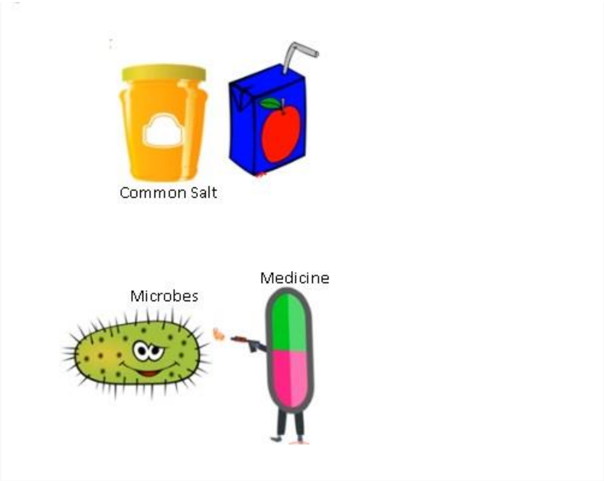
Artificial sweetener	Structural formula	Sweetness value in comparison to cane sugar
Aspartame	Aspartic acid part Phenylalanine methyl ester part	100
Saccharin		550
Sucralose		600
Alitame		2000

Food Preservatives

- Food preservatives prevent spoilage of food due to microbial growth. The most commonly used preservatives include table salt, sugar, vegetable oils and sodium benzoate, C_6H_5COONa.
- Sodium benzoate is used in limited quantities and is metabolised in the body. Salts of sorbic acid and propanoic acid are also used as preservatives.

- There are 3 categories of food preservatives:-
  - Anti-microbial
    - It inhibits the growth of bacteria.
  - Anti-oxidant
    - They prevent damage to the cells, cell proteins and lipids. They neutralize the free radicals which causes aging and degeneration of body.
    - For Example: - BHT(butylated hydroxytoluene) and BRA(Butylated hydroxyanisole).

    - Anti-ripening
        - It will remove the oxygen from the substance. It is used to preserve fruits and vegetables.



Cleansing Agents

- The word detergent means “cleansing agent”. Detergent is derived from Latin word “detergere” means “to wipe off”.
- Cleansing agents are the substances which remove dirt and have cleansing action in water.
- Detergents can be classified into 2 types”
    - Soapy detergents or soaps.
    - Synthetic detergents

<u>Soaps</u>

- Soaps are sodium or potassium salts of long chain fatty acids (containing 15-18 carbon atoms), e.g., stearic, oleic and palmitic acids.
- Sodium salts of fatty acids are known as hard soaps and potassium salts of any fatty acids are known as soft soaps.

<u>Preparation of Soap</u>

- Soaps containing sodium salts are formed by heating fat (i.e., glyceryl ester of fatty acid) with aqueous sodium hydroxide solution. This reaction is known as <u>saponification</u>.
- In saponification esters of fatty acids are hydrolysed and the soap is obtained remains in colloidal form.
- It is then precipitated from the solution by adding sodium chloride.
- The solution left after removing the soap contains glycerol, which can be recovered by fractional distillation.
- Only sodium and potassium soaps are soluble in water and are used for cleaning purposes.
- As compared to sodium, potassium soaps are soft to the skin. These can be prepared by using potassium hydroxide solution in place of sodium hydroxide.

Types of Soaps

- By using different types of raw materials different kinds of soaps are made.

1. Toilet Soaps:-
    1. They are prepared by using better grades of fats and oils and care is taken to remove excess alkali.
    2. Colour and perfumes are added to make these more attractive.
2. Floating Soaps:-
    1. Soaps that float in water are made by beating tiny air bubbles before their hardening.
3. Transparent Soaps:-
    1. They are prepared by dissolving the soap in ethanol and then evaporating the excess solvent.
4. Medicated Soaps:-
    1. In this type of soaps substances of medicinal value are added.
5. Shaving Soaps:-
    1. Shaving soaps contain glycerol to prevent rapid drying. A gum called, rosin is added while making them. It forms sodium rosinate which lathers well.
6. Laundry Soaps:-
    1. They contain fillers like sodium rosinate, sodium silicate, borax and sodium carbonate.
7. Soap Chips:-
    1. Soap chips are made by running a thin sheet of melted soap onto a cool cylinder and scraping off the soaps in small broken pieces.
8. Soap Granules:-
    1. They are dried miniature soap bubbles.
9. Soap powders and scouring:-
    1. Soaps contain some soap, a scouring agent (abrasive) such as powdered pumice or finely divided sand, and builders like sodium carbonate and trisodium phosphate.

Why Soaps don't work in hard water

- Hard water contains calcium and magnesium ions. These ions form insoluble calcium and magnesium soaps respectively when sodium or potassium soaps are dissolved in hard water.

$C_{17}H_{35}COONa + CaCl_2$ à $2NaCl + (C_{17}H_{35}COO)_2Ca$

Soap Insoluble calcium stearate (Soap)

- These insoluble soaps separate as scum in water and are useless as cleansing agent. In fact these are hindrance to good washing, because the precipitate adheres onto the fibre of the cloth as gummy mass.
- Soaps cannot be used in acidic solutions since acids precipitate the insoluble free fatty acids which stick to the fabrics and thus reduce the ability of the soaps to remove oil and grease from fabrics.

$RCOONa + H^+$ à $RCOOH + Na^+$

Soap Free fatty

acid precipitate out

- Hair washed with hard water looks dull because of this sticky precipitate. Dye does not absorb evenly on cloth washed with soap using hard water, because of this gummy mass.

Synthetic Detergents

- Synthetic detergents are cleansing agents which have all the properties of soaps, but which actually do not contain any soap.
- These can be used both in soft and hard water as they give foam even in hard water. Because calcium and magnesium salts are also detergents like their sodium salts are also soluble in water.
- Some of the detergents give foam even in ice cold water.
- Straight chain alkyl group contains detergents which are biodegradable whereas branched alkyl group containing detergents are non-biodegradable.
- Synthetic detergents are mainly classified into three categories:
- (i) Anionic detergents (ii) Cationic detergents and (iii) Non-ionic detergents

- Anionic detergents:-
    1. Anionic detergents are sodium salts of sulphonated long chain alcohols or hydrocarbons.
    2. Alkyl hydrogen sulphates formed by treating long chain alcohols with concentrated sulphuric acid are neutralised with alkali to form anionic detergents. Similarly alkyl benzene sulphonates are obtained by neutralising alkyl benzene sulphonic acids with alkali.
    3. In anionic detergents, the anionic part of the molecule is involved in the cleansing action.

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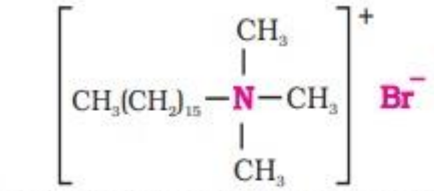
    1. Sodium salts of alkylbenzenesulphonates are an important class of anionic detergents.
    2.
        1. They are mostly used for household work. Anionic detergents are also used in toothpastes.
- Cationic Detergents:
    1. They are quaternary ammonium salts of amines with acetates, chlorides or bromides as anions.
    2. Cationic part possesses a long hydrocarbon chain and a positive charge on nitrogen atom.
    3. Hence, these are called cationic detergents. Cetyltrimethylammonium bromide is a popular cationic detergent and is used in hair conditioners.
    4. Cationic detergents have germicidal properties and are expensive, therefore, these are of limited use.

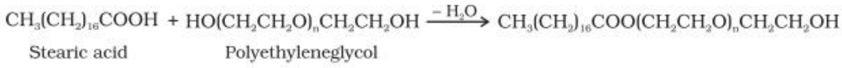


$$\left[CH_3(CH_2)_{15}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}}-CH_3\right]^{+} Br^{-}$$

Cetyltrimethyl ammonium bromide

- Non-ionic Detergents:
    1. They do not contain any ion in their constitution.
    2. One such detergent is formed when stearic acid reacts with polyethylene glycol.
    3. Liquid dishwashing detergents are non-ionic type. Mechanism of cleansing action of this type of detergents is the same as that of soaps.

4. These also remove grease and oil by micelle formation. Main problem that appears in the use of detergents is that if their hydrocarbon chain is highly branched, then bacteria cannot degrade this easily.

- 

  $$\underset{\text{Stearic acid}}{CH_3(CH_2)_{16}COOH} + \underset{\text{Polyethyleneglycol}}{HO(CH_2CH_2O)_nCH_2CH_2OH} \xrightarrow{-H_2O} CH_3(CH_2)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$$

1. These days the branching of the hydrocarbon chain is controlled and kept to the minimum. Unbranched chains can be biodegraded more easily and hence pollution is prevented.

Advantages of Synthetic detergents over Soaps

1. They can be used with hard water which soap cannot do.
2. They can be used in acidic medium unlike soaps.
3. They are more soluble in water so form better latter than soaps.
4. They have stronger cleaning action than soaps.