ENGINEERING CHEMISTRY

Life is Chemistry :
Dilute your Sorrow,
Evaporate your Worries,
Filter your Mistakes,
Boil your Ego.
You will get the crystal of Happiness.
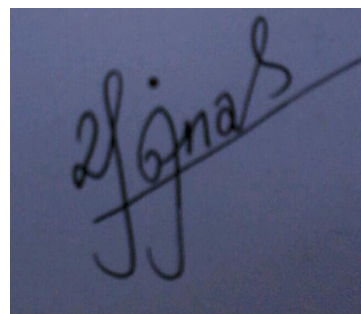
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Inorganic Chemistry

1)Difference between Electronegativity(EN),Ionization energy(IE) and Electron affinity(EA).

Ionization energy	Electronegativity	Electron affinity
IE is defined as the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to produce a cation. Eg: $M(g)+IE_1 \longrightarrow M^+(g)+e^-$ where,$M(g)$ and $M^+(g)$ represent gaseous atom and resultant gaseous cation respectively. **2nd ionization energy:** The energy required to remove a second electron from a singly charged gaseous cation. For Example: $M^+(g) +IE_2 \to M^{++}(g) + e^-$ It is minimum for the alkali metals which have a single electron outside a closed shell.It always requires an absorption of energy for an electron to be removed from the outer shell of an atom. So,IE are usually endothermic.	EN of an element is defined as the relative tendency of an atom in a molecule to attract a shared pair of electrons towards itself. Eg:Consider a bond between two atoms,A and B, $A \overset{\bullet}{\underset{\bullet}{\rule{2em}{0pt}}} B$. If the atoms are equally electro negative,both have the same tendency to attract the bonding pair of electrons, and so it will be found on average half way between the two atoms.To get a bond like this,A and B would usually have to be the same atom.If B is slightly more electronegative than A,B will attract the electron pair rather more than A does. $A \overset{\delta+}{\underset{\bullet}{\rule{2em}{0pt}}} \overset{\delta-}{B}$ The 'δ^+' and 'δ^-' symbols indicate partial positive and negative charges.The most commonly used scale of EN is that developed by Linus Pauling in which the value 4.0 is assigned to fluorine,the most EN element. **Mulliken Electronegativity :** $\chi = \dfrac{[EA+IE]}{2}$	EA of an element is defined as the energy released when an electron is added to an isolated gaseous atom to form anion or negative ion. Eg: $X(g)+e^- \longrightarrow X^-(g)+EA_1$ Where,$X(g)$ and $X^-(g)$ represent gaseous atom and resultant gaseous anion respectively.For example,the first electron affinity of chlorine is -349 $kJmol^{-1}$.By convention,the negative sign shows a release of energy. Second EA is positive because electron is being added to an already negatively charged ion.Thus,it requires more energy to overcome the repulsion. $X^-(g)+e^- \to X^{--}(g) +EA_2$ Groups VIA and VIIA in the periodic table have the largest electron affinities values.First EA is negative because energy is released during addition of electron.
An atom has absolute value of IE.	An atom has relative value of EN.	An atom has absolute value of EA.
It is measured in eV/atom or Kcal/atom or KJ/mole.	It is unit less as it a number.	It is measured in eV/atom or Kcal/atom or KJ/mole.
It is property of isolated atom.	It is property of bonded atom.	It is property of isolated atom.

2)Why IE of Nitrogen is greater than Oxygen?
=Nitrogen has exactly half filled p-subshell i.e $1s^2 2s^2 2p^3$ while oxygen has electronic configuration $1s^2 2s^2 2p^4$ which is neither half filled nor completely filled.Therefore,it is difficult to remove an electron from N than from O.Thus first ionization energy of N is greater than O although nuclear charge of Oxygen is greater than that of Nitrogen.

3)EA of Be and Mg are almost zero.Why?
=Be($1s^2 2s^2$) and Mg($1s^2 2s^2 2p^6 3s^2$) have completely filled s-orbital.They don't have tendency to accept an extra electron.So,EA of Be and Mg are almost zero.

4)Why EA of Fluorine is less than that of chlorine?
=As a result of small size of Fluorine,the inner electronic repulsion in the relatively compact 2p sub shell are comparatively large and repels the incoming electron thereby reducing the force of attraction of the nucleus towards the adding electron and hence decreasing the electron affinity.Consequently,the EA of F is less than that of chlorine.

5)Why inert gas shows highest IP ?
=Inert gases have completely filled orbitals.We know that more the stable electronic configuration greater will be the ionization energy.For eg:Neon($1s^2 2s^2 2p^6$),it has stable electronic configuration and as a result high ionization energy,

6)EA of halogens is high.Explain.
=Halogen have valence shell electronic configuration $ns^2 ns^5$.Due to this electronic configuration,these element have great tendency to accept an additional electron so they acquire noble gas($ns^2 np^6$)configuration.Hence their EA is high.

7)Why EN of Gallium is higher than Aluminium?
=Ga has a higher EN than Al due to the 10 extra electrons in the d orbitals, and protons in the nucleus.With a greater nuclear charge,the electrons are held more tightly to the nucleus and the size of Gallium decreases and EN increases.

8)What are the factors affecting Ionization energy?
a)**Atomic size:**
Ionization energy decreases with increase in atomic size.This is because larger the distance of the outer electron from the nucleus,the lesser will be the coulombic force of attraction between the nucleus and outer electron.In bigger atoms,outer electrons are held less firmly and it becomes easier to remove the electron.Thus ionization energy decrease with increase in atomic size.Therefore,IE is inversely proportional to atomic size.
i.e IE α $\dfrac{1}{\text{Atomic size}}$

b)**Nuclear charge:**
By increasing the nuclear charge,electrons feel more nuclear attraction.Hence more ionization energy is required.Therefore,ionization energy is directly proportional to Nuclear charge.
i.e IE α Nuclear charge

c)Penetration Power:

Tendency of becoming nearer to the nucleus is called penetration power.The order of penetration power of different sub-shells is s > p > d > f.Therefore,IE is directly proportional to penetration power.This is the reason that first ionization energy of B is less than Be.

d)Stability:

In stable configuration,more energy is required to release the electron as compared to non stable configuration.Therefore,Ionization energy is directly proportional to stability. Ionization energy is more of full-filled shell as compared to half-filled shell.

e)Screening & Shielding effect:

Presence of other orbits between nucleus and last orbit decreases the nuclear attraction. This effect is called screening effect but electron-electron repulsion is called shielding effect which also decreases the nuclear attraction.Due to presence of these effects ionization energy decreases.

Downwards in a group ionization energy decreases due to increase in size of atoms while in a period from left to right ionization energy increases due to increase in nuclear charge.

9)What are the factors affecting Electron affinity?

a)**Nuclear charge**:

Effective nuclear charge is a measure of the attraction between a nucleus and its outer shell electrons.Clearly,it depends on the number of protons in the nucleus(i.e actual nuclear charge),but it also depends on the number of inner shells which screen the outer shell from the effect of the nucleus.Greater the nuclear charge,greater will be the attraction for the incoming electron and as a result larger will be the value of electron affinity.i.e EA α Nuclear charge.

b)Atomic size:

Larger the size of an atom,larger will be the distance between the nucleus and the incoming electron.Thus,smaller will be force of attraction felt by incoming electron and hence smaller will be the value of Electron affinity.In common,electron affinity reduces in going down the group and raise in going from left to right across the period.On moving down the group atomic size rises and on going from left to right in a period atomic size reduces. i.e EA α $\dfrac{1}{\text{Atomic size}}$

c)Electronic configuration:

Stable the configuration of an atom,lesser will be its tendency to accept an electron and hence lower the value of its electron affinity.Electron affinity of magnesium,beryllium, and calcium is practically zero.This is accredited due to extra stability of the fully completed s-orbitals in them.Therefore, if an atom has completely filled or half filled orbitals,its electron affinity will be less.

Variation of electron affinity:

Across the rows of the periodic table:
On moving from left to right in the periodic table,the electron affinity of the elements increases.The atomic size gets smaller as we move across the rows of the periodic table from left to right,and the nuclear charge/atomic number also increases simultaneously. This causes the electron affinity of atoms to be increased tremendously.Thus,we find that, on moving from left to right in the periodic table,the elements become more non metallic.

Down the groups of the periodic table:
The atomic size and nuclear charge of elements increases down the groups of the periodic table as the atomic number increases.But the effect of the increase in atomic size compensates the increase in nuclear charge.Thus,the attractive force of the nucleus on the outermost orbit electrons decreases and hence the electron affinity of the elements decreases.

10)What are the factor affecting the electronegativity?
A)Atomic size:
The electronegativity increases with a decrease in size of the atom.The smaller the size of an atom,greater is the tendency to attack the share paired of electron towards itself. Therefore,smaller atom have higher electronegativity values then larger atom.

B)Number of inner shell:
The atom having large number of inner shell has lower value of electronegativity.This is because the atom with more shell are bigger than the atom having less number of inner shells.

C)Types of hybridization:
The electronegativity increases as the s-character in hybrid orbitals increases.For e.g:the electronegativity in methane,ethene & ethyne is the increasing order as:

Methane	Ethene	Ethyne	
sp^3	sp^2	sp^1	hybridization
25 %	33 %	50 %	s-character

The highest value of electronegativity of carbon atom in ethtyne account for its highly acidic hydrogen atom.Hence,carbon of ethyne has more electronegativity value than carbon of methane and ethene.

D)Ionization energy and electron affinity:
Higher Ionization energy and higher electron affinity lead to higher electronegativity. Higher value of ionization means large capacity of energy is required to remove the valence electron.This shows that the tendency of an atom to hold the shared pair of electron towards itself is high.It is due to this reason that element of group VIIA have highest electronegativity.

E)Charge on the ion:
A cation is the smaller in size of corresponding atom.As a result,a cation attract electron

more readily than its parents atom.Thus,a cation has higher electronegativity than its parents atom.Since,the electron accepting tendency increases with an increasing in the charge on the cation,hence the cation having higher positive charge is more electronegative.Size of anion is larger as compared to that atom is less than that of its parents atom.So electron attracting tendency of an anion is less than that of its parent atom.The electronegativity of F(EN=0.8) is less than that of F atom (EN = 4).

F)Number and nature of atoms bonded to it:
The electronegativity of an atom depends upon the number and nature of the atom bonded to it.For e.g.the electronegative of phosphorous atom in PCl_3 is higher than in PF_5.Since F is more electronegative than Cl.Also, In PCl_3 and PCl_5,p of PCl_5 has electronegativity value more as oxidation state of P is higher than P of PCl_5.

Note:
A) Effective nuclear charge increases across each period.
B) IE,EA,EN generally increase across the periods.
C) IE,EA,EN generally decrease across the periods.
D) Removal of electrons from half filled and full filled shells requires higher energy.
E) Metals have low IE and non metals have high IE.
F) The elements with a higher IE have higher EA also.
G) Metals have low EN whereas and nonmetals have high EN.
H) Fluorine is most electronegative element.
I) First EA is exoergic while second and subsequent EA are endoergic in nature.

11)S block element:
In the s-block elements the last electron enters the outermost s-orbital and as the s-orbital can accommodate only two electrons,that is why only two groups i.e group 1 & 2 belong to the s-block of the periodic table.Thus the outermost orbital of s block elements consists of one or two electrons and the orbital next to the outermost shell i.e the penultimate shell has either 2 or 8 electrons.This is the reason why the s-block elements show a fixed valency which depends on the number of electrons present in the outermost shell.

a)Electronic Configuration:
The general electronic configuration of s-block elements is ns^1 for Alkali metals and ns^2 for alkaline earth metals where n = 2 to 7.All the alkali metals have one valence electron and these loosely held s-electron in the outermost valence shell of these elements makes them the most electropositive metals.The alkaline earth metals have two electrons in the s-orbital of the valence shell.Like alkali metals,these elements are also very electropositive.

b) **Metallic character**:
All the Alkali metals are silvery white, soft and light metals.The Alkaline Earth metals,in general are silvery white,lustrous and relatively soft but harder than the Alkali metals. Beryllium and magnesium appear to be somewhat greyish.The Metallic character increases as we go down both groups.Both the alkali metals and the alkaline earth metals

are highly malleable and ductile and have a very high tendency to lose electrons to form positive ions and hence they are highly electropositive.

c)**Atomic Density:**
The Alkali metals and the Alkaline Earth metals both have low density.This is because they have large ionic size due to which their atomic nuclei are widely separated in their crystal lattices.The density increases down both the groups and periods.

d)**Melting and Boiling Points**:
The melting and boiling points of the alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them.The melting and boiling points of alkaline Earth metals are higher than the corresponding alkali metals due to their smaller sizes.The trend is however not systematic but it slightly decreases down the group.

e)**Oxidation state**:
The Alkali metals show only +1 oxidation state,while alkaline Earth metals show +2 oxidation state only.Because of their low ionization energies, they easily lose the outermost s electron to form the uni positive ions.Once they lose the first electron,in case of alkali metals,they achieve the noble gas configuration.The same is true with respect to alkaline earth metals,when they lose the 2 electrons present in the valence shell.

f)**Atomic and Ionic radii**:
Both the Alkali metals and the alkaline earth metals have large atomic and ionic radii. The Atomic and the Ionic radii increases as we move down both groups.But as we go from group I to group II in the same period the atomic and the ionic radii decreases.

g)**Electrode potential:**
The alkali metals are strong reducing agents.The standard electrode potentials of all alkali metals lie between -2.7V and -3.0V,indicating a strong tendency to form cations in solution.The alkaline earth metals also have negative values of their standard electrode potentials.

h)**Ionization Energies**:
The ionization energies of the alkali metals are considerably low and decreases down the group from Lithium (Li) to Cesium(Cs).This is due to the increasing size,increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge. The alkaline earth metals have low ionization energies due to their large size of the atoms.Since the atomic size increases down the group,their ionization energies decreases down the group.But as we go from group I to group II in the same period ionization energies increases.The first ionization energies of the alkaline earth metals are higher than those of the corresponding Group I metals.This is due to their small size as compared to the corresponding alkali metals.But the second ionization energies of the alkaline earth metals are smaller than those of the corresponding alkali metals.
$Na \rightarrow Na^+ + e^-$
$Ca \rightarrow Ca^{++} + 2e^-$

i)**Magnetic Properties:**
Alkali metals are attracted by the applied magnetic field and hence are paramagnetic in nature whereas the alkaline earth metals are repelled by the magnetic field and hence are diamagnetic in nature.

J)**Complex Formation**:
 Both the alkali metals and the alkaline earth metals show weak tendency to form complexes because they have no low energy vacant orbital available for bonding with lone pair of ligands.This is due to large size,low nuclear charge and poor ability to attract electrons.

K)**Flame colouration:**
The alkali metals and their salts,when introduced into the flame,give characteristic color to the flame.

Li	Na	K	Rb	Cs
Crimson red	Golden yellow	Pale violet(Lilac)	Red-Violet	Blue

This property of the alkali metals offers a very sensitive and reliable test for alkali metals. This property is due to the ease of excitation of the valence electrons.When elements or their compounds are introduced to flame,the electrons absorbs energy from the flame and gets excited to higher energy levels.When these electrons return to their ground state,they emit absorbed energy in form of visible light having characteristic wavelengths. Depending upon the wavelength of light emitted, different colors are imparted to the flame.Salts (generally chlorides)impart characteristic colors to the Bunsen flame.Be and Mg does not impart characteristic color to the flame.

12)P block element:
Elements belonging to the group 13 (i.e group IIIA) to group 17 (i.e group VIIA) of the periodic table along with the group 18 i.e the zero group elements together form the p-block of the periodic table. https://www.blogger.com/blogger.g?blogID=8132942763032855786In the p-block elements the last electron enters the outermost p orbital.They have 3 to 8 electrons in the outermost shell.As we know that the number of p orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of p orbitals is six.Hence there are six groups of p-block elements in the periodic table numbering from 13 to 18.The First group of the p-block i.e the group IIIA is commonly called as Boron group,the second group i.e the group IVA is called Carbon group,the third group i.e the group VA is called Nitrogen group,the fourth group i.e the group VIA is called Chalcogens,the fifth group i.e the group VIIA is called Halogens and the sixth group i.e the zero group or group 18 is called Inert or Noble gases group.In the p-block all the three types of elements are present i.e.The metals,nonmetals and metalloids .

Characteristic Properties of elements in p-block of Modern Periodic Table :
a)Electronic Configuration:
The general valence shell electronic configuration of p-block elements is $ns^2\ np^{1-6}$ (except for He).The inner core of the electronic configuration may,however,differ.The General electronic configuration shown by elements from group13 to 18 of p-block is as given

below :
Group 13 (Boron family)   - $ns^2 np^1$
Group 14 (Carbon family)   -$ns^2 np^2$
Group 15 (Nitrogen family) - $ns^2 np^3$
Group 16 (Oxygen family) -$ns^2 np^4$
Group 17 (Halogen family)   -$ns^2 np^5$
Group 18 (Noble gases)   -$ns^2 np^6$ (except Helium)
The general electronic configuration of Helium is $1s^2$.Due to their distinct electronic configuration p-block elements show a lot of variation in properties.

b)Metallic Character:
As stated earlier p-block contains all types of elements i.e metals,non-metals and metalloids.The p-block is the only region of the periodic table to contain metalloids.The non metallic character decreases down the group whereas there is a gradual increase in non-metallic character from left to right in the p-block.The metallic character tends to increase down each group whereas it decreases as we go from left to right across a period. In fact,the heaviest element in each p-block group is the most metallic in nature.Metallic character increases as we move down the group,from B to Tl.Boron is a non metal,while all the others are metallic and good conductors of electricity.

c)Atomic Density:
The Atomic Density of elements in p-block increases down the group,this is due to increase in the size of the atom down the group.Whereas it decreases as we move from left to right across the period,this is due to the decrease in atomic size of all elements in the p- block across the period.Of all the elements,aluminium is of very low density and is widely used as a structural material.

d)Melting and Boiling points:
Melting points decreases from Barium to gallium and then increases up to Tl.The low melting point of Ga is explained on the basis that Ga is diatomic in nature.Heat of sublimation and boiling points show a steady decrease.The melting and boiling points gradually increases down the group because the molecular mass increases down the group and hence the intermolecular forces increases.

e)Oxidation state:
The p-block elements show a variable oxidation state.The oxidation states increases as we move from left to right in the periodic table.The maximum oxidation state shown by a p-block element is equal to the total number of valence electrons.According to this,the oxidation states shown by different groups is as follows :
Boron family (Group 13)   : +3 , Carbon family (Group 14)   :+4
Nitrogen family (Group 15) :+5 , Oxygen family (Group 16) : +6
Halogen family (Group 17) :+7 , Noble gases (Group 18)   : +8
Since Boron is very small, it has high ionization energy and does not lose all three valence shell electrons.So, it cannot form B^{3+} ion.Aluminium forms +3 ion,while Ga,In and Tl show +1 and +3 oxidation states.

f)Atomic and Ionic radii:
As we move down the group in the p-block one extra shell than the preceding element gets added into the next element.This ultimately increases the atomic and the ionic radius of every next element down the group ,which finally shows that the atomic and the ionic radii increases down the group.The trend is not same across the period.As we move from left to right in a period the atomic radii and the Ionic radii of p-block elements decreases . The atomic radius increases greatly from Boron to Aluminium.This increase is due to greater screening effect caused by the eight electrons present in the penultimate shell.

g)Electrode Potential:
The p-block elements generally have a positive electrode potential.It generally decreases down the groups.

h)Ionization Energies:
The p-block elements have high ionization potentials.The ionization energies of p-block elements increases from left to right in a period due to increasing effective nuclear charge.According to the general trends the ionization energy values decreases down the group but do not decrease smoothly as expected.Non-metals have high ionization energies than metals.It is maximum for a noble gas because noble gases have completely filled configuration.Some elements at the bottom of a group like Lead,Tin,Thallium, Bismuth etc behaves almost as a metal with very low ionization energies.

i) Magnetic Properties:
The elements Radon,Astatine,Iodine and Polonium of the p-block are non-magnetic in nature.The element Tin is paramagnetic and the rest all elements of the p-block are diamagnetic in nature.

j) Complex Formation:
The smaller size and the greater charge of the elements of different groups of p-block enable them to have a greater tendency to form complexes than the s-block elements.The complex formation tendency decreases down the group as the size of the atoms increases down the group.

k)Chemical Reactivity:
The chemical reactivity of elements in the p-block increases as we move from left to right in a period. But as we move down in a group the chemical reactivity of elements decreases down the group.

l)Reactivity of Noble gases:
All the orbitals of the noble gases are completely filled by electrons and it is very difficult to break their stability by the addition or removal of electrons.Thus the noble gases exhibit very low chemical reactivity.Because of their low reactivity noble gases,are often used when an nonreactive atmosphere is needed,such as in welding.

m)Conductivity:

The conductivity of elements in p-block increases down the group.Generally the metals in the p-block are good conductors of heat and electricity whereas the non-metals are poor conductors of heat and electricity.The conductivity of metalloids lies in between the metals and non-metals.

n)Electron Negativity:
EN increases from left to right in a period and decreases down the group.On account of high values of EN,they usually form covalent compounds.

13)General Characteristics of Transition Elements:
The elements that lie in between S-block and P-block are the d-block elements.These elements are called transition elements as they show transitional properties between 's' and p-block elements.These elements contain partially filled d-orbitals and hence they are called as d-block elements.The general electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{1-2}$.

A)Electronic Configuration:
The general electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{1-2}$.All the d-block elements except zinc,cadmium and mercury have partially filled d-orbitals.But,zinc, cadmium and mercury have completely filled d-orbitals and they exhibit common oxidation state.So,they do not come under transition elements but are studied along with d-block elements.In all the other transition elements the last electron enters the (n-1)d orbital which is called the penultimate shell.

B)Variable oxidation states:
By the study of electronic configuration of transition metals it is understood that variable oxidation state can be formed as there are both ns and (n-1)d electrons in bonding.The participation of ns electrons in bonding leads to +2 oxidation state which is a lower oxidation state.The participation of (n-1)d electrons in bonding leads to higher oxidation states like +3,+4,+5,+6 etc.These oxidation states depend upon the nature of combination of transition metals with other elements.The oxidation state increases with atomic number.This increase is related to groups.The most common oxidation state of the elements of first transition series is +2.Ionic bonds are formed in lower oxidation state transition elements whereas covalent bonds are formed in higher oxidation states.

C)Magnetic properties:
By the study if electronic configuration of transition metals it is understood that they generally contain one or more unpaired electrons in the (n-1)d orbital.Due to these unpaired electrons they behave as paramagnetic substances.These substances are attracted by the magnetic field.The transition elements that contain paired electrons behave as diamagnetic substances.These substances are repelled by the magnetic field.The para-magnetic character increases as the number of unpaired electrons increases.Formation of colored compounds.Most of the transition elements form colored compounds both in solid state as well as in aqueous solution.It is already studied that the transition metals have incomplete d-orbital.The electrons are to be promoted from a lower energy level to a higher energy level.Some amount of energy is required for this process and the radiations

of light are observed in the visible region.The compounds absorb a particular color from the radiation and the remaining ones are emitted.

For e.g.Cu^{++} are bluish green in color due to absorption of red light wavelength.As Zn has completely filled d-orbitals it cannot absorb radiation and hence Zn^{++} salts are white.

D)Formation of complexes:

Transition metals form many complex ions.They are the electrically charged complexes with a metal ion in the centre which is surrounded and linked by a number of neutral molecules or negative ions.These neutral molecules or negative ions are called as **ligands.** As the transitions metals are small in size they form large number of complexes. For Eg: $Fe(CN)6]^{4-}$, $[Cu(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{--}$.

General trends in the chemistry of first row transition series:
A)Metallic character:

Most of the transition elements of the first row form metallic bonds due to the presence of incomplete outermost energy level.So,all the transition elements exhibit metallic characters.The strength of the metallic bond depends upon the number of unpaired d-electrons.As the number increases the strength also increases.Due to the absence of unpaired electrons 'Zn' is not a hard metal.

B)Ionization energy:

The ionization energies of first row elements gradually increases with increase in atomic number.The ionization energy of Zn is very high than all the other metals which is due to its fully filled d-orbital.The third ionization energy of Mn is very high than the others.

C)Oxidation State:

The first row transition elements show variable oxidation states.Zn is an exception among them.As it has fully filled d-orbital,it exhibits only +2 oxidation state.

D)Ionic radii:

In the first row transition elements the ionic radii decreases with increase in atomic number.The value of ionic radii also depends on the oxidation state of metals.As the oxidation state increases the ionic radii decreases and as the oxidation state decreases the ionic radii increases.

E)Catalytic property:

The first row transition elements exhibit catalytic properties due to the presence of unpaired electrons which can form complexes.Iron and vanadium are the most important catalysts.Iron is used as catalyst in the manufacture of ammonia.Vanadium is used in the form of vanadium pentoxide in the manufacture of sulphuric acid.

F)Coloured ions:

In the first row transition elements all the elements except Zn form colored ions.As these elements have incomplete d-orbital,some amount of energy is required to promote the electrons from lower energy level to higher energy level.This process exhibits radiations

from which the compounds absorb a particular color.But some elements other than Zn also appear colorless depending on their oxidation state.

G)Alloy formation:
When one metal mixes up with another metal alloys are formed.As the d-block elements have same atomic sizes they can easily take up positions of one another.This causes alloy formation.For example:Cr,V, Mn are used in formation of alloy steels.

14)Why Cu, Zn, Hg are not considered as transition metal?
   Cu=atomic number =29=$3d^{10}\ 4s^1$
   Zn=atomic number =30=$3d^{10}4s^2$
   Hg=atomic number =80=$5d^{10}\ 6s^2$
As to be a transitional element,atom should have incomplete d-orbitals,these three elements have completely filled d-orbitals i.e having $(n-1)d^{10}\ ns^2$ configuration.so they cannot be regarded as true transition element.

15)Transitional element exhibit variable oxidation states.Explain.
=The variable oxidation state of transitional element is due to availability of both (n-1)d and ns electron for bond formation,as the energies of d-orbital and s orbital are nearly equal.Most of the transitional element has two ns electron,so generally exhibit +2 oxidation state.In addition,they may also utilize one more (n-1)d electron for bond formation.So oxidation state of +3 and higher will be occur.The sum of ns and unpaired (n-1)d electron determines the highest oxidation state shown by Transitional element.

16)Why Zn^{++} salts are colourless?
=The colour of transition metal ions is associated with incompletely filled (n-1)d orbitals. The transitional metals ions containing unpaired d-electron undergo electronic transitions from one d orbital to another d-orbital.During d-d transition process,they absorb certain radiation from visible light and emit the remainder as coloured light.But,in Zn^{++} ($3d^{10}\ 4s^0$) has no unpaired d electron,so it's salts are white.

17)Why transitional element form significant number of complexes?
=Transitional element forms significant number of complexes because transitional metals yields small,highly charged ions,which have vacant (n-1)d orbitals of approximately the appropriate energy to accept the pairs of electrons donated by other group or molecules. The molecules or ions which add themselves to the cation of transitional metals are called ligands. For eg:$[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$

18)Why Transitional elements are mostly para magnetic?
=Transitional elements are mostly paramagnetic because there is presence of unpaired electron in the (n-1)d orbital or (n-2)f orbital.Thus only those atoms or ions having unpaired electron shows para magnetism.The greater the number of unpaired electron in a atom or ions,the more strongly paramagnetic it is.

For Eg:Fe^{+++} is more strongly paramagnetic than Fe^{++} because Fe^{+++} possesses greater number of unpaired electrons.

19)Why is Cu(I) dimagnetic while Cu(II) is paramagnetic?
=$Cu^+(3d^{10})$is dimagnetic due to absence of unpaired d-electron whereas $Cu^{++}(3d^9)$ is paramagnetic due to presence of one unpaired d-electron.

20)Why are transitional elements metals?
=Transitional elements are called metals because they have low IE,they lose electrons to form cations and exhibit metallic character.

21)Define Transitional element.
=Transitional elements are those elements whose atom or atleast one of its ions has incompletely filled d or f orbitals. Eg:Sc,Fe,Cr,Pd.

22)Define and explain inert pair effect.Clarify the reason of inert pair effect with suitable examples.
=The inert pair effect is the tendency of the electrons in the outermost atomic s orbital to remain unionized or unshared in compounds of post-transition metals.The term inert pair effect is often used in relation to the increasing stability of oxidation states that are 2 less than the group valency for the heavier elements of groups 13,14,15 and 16.

In the elements of 4th,5th and 6th period of p-block elements which come after d-block elements the electrons present in intervening d and f-orbitals do not shield the s-electrons of the valence shell effectively as a result ns^2 electrons remain more tightly held by nucleus and hence do not participate in bonding.This is called inert pair effect.
In other words tendency of s-electrons of valence shell to participate in bond-formation decreases.Another reason for inert pair effect is that as the size of atoms increases down the group in p-block elements the energy required to unpair the ns^2 electrons is not compensated by the energy released in forming two additional bonds.So the bond formation by valence 's' electrons is not energetically favorable.The inert pair effect becomes more predominant down the group in p-block elements because of increased nuclear charge which outweighs the effect of corresponding increase in atomic size.The s-electrons thus become more tightly held and therefore become more reluctant to participate in bond formation.

For example:
1)In 3rd A group,thallium($1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^2\,5p^6\,4f^{14}\,5d^{10}\,6s^2\,6p^1$)can exhibit +1 and+3 oxidation states but it is stable in +1 oxidation state only due to inert pair effect.

2) In 4th A group,lead([Xe] $4f^{14}\,5d^{10}\,6s^2\,6p^2$)shows both +2 and +4 oxidation states but it is stable in +2 oxidation state due to inert pair effect.

Questions for Practice :
A)The IE of Na^+ is more than that of Ne although both have same electronic configuration.Explain.
B)Why 1st IE of Li is less than Be?

C)Why IE value of an ion increases as number of positive charge increases?

D)Why zinc sulphate salt is colorless whereas copper sulphate salt is colorful in nature?

E)Why Mn can form complex but not Mg?

F)Why ionic radii of Fe^{+++} ion is greater than Fe^{++}?

G)Why 2nd ionization energy of chromium and copper are exceptionally high?

H)Explain why Ti^{3+} compounds are colored but those of Ti^{4+} are colorless?

I)Why Transitional element show variable valency?

J)Why Cu^+ and Ag^+ are colorless?

K)In PCl_3 & PCl_5, P of which compound has more EN?Why?

L)In PCl_3 & PF_5, P of which compound has more EN?Why?

M)Which would have higher second ionization energy, Na or Mg?

N) Explain why ionization potential increases across a period.

O)Why electronegativity increase with increase in oxidation state ?

P)Why is that first IE of of transitional elements reasonably constant?

Q)Which of the following element has highest EN and Why ?
1)Cl, Br, I, F   2)N,O,F

R)Which of the following element has highest EA and why?
1)N,P,As   2)B,C,N   3)N,Cl,Si

S)Suggest the reason for the decrease in 1st IE from Be to B and Mg and Al.

U)Explain why 1st IE of Na is smaller than that of Mg but 2nd IE of Mg is smaller than that of Na.

T)Why do transition metals element make colored compound both in solid form and in solution? Is it related with their electrons or something else?

U)Why do the transition metals Cu and Cr donot follow the usual electronic structure pattern?

V)What is a transitional metal?

W)The incorrect statement among the following is:
1)The first ionization potential of Al is less than the first ionization potential of Mg.
2)The second ionization potential of Mg is greater than the second ionization potential Na.
3)The first ionization potential of Na is less than the first ionization potential of Mg.
4)The third ionization potential of Mg is greater than that of Al.

X)Why $IE_3 > IE_2 > IE_1$?

Y)Which of the following has highest IE and why?
A)Na^+ ,Mg^{++} ,F^- B)I, I^+ ,I^-

Z)Describe EN concept of Pauling.

Ionic equilibrium

1)Define buffer solution with example.Calculate pH of solution formed by mixing 500ml of 0.2M acetic acid and 400 ml of 0.4 sodium acetate if $K_a=1.8*10^{-5}$.

=A buffer solution is that which resist change in pH even on addition of small amount of acid or base or on dilution.There are two types of buffer solution.

For example: i) $CH_3COOH + CH_3COONa$ (Acid buffer solution)

ii)$NH_4Cl + NH_4OH$ (Basic buffer solution)

Solution:

pH=?

Volume of acetic acid(V_1)=500ml

Volume of sodium acetate(V_2)=400 ml

Strength of acetic acid (C_1)=0.2M

Strength of sodium acetate(C_2)=0.4M

K_a=1.8*10^{-5}

We know that,

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

or,pH=-log(K_a)+log$\dfrac{[salt]}{[acid]}$

or,pH=-log(1.8*10^{-5})+log$\dfrac{[C_2*V_2]}{[C_1*V_1]}$

pH=-log(1.8*10^{-5})+log$\dfrac{[0.4*400]}{[0.2*500]}$

or,pH= 4.744+0.204

Hence,pH=4.948

2)Define acid buffer solution and basic buffer solution.A buffer solution contains 0.2mole of acetic acid and 0.25 mole of potassium acetate.pH value of solution is found to be 4.8416 at 25°C.Calculate dissociation constant of acetic acid.

=A buffer solution prepared by mixing weak acid and its salt with strong base is termed as acidic buffer solution.

For Eg: $C_6H_5COOH+C_6H_5COONa$

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

A buffer solution prepared by mixing weak base and its salt with strong acid is called basic buffer.

pOH=pK_b+log$\dfrac{[salt]}{[base]}$

pH=14-[pK_b+log$\dfrac{[salt]}{[base]}$]

For eg: $H_2CO_3+NaHCO_3$,

Solution:

No of moles of acetic acid(n_1)=0.2

No of moles of potassium acetate(n_2)=0.25

Concentration of acetic acid(M_1)=?

Concentration of potassium acetate(M_2)=?

pH of solution: 4.8416

Dissociation constant of acid(K_a)=?

We know that ,

$M_1 = \dfrac{n_1}{V}$,

$M_2 = \dfrac{n_2}{V}$

Now,

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

or, $pH = -\log(K_a) + \log\dfrac{[M_2]}{[M_1]}$

or, $pH = -\log(K_a) + \log\dfrac{[n_1]}{[n_2]}$

or, $4.8416 = -\log(K_a) + \log\dfrac{[0.25]}{[0.2]}$

or, $4.8416 = -\log(K_a) + 0.09691$

or, $-4.74469 = \log(K_a)$

or, $K_a = 10^{(-4.74469)}$

Hence, $K_a = 1.80 * 10^{-5}$.

Dissociation constant of acetic acid is $1.80 * 10^{-5}$.

3)Write the buffer mechanism of acidic buffer solution.

=A buffer solution prepared by mixing weak acid and its salt with strong base is termed as acidic buffer solution.

For Eg:$C_6H_5COOH + C_6H_5COONa$

We'll take a mixture of ethanoic acid and sodium ethanoate.Ethanoic acid is a weak acid, and the position of this equilibrium will shift to the left:

$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$ (feebly ionized)

$CH_3COONa \rightarrow CH_3COO^- + Na^+$ (highly ionized)
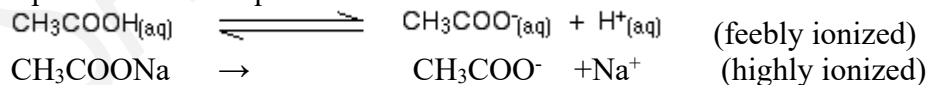
Ionization of CH_3COOH is suppressed due to high concentration of CH_3COO^- ions.

Adding an acid to this buffer solution:

The buffer solution must remove most of the new hydrogen ions otherwise the pH would drop markedly.Hydrogen ions combine with the ethanoate ions to make ethanoic acid. Although the reaction is reversible,since the ethanoic acid is a weak acid,most of the new hydrogen ions are removed in this way.

$CH_3COO^-_{(aq)} + H^+_{(aq)} \longrightarrow CH_3COOH_{(aq)}$
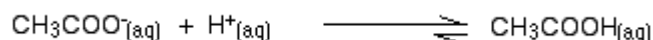
Since most of the new hydrogen ions are removed,the pH won't change very much but because of the equilibria involved,it will fall a little bit.

Adding an alkali to this buffer solution:
Alkaline solutions contain hydroxide ions and the buffer solution removes most of these. This time the situation is a bit more complicated because there are two processes which can remove hydroxide ions.

Removal by reacting with ethanoic acid:
The most likely acidic substance which a hydroxide ion is going to collide with is an ethanoic acid molecule.They will react to form ethanoate ions and water.

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H_2O_{(l)}$$
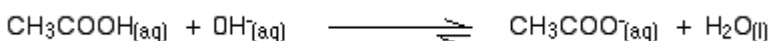
Because most of the new hydroxide ions are removed,the pH doesn't increase very much.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$
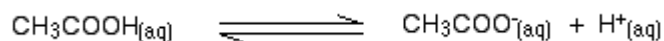
Hydroxide ions can combine with these to make water. As soon as this happens,the equilibrium tips to replace them.This keeps on happening until most of the hydroxide ions are removed.

Equilibrium moves to replace the removed hydrogen ions.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

Hydroxide ions combine with these to make water.
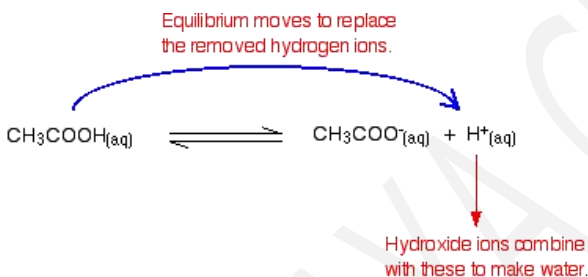
Again,because equilibria involved,not all of the hydroxide ions are removed just most of them.The water formed re-ionizes to a very small extent to give a few hydrogen ions and hydroxide ions.

4)Write the mechanism of basic buffer solution.
Consider a basic buffer solution containing mixture of weak base (NH$_4$OH)and its salt(NH$_4$Cl).They ionizes as,

NH$_4$OH $\leftrightarrow$ NH$_4^+$ + OH$^-$ (Feebly ionized)
(Weak base)

NH$_4$Cl $\rightarrow$ NH$_4^+$ + Cl$^-$ (highly ionized)
(Strong electrolyte)
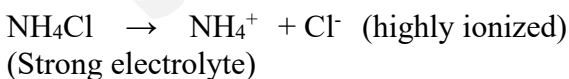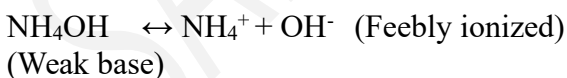
Effect of addition of acid:
When small amount of acid like HCl is added to this buffer solution,the H$^+$ ion coming from added acid undergo combination with OH$^-$ ion in buffer solution to give H$_2$0.
    H$^+$ +   OH$^-$ $\rightarrow$ H$_2$0
(From acid) (Buffer)
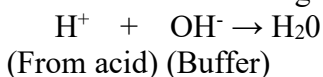
Addition of acid decreases the number of OH^- ion.Due to decrease in concentration of OH^- ions,more number of unionised ammonium hydroxide will ionize to give the same amount of OH^- ions as were present before addition of acid.Hence pH will remain constant.
$$NH_4OH \rightarrow NH_4^+ + OH^-$$
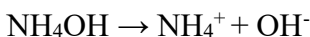
Effect of addition of base:
When few drops of NaOH is added to it,excess of OH^- ions combine with NH_4^+ ions of buffer solution to form feebly ionized NH_4OH.The additional OH^- are consumed by NH_4^+ ions in the solution and there will be no change in pH value.Due to increase in concentration of unionized NH_4OH,there is negligible change in pH.i.e remains constant.
$$NH_4^+ + OH^- \rightarrow NH_4OH$$
(Buffer) (added base)
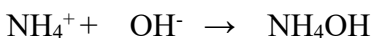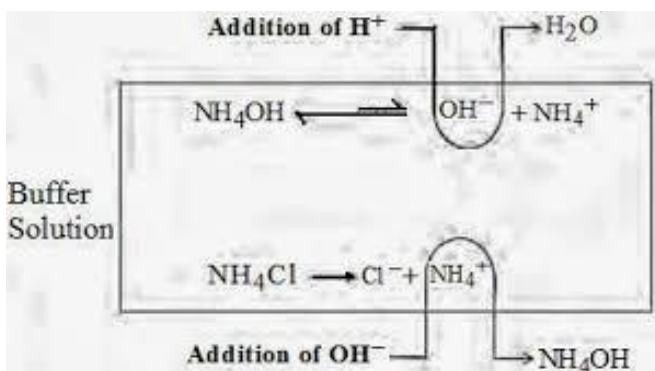
Henderson equation
$$pH = pK_a + \log\frac{[salt]}{[acid]}$$
$$pOH = 14 - pH$$
$$pOH = pK_b + \log\frac{[salt]}{[Base]}$$

5)Calculate pOH of 0.02M benzoic acid if degree of ionization is 1.4 %.
Soln,
$$C_6H_5COOH \leftrightarrow C_6H_5COO^- + H^+$$
$\quad$ C $\qquad\qquad$ 0 $\qquad\qquad$ 0 $\qquad$ (Initially)
$(1-\alpha)C \qquad C\alpha \qquad\qquad C\alpha$
Here,
$\alpha = 1.4\% = \dfrac{1.4}{100} = 0.014$
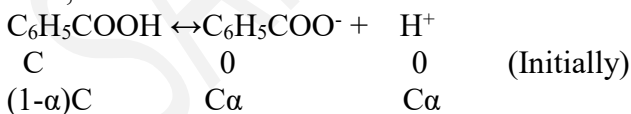
Concentration(C)=0.02M
$pH = -\log[H^+]$
$pH = -\log[C\alpha]$
$\quad = -\log(0.02*0.014)$
$pH = 3.55$
$pOH = 14 - pH$

pOH=14-3.55
So,pOH=10.45

6)Calculate pOH of 10^{-9} M NaOH.
Soln,

pOH= -log[OH$^-$]
   = -log[10^{-9}]
   =9
   =Wrong

Correct Method:
When the amount of acid or base present in aqueous solution is extremely small,the concentration of OH$^-$ ions of water in case of base and H$^+$ ions of water in case of acid also becomes significant.

[OH$^-$]$_{water}$ =10^{-7}
[OH$^-$]$_{NaOH}$ =10^{-9}
[OH$^-$]$_{total}$ =10^{-7} + 10^{-9}
       =$1.01*10^{-7}$
So,pOH=-log($1.01*10^{-7}$)
       =6.995
And,pH=7.00432

Note:
A)For weak acid and weak base:
pH   = -log[H$^+$] = -logCα
pOH =-log[OH-]= -logCα
C= concentration
α=degree of ionization

B)For Strong acid and base:
I)For monobasic acid (Like HCL,HCN) and monoacidic base(Like NaOH):
 pH = -log[H$^+$] = -log[M] = -log[N]
pOH=-log[OH$^-$] =-log[M] = -log[N]

II)For polybasic acid(like H$_2$SO$_4$,H$_3$PO$_4$) or polyacidic base(Like Ca(OH)$_2$):
 pH = -log[N] = -log[H$^+$]   = -log[M * basicity of acid]
pOH= -log[N] = -log[OH$^-$] = -log[M * acidity of base]

M= Molarity
N=Normality

7)Find pH of 0.03N sulphuric acid.
solution,
Normality(N)=0.03N
pH =-log(H$^+$)
   =-log[M * basicity of acid]   {M=<u>N</u> ,Basicity=2(H$_2$SO$_4$)}
   =-log[0.015*2]   2

pH = 1.522

8)Calculate pH and pOH of a buffer solution prepared by mixing 450 ml of 0.4M sodium acetate and 600 ml of 0.2 M acetic acid which is 1.5% ionized in dilute solution.

Solution,

pH=?

Volume of sodium acetate(V_1)=450ml

Volume of acetate acid   (V_2)=600ml

Strength of sodium acetate(C_1)=0.4M

Strength of acetate acid   (C_2)=0.2M =C

Degree of ionization of acid(α)=1.5%=0.015

We know that,

$CH_3COOH \leftrightarrow CH_3COO^- + H^+$
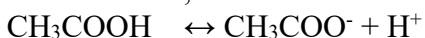
C   0   0

$(1-\alpha)C$ $C\alpha$ $C\alpha$

$K_a = \dfrac{C\alpha * C\alpha}{C-C\alpha}$

$= \dfrac{C\alpha^2}{1-\alpha}$

$= \dfrac{0.2*(0.015)^2}{1-0.015}$

$=4.568*10^{-5}$

Then,

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

$=-\log(4.568*10^{-5}) + \log\dfrac{[0.4*450]}{[0.2*600]}$

$=4.340+ 0.176$

pH =4.516

And,pOH=14-pH

=14-4.516

=9.484

Questions for practice :

A)0.1M NH$_4$OH is 1.34 % ionized at 25ºC,

I)Calculate ionization constant of the base. (Ans=1.82*10^{-5})

II)Calculate the degree of ionization of NH$_4$OH in presence of 0.5M NH$_4$Cl solution. (Ans=3.60*10^{-5})

[Hint : $K_b = \dfrac{[NH^+_4][OH^-]}{[NH_4OH]} = \dfrac{[0.5+\alpha c]*[\alpha c]}{[(1-\alpha)c]}$

III)Calculate the pH of 0.1 M NH$_4$OH in absence and in presence of 0.5M NH$_4$Cl solution.(Ans=11.13 , 8.56)

B)Calculate the H$^+$ & OH$^-$ ions concentration of solution containing 0.1M NH$_4$OH in

presence of 0.5 M NH_4Cl, $K_a=1.8*10^{-5}$.(Ans=H^+=2.77*10^{-9} ,OH^-=3.60*10^{-6} M)

C)An acidic buffer of total molarity 0.29 has pH value of 4.4.calculate the individual molarities of acid and salt,if dissociation constant of acid is $1.80*10^{-5}$.
(Ans=0.199 , 0.091 mol/l)

D)A buffer solution contains 0.5 mole of acetic acid and 0.3 mole of potassium acetate.pH value of solution is found to be 4.66 at 25^oC.Calculate dissociation constant of acetic acid. (Ans=$1.312*10^{-5}$)

E)Calculate pH of solution formed by mixing 500ml of 0.2M acetic acid and 400 ml of 0.4 sodium acetate if $K_a=1.8*10^{-5}$.Calculate the pH of solution after the addition of
i)0.01 mole of HCl   (Ans=5.042)
ii)0.03 mole of NaOH. (Ans=5.158)
(Ans=4.948)

F)Calculate pH if :
1)0.1M   acetic acid solution having $K_a=1.8*10^{-5}$. (Ans=4.744)
2)10^{-7} moles NaOH per litre.   (Ans=7.302)

G)The ionization constant of methanoic acid is $1.8*10^{-4}$.Find the degree of ionization of the solution containing 4.6g of the acid per litre of its solution.(Ans=4.24 %)

H)Find H^+ in a solution of 1M HNO_2 and 0.225
M $NaNO_2$.The K_a for HNO_2 is $5.6×10^{-4.}$
(Ans=$1.6*10^{-4}$)

I)Calculate molar concentration of CH_3COOH solution which is 2.0% ionized,k_a for CH_3COOH is $1.8*10^{-5}$.(Ans=0.044 M)

J)Write the mechanism of buffer action of solution containing a mixture of benzoic acid and sodium benzoate.

K)Write the mechanism of buffer action of solution containing a mixture of H_2CO_3 and $NaHCO_3$ Solution.

L)A aq.solution composed of 0.01M propanoic acid and 0.02M sodium propanoate.Find degree of ionization of the acid,the hydrogen ion concentration and pH if $K_a=1.84*10^{-5}$.
Ans=4.28%,$9.20*10^{-6}$,pH=5.036)

M)A 1 litre buffer solution prepared by mixing 0.1 mole of benzoic acid and 0.2 mole of sodium benzoate solution.The pH of solution is 5.0.Calculate the pH of the solution after the addition of
A)0.05 mole HCL   (Ans=4.698)
B)0.002 mole NaOH   (Ans=5.012)

Electro Chemistry

1)Measurement of standard Hydrogen electrode (SHE):

Hydrogen electrodes are electrodes that produce or consume hydrogen.Hydrogen electrodes are used as reference electrodes when measuring electrode potentials.The standard hydrogen electrode or the normal hydrogen electrode are the most important reference electrodes,since their potential is defined as the zero point of the electro-chemical series.They consist of a platinized platinum plate that is immersed into an HCl solution.Platinum is not affected by HCl solution i.e there is no reaction between electrode and electrolyte.Hence,net charge separation doesnot takes place between electrolyte and electrode.Platinum plate has large surface area for absorption of Hydrogen.

$2H^+(aq) + 2e^- \rightarrow H_2(g)$

It is immersed into a hydrochloric acid with a concentration of 1 mol/l and is surrounded by hydrogen gas at atmospheric conditions(1 atm,25°C)
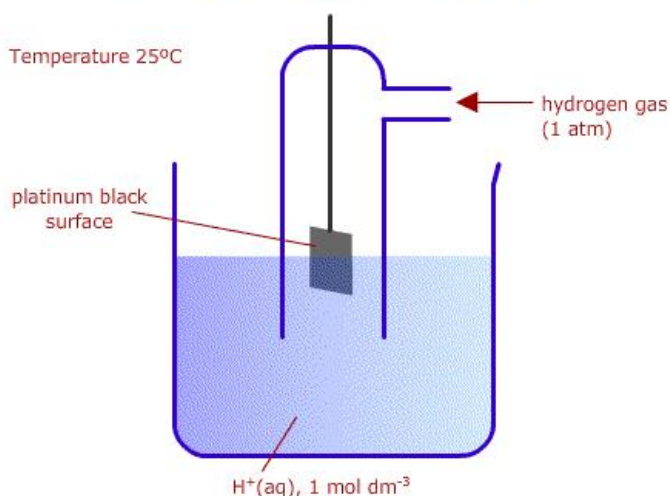
Conditions:

298 K for temperature (25°C), for any standard electrode
1 atmosphere pressure of hydrogen gas $H_2(g)$ for hydrogen electrode,
1 moldm^{-3} concentration of $H^+(aq)$ (hydrogen ions for hydrogen electrode),

2)Define electrochemical cell and describe construction of simple electrochemical cell.

=The cell in which electrical energy is produced as a result of chemical reaction is called electrochemical cell or galvanic cell.

It is composed of two electrodes dipped in two different electrolytes usually in two different containers.Oxidation takes place at anode half cell and reduction takes place at cathode half cell.These two half cells are connected by salt bridge which usually consists of inert ionic compounds such as KNO_3,KCl,NH_4NO_3 etc in which the mobility of cation and anion are expected to be equal or nearly equal.Two half cells are externally connected with highly sensitive potentiometer or galvanometer or ammeter.This type of cell is known as galvanic cell.

Construction of simple galvanic cell :

In the process of the reaction, electrons can be transferred from the corroding zinc to the copper through an electrically conducting path as a useful electric current. Zinc more readily loses electrons than copper, so placing zinc and copper metal in solutions of their salts can cause electrons to flow through an external wire which leads from the zinc to the copper. The salt bridge, in that case, provides the electrolytic path that is necessary to complete an electrochemical cell circuit. salt bridge also maintains electrical neutrality of the electrolyte of anode and cathode half cells.

The half-cell called the anode is the site at which the oxidation of zinc occurs as shown below.

$$Zn \, (s) \rightarrow Zn^{+2} \, (aq) + 2e^-$$
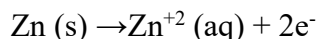
During the oxidation of zinc, the zinc electrode will slowly dissolve to produce zinc ions (Zn^{+2}), which enter into the solution containing $Zn^{+2}(aq)$ and $SO_4^{-2}(aq)$ ions. The half-cell, called the cathode, is the site at which reduction of copper occurs as shown below.
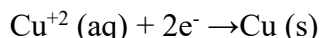
$$Cu^{+2} \, (aq) + 2e^- \rightarrow Cu \, (s)$$

When the reduction of copper ions (Cu^{+2}) occurs, copper atoms accumulate on the surface of the solid copper electrode.
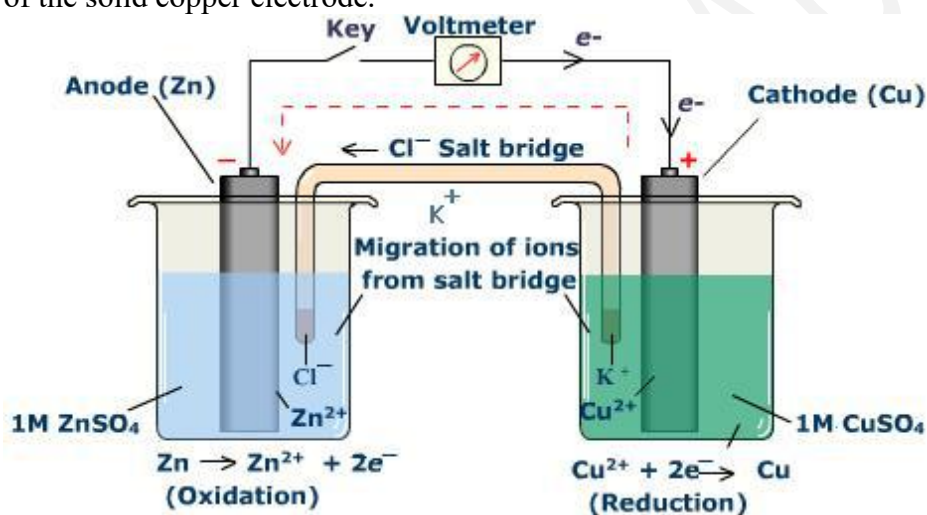
Or,
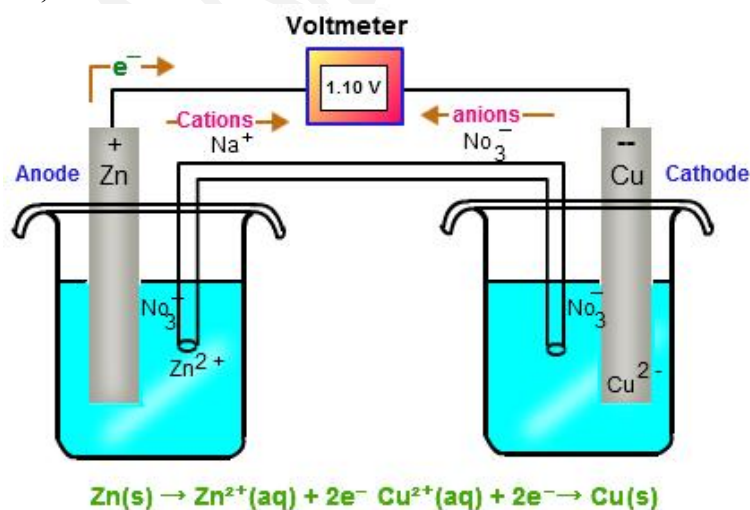
The overall cell reaction is :
At anode : $Zn \rightarrow Zn^{+2}$ (aq) + 2e⁻   (oxidation)
At cathode : Cu^{+2} (aq) + 2e⁻ → Cu (s)   (reduction)
Cell reaction : $Zn + Cu^{++} \rightarrow Zn^{++} + Cu$ (Redox reaction)

The reaction in each half-cell does not occur unless the two half cells are connected to each other.This difference in potential energy is called an electromotive force (emf) and is measured in terms of volts.The zinc/copper cell has an emf of about 1.10 volts under standard conditions.
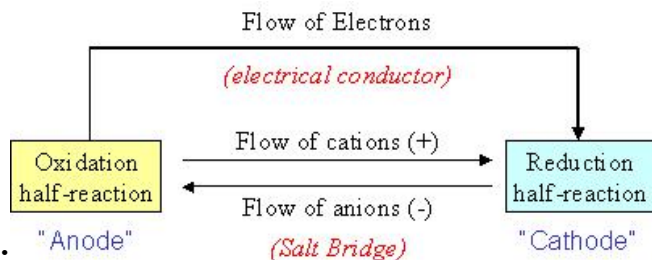
Note :

A)Oxidation= anode / -ve terminal/ left / Less emf value

B)Reduction= cathode/ +ve terminal/right/High emf value

Cell Notation and Conventions:
 Zn│ZnSO₄(aq) ‖ CuSO₄(aq)│Cu
     Anode   cathode
 Zn | Zn⁺⁺   ‖Cu⁺⁺| Cu
The components of the cell are written in order,starting with the left-hand and moving across the salt bridge to the right.A single vertical line indicates a phase boundary.The double vertical line represents a salt bridge.

By convention,the electrode written to the left of the salt bridge in this cell notation is always taken to be the anode,and the associated half-equation is always written as an oxidation.The right-hand electrode is therefore always the cathode,and the half-equation is always written as a reduction.

3)Nernst equation for electrode and cell potential :
A)$E_{cell} = E°_{cell} - \dfrac{0.0591}{n} \log \dfrac{[Product's\ concentration]}{[Reactant's\ concentration]}$
Where,n =number of electrons indicated in the balanced equation.
$E°_{cell} = E°_{cathode} - E°_{anode}$ (For reduction potential)
$E°_{cell} = E°_{cathode} + E°_{anode}$ (For oxidation potential and reduction potential)
$E°_{cell}$ must be positive for the feasibility of the cell.

B)$E_{cell} = E°_{cell} - 2.303 \dfrac{RT}{nF} \log \dfrac{[Product's\ concentration]}{[Reactant's\ concentration]}$
R = universal gas constant $= 8.314\ Jmol^{-1}K^{-1}$

T = temperature in Kelvin (0°C =273 K)
F = Faraday's constant=96500 C
n = number of electrons transferred(oxidised/reduced)

4)Define standard electrode potential.How is single electrode potential originated?
=The potential difference produced between metal and its ions in the solution is called electrode potential.
Standard electrode potential is the potential difference produced between the metal electrode and its solution under standard conditions(25°C,1 M concentration of ions and 1 atmospheric pressure).It is measured with the help of standard hydrogen electrode.

The single electrode potential is originated by the separation of of charges between the metal electrode and its solution.When a metal is dipped into a solution of its own ions at certain concentration,its atom either lose electrons with respect to the solution or some of positively charged ion gain electrons and get converted into atoms.This process results in the separation of charges.Similarly,if the metal ions have relatively greater tendency to take electrons from the electrode,the process is reversed with result in the separation of charges.This causes the origin of single electrode potential.

5)Calculate emf of cell at 30°C when the given electrodes are coupled together.$E°_{Ni/Ni^{++}}$=0.25 V,$E°_{Cd/Cd^{++}}$=0.40 V,R=8.314 JK^{-1}mol^{-1}, [Ni^{++}=0.01M], [Cd^{++}=0.10M],F=96500C.
Solution:
The cell can be represented as :
Ni|Ni^{++}(0.01M)||Cd^{++}(0.1M)|Cd
Anode   Cathode
Reaction:

$$Ni \rightarrow Ni^{++} +2e^- \quad (Oxidation)$$
$$Cd^{++} + 2e^- \rightarrow Cd \quad\quad (Reduction)$$
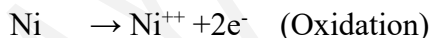
Overall reaction: Ni + Cd^{++} →Ni^{++}+Cd
Since reaction involves loss or gain of two electrons,therefore n=2,emf of cell is given as:
$$E_{cell}=E°_{cell} +2.303\frac{RT}{nF} log\frac{[cathode's\ concentration]}{[Anode's\ concentration]}$$

or,$E_{cell=}$(0.40-0.25)+$\frac{2.303*8.314*(30+273)}{2*96500}$ log$\frac{[0.1]}{[0.01]}$ {Temperature(T)=273+30 K)}

or,$E_{cell=}$0.15+0.03006
Hence, $E_{cell=}$0.180 V.

6)Define electrochemical series.Explain its applications.
The vertical arrangement of elements according to increasing reduction potential value from top to bottom is called electrochemical series.
The series in which elements are arranged in increasing order of standard reduction potential or decreasing order of standard oxidation potential as compared to the electrode potential of standard hydrogen electrode is called electrochemical series.It is also called activity series.

Applications of Electrochemical Series:
A)To predict reactivity of metals:
The activity of the metal depends on its tendency to lose electron or electrons i.e tendency to form cation.This tendency depends on the magnitude of standard reduction potential.The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into cation. Such a metal is said to be chemically active.The chemical reactivity of metals decreases from top to bottom in the series.The metal higher in the series is more active than the metal lower in the series.For example:

a)Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active.These react with cold water and evolve hydrogen.These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.

(b)Metals like Fe, Pb, Sn, Ni, Co etc.which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.

(c)Metals like Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

Electrode	E^0
Li^+/Li	-3.045
Rb^+/Rb	-2.925
K^+/K	-2.925
Cs^+/Cs	-2.923
Ba^{2+}/Ba	-2.905
Ca^{2+}/Ca	-2.866
Na^+/Na	-2.714
Mg^+/Mg	-2.37
Al^{3+}/Al	-1.66
Ti^{2+}/Ti	-1.630
Zr^{4+}/Zr	-1.539
Mn^{2+}/Mn	-1.179
V^{2+}/V	-1.175
Cr^{2+}/Cr	-0.913
Zn^{2+}/Zn	-0.763
Cr^{3+}/Cr	-0.744
Fe^{2+}/Fe	-0.44

Cd^{2+}/Cd	-0.403
Co^{2+}/Co	-0.277
Ni^{2+}/Ni	-0.250
Sn^{2+}/Sn	-0.136
Pb^{2+}/Pb	-0.126
Fe^{3+}/Fe	-0.037
H^{+}/H_2	0.000
Cu^{2+}/Cu	+0.337
Cu^{+}/Cu	+0.521
Ag^{+}/Ag	+0.799
Hg^{2+}/Hg	+0.851
Pd^{2+}/Pd	+0.987
Pt^{2+}/Pt	+1.188
Au^{3+}/Au	+1.50
Au^{+}/Au	+1.692

B)To predict electropositive character of metals:
The electropositive character also depends on the tendency to lose electron or electrons. Like reactivity,the electropositive character of metals decreases from top to bottom in the electrochemical series.On the basis of standard reduction potential values,metals are divided into three groups:

(a)Strongly electropositive metals:Metals having standard reduction potential near about – 2.0 volt or more negative like alkali metals,alkaline earth metals are strongly electropositive in nature.

(b)Moderately electropositive metals:Metals having values of reduction potentials between 0.0 and about – 2.0 volt are moderately electropositive Al,Zn,Fe,Ni,Co etc. belong to this group.

(c)Weakly electropositive:The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals.Cu,Hg,Ag etc belong to this group.

C)To predict thermal stability of metallic oxides:
The thermal stability of the metal oxide depends on its electropositive nature.As the electropositivity decreases from top to bottom,the thermal stability of the oxide also decreases from top to bottom.The oxides of metals having high positive reduction potentials are not stable towards heat.The metals which come below copper form unstable oxides i.e these are decomposed on heating.

$$Ag_2O \xrightarrow{Heat} 2Ag + O_2$$
$$2HgO \xrightarrow{Heat} \frac{1}{2}O_2 + 2Hg$$
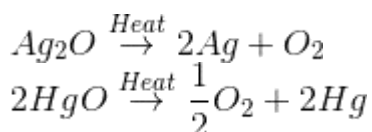
D)To predict Reducing power of metals:

Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential,more is the tendency to lose electron or electrons.Thus reducing nature decreases from top to bottom in the electrochemical series.The power of the reducing agent increases,as the standard reduction potential becomes more and more negative.Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron.(decreasing order of reducing nature)

Element :   Na >   Zn >   Fe
Reduction potential :   − 2.71   − 0.76   − 0.44

Alkali and alkaline earth metals are strong reducing agents.

E)To predict Oxidising nature of non-metals :
Oxidising nature depends on the tendency to accept electron or electrons.More the value of reduction potential, higher is the tendency to accept electron or electrons.Thus, oxidising nature increases from top to bottom in the electrochemical series.The strength of an oxidising agent increases as the value of reduction potential becomes more and more positive.Thus,in electrochemical series:

Top   (Strongest reducing agent)

Highest negative reduction potential

Or

(Minimum reduction potential)

Bottom (Strongest oxidising agent)

Highest positive value of reduction potential
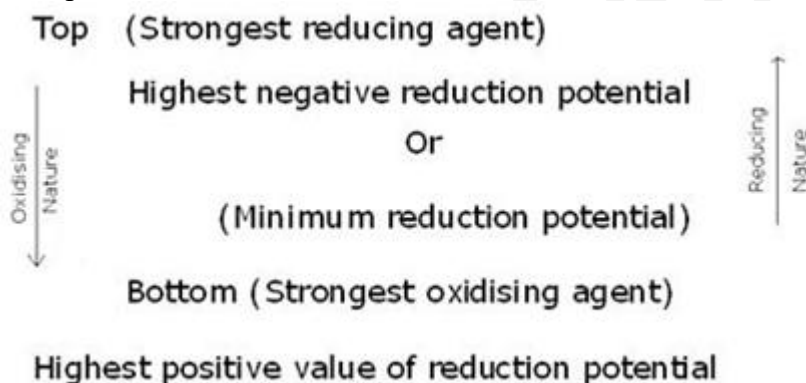
F)To calculate emf of cell :
The following steps determine the reduction potential of the cathode and anode:

Step I:
The two half-cell reactions are written in such a way that the reaction taking place at the left hand electrode is written as an oxidation reaction and that taking place at the right electrode is written as reduction reaction.

Step II:
The number of electrons in the two equations are made equal by multiplying one of the equations if necessary by a suitable number.However,electrode potential values ($E°$) are not multiplied.

Step III:
The electrode potentials of both the electrodes are taken to be reduction potentials and so

the EMF of the cell is equal to the difference between the standard potential of the right hand side and the left hand side electrode.

$E_{cell} = E_R - E_L$

Step IV:

If the EMF of the cell is +ve, the reaction is feasible in the given direction and the cell is correctly represented i.e oxidation occurs at left electrode (anode) and reduction occurs at the right electrode (cathode). If it is -ve, the cell reaction is not feasible in the given direction and the cell is wrongly represented. Thus, to get positive value for the EMF the electrodes must be reversed.

The emf of the galvanic cell generated can be calculated by subtracting reduction potential of anode from the reduction potential of cathode or it is calculated by algebraic summation of oxidation potential of anode and reduction potential of cathode.

$E^o_{cell} = E^o_{cathode} - E^o_{anode}$ (For reduction potential)

$E^o_{cell} = E^{ox}_{anode} + E^{red}_{cathode}$ (For oxidation and reduction potential)

The value so calculated must be positive.

The cell reaction is spontaneous in the forward direction if $E_{cell} > 0$, $\Delta G < 0$

The cell reaction is not spontaneous in the forward direction if $E_{cell} < 0$, $\Delta G > 0$.

G) Predicting the Liberation of Hydrogen Gas from Acids by Metals:

All metals having negative electrode potentials (negative E° values) show greater tendency of losing electrons as compared to hydrogen. So, when such a metal is placed in an acid solution, the metal gets oxidized and H^+ (hydrogen) ions get reduced to form hydrogen gas. Thus, the metals having negative E° values liberate hydrogen from acids.

$$M_{(s)} \rightleftharpoons M^{n+}_{(aq)} + ne^-$$

$$nH^+_{(aq)} + ne^- \rightleftharpoons n/2 \, H_{2(s)}$$

$$\text{Thus,} \quad M + nH^+_{(aq)} \rightleftharpoons M^{n+}_{(aq)} + n/2 \, H_{2(g)}$$

$Zn + 2H^+ \rightarrow Zn^{++} + H_2 (\uparrow)$
    (dil)

$Cu + H^+ \rightarrow$ No evolution of H_2
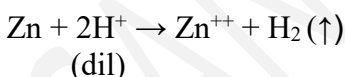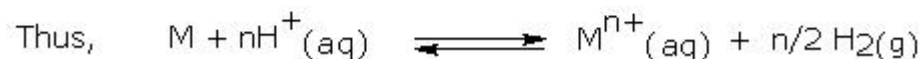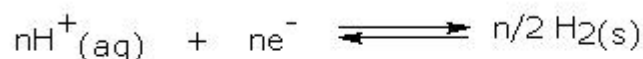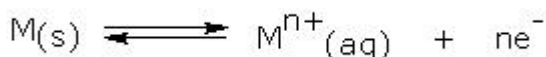
For example, metals such as Mg (E°= - 2.37 V) can displace hydrogen from acids such as HCl and H_2SO_4. But metals such as Copper(E °= +0.34V) and gold (E°= +1.42 V) cannot displace hydrogen from acids because of their positive reduction potential value.

H) To predict whether a given metal will displace another, from its salt solution:

A metal higher in the series will displace the metal from its solution which is lower in the series i.e the metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential. A metal higher in the

series has greater tendency to provide electrons to the cations of the metal to be precipitated.

$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$ (Displacement or redox reaction)
$Cu + ZnSO_4 \rightarrow$ No reaction.
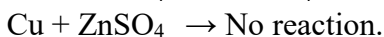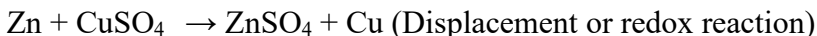
7)What is standard electrode potential?How can we measure the standard electrode potential experimentally?
=Standard electrode potential is the potential difference produced under standard conditions(25°C ,1 M concentration of ions and 1 atmospheric pressure).It is measured with the help of standard hydrogen electrode.

Standard reduction potential = - (Standard oxidation potential)

Standard oxidation potential = - (Standard reduction potential)

Oxidation potential:The tendency of an electrode to lose electrons or to get oxidized is called Oxidation potential.

Reduction potential:The tendency of an electrode to gain electrons or to get reduced is called Reduction potential

Measurement of Electrode Potential :
The measurement of electrode potential of a given electrode is made by constituting a voltaic cell i.e by connecting it with a standard hydrogen electrode (SHE) through a salt bridge.1 M solution is used in hydrogen half-cell and the temperature is maintained at 25°C.

Determination of standard electrode potential of Zn/Zn^{++} electrode:
For measuring the standard electrode potential of a given electrode,a voltaic cell is constructed with a reference electrode like standard hydrogen electrode.1 M solution is used in both the half cell and the temperature is maintained at 25°C.The electrodes are connected with a voltmeter to measure emf of the cell.The reading noted in voltmeter gives the standard electrode potential of the electrode with respect to hydrogen electrode.

In order to determine the eletrode potential of Zn,Zn electrode is dipped in 1M $ZnSO_4$,it is coupled with SHE.Zn electrode acts as anode whereas SHE acts as cathode.The electrons given off in this half-reaction flow through the circuit and eventually accumulate on the platinum wire to give this wire a net negative charge.The H^+ ions from the HCl are attracted to this negative charge and migrate toward the platinum wire.When the H^+ ions touch the platinum wire,they pick up electrons to form hydrogen atoms, which immediately combine to form H_2 molecules.

$$\text{Oxidation:} \quad Zn \longrightarrow Zn^{++} + 2e\text{-}$$

$$\text{Reduction:} \quad 2H^+ + 2e^- \longrightarrow H_2$$
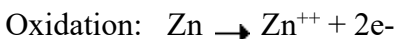
The oxidation of zinc metal releases Zn^{++} ions into the Zn/Zn^{++} half-cell.This half-cell therefore picks up a positive charge that interferes with the transfer of more electrons. The reduction of H^+ ions in the H_2/H^+ half-cell leads to a net negative charge as these

H^+ ions are removed from the solution.This negative charge also interferes with the transfer of more electrons.To overcome this problem,we complete the circuit by adding a U-tube filled with a saturated solution of a soluble salt such as KCl.Negatively charged Cl^- ions flow out of one end of the U-tube to balance the positive charge on the Zn^{++} ions created in one half-cell.Positively charged K^+ ions flow out of the other end of the tube to replace the H^+ ions consumed in the other half cell.The U-tube is called a salt bridge because it contains a solution of a salt that literally serves as a bridge to complete the electric circuit.

The zinc electrode acts as an anode and the hydrogen electrode as cathode and the cell can be represented as :

Cell Representation	Oxidation half reaction	Reduction half reaction
$Zn|Zn^{++}$ (aq) $||$ H^+(aq)$|H_2$ (g),pt	$Zn \rightarrow Zn^{++}+$ 2e-	$2H^+$+ 2e- $\rightarrow H_2\uparrow$
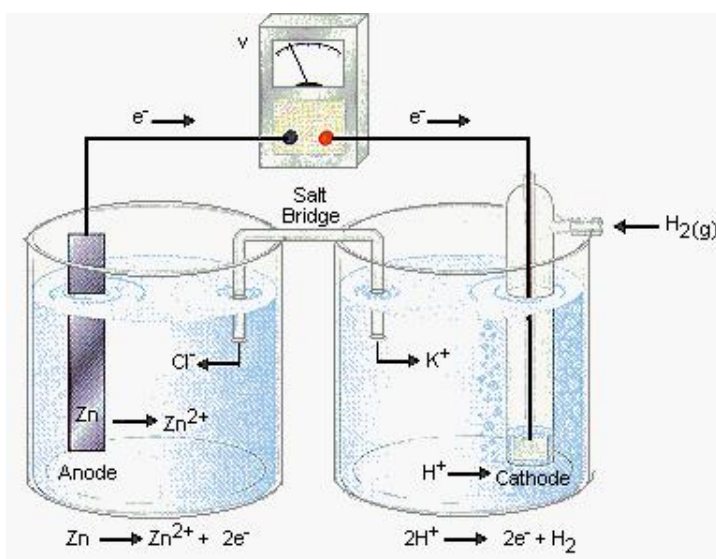
The EMF of the cell is 0.76 volt.
$E_{Cell} = E°_{Anode} + E°_{Cathode}$
or, $0.76 = E°_{Anode} + 0$
or,$E°_{Anode} = +0.76$ V
As the reaction on the anode is oxidation, i.e.,
$Zn \rightarrow Zn^{++} + 2e^-$,
$E°_{Anode}$ is the standard oxidation potential of zinc.This potential is given the positive sign.
$E°_{ox} (Zn/Zn^{++}) = +0.76$ volt
So standard reduction potential of Zn i.e $E^0(Zn/Zn^{++})$
$E^0_{ox} = -(+0.76)$
     $= -0.76$ volt
The EMF of such a cell gives the positive value of standard oxidation potential of metal M. The standard reduction potential(E_o) is obtained by reversing the sign of standard oxidation potential.
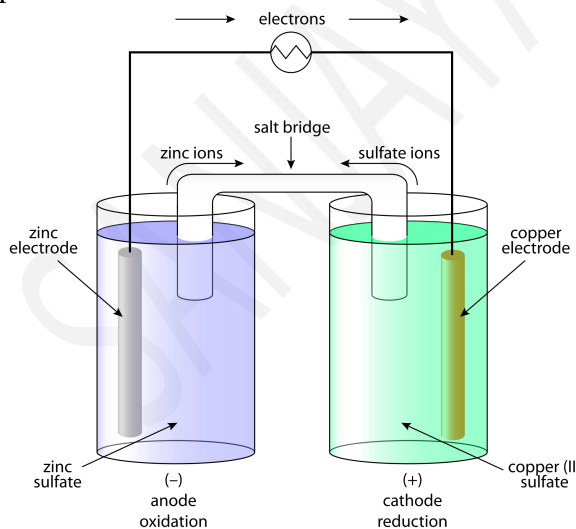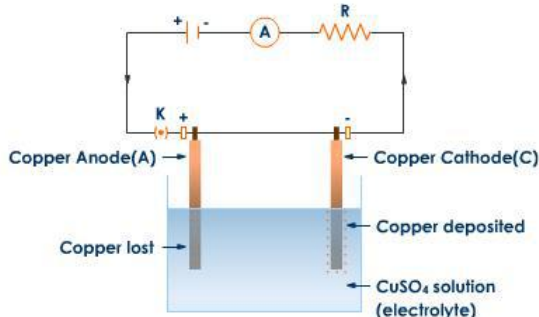
8)Difference between an electrolytic cell and a galvanic cell.

Galvanic cell	Electrolytic cell
A Galvanic cell is a device which converts chemical energy into electrical energy. Eg:Voltaic cell.	An electrolytic cell is a device in which external source of emf is supplied in order to bring a chemical reaction. Eg:Electrolysis of $CuSO_4$ solution.
Here, the redox reaction is spontaneous and is responsible for the production of electrical energy.	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
The two half-cells are set up in different containers,being connected through the salt bridge or porous partition.	Both the electrodes are placed in a same container in the solution of molten electrolyte.
Here the anode is negative and cathode is the positive electrode.The reaction at the anode is oxidation and that at the cathode is reduction.The electrons are supplied by the species getting oxidized.They move from anode to the cathode in the external circuit	Here,the anode is positive and cathode is the negative electrode.The reaction at the anode is oxidation and that at the cathode is reduction.
The electrons are supplied by the species getting oxidized.They move from anode to the cathode in the external circuit	The external battery supplies the electrons. They enter through the cathode and come out through the anode.
Salt bridge is used.	Salt bridge is not used.
Electrode materials are different.	Electrode materials may be of same or different.
Oxidation-reduction or redox reactions take place in electrochemical cells. The figure above shows that Zn(s) is continuously oxidized,producing aqueous Zn^{++}: $Zn(s) \rightarrow Zn^{++}(aq)+ 2e^-$ Conversely,in the cathode,Cu^{++} is reduced and	The electrolysis of an aqueous solution of copper sulphate using copper electrodes results in transfer of copper metal from the anode to the cathode during electrolysis. The copper sulphate is ionised in aqueous solution. $CuSO_4 \rightarrow Cu^{++} + SO_4^{--}$ The positively charged copper ions migrate to the cathode, where each gains two electrons to become copper atoms

continuously deposits onto the copper rod.$Cu^{++}(aq)+ 2e^- \rightarrow Cu(s)$

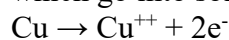As a result,the solution containing Zn(s) becomes more positively charged as the solution containing Cu(s) becomes more negatively charged.For the voltaic cell to work,the solutions in the two half cells must remain electrically neutral.Therefore,a salt bridge containing KNO_3 is added to keep the solutions neutral by adding NO_3^- anion into the anode solution and K^+ cation into the cathode solution.As oxidation and reduction proceed,ions from the salt bridge migrate to prevent charge buildup in the cell compartments.
$Zn(s)|Zn^{++}(aq)||Cu^{++}(aq)|Cu(s)$

that are deposited on the cathode.
$Cu^{++} +2e^- \rightarrow Cu$
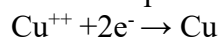
At the anode, each copper atom loses two electrons to become copper ions, which go into solution.
$Cu \rightarrow Cu^{++} + 2e^-$
The sulphate ion does not take part in the reaction and the concentration of the copper sulphate in solution does not change.This process is used in electroplating.As a consequence,copper is deposited in the cathode at the same rate as it's removed from the anode and no new substances are produced in this reaction.The cathode must be pure copper(metal) & anode must be impure copper.

9)How can single electrode potential measured experimentally?
=The potential difference produced between metal and its ions in the solution is called electrode potential.

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$$
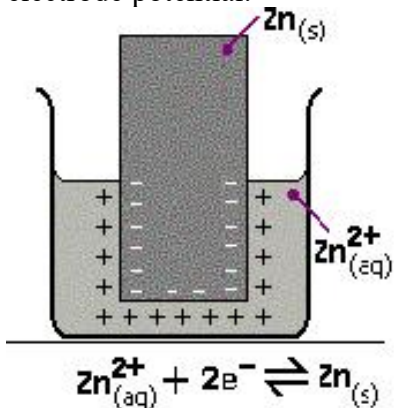
When Zn plate is placed in solution containing Zn^{++} ions,Zn atom loses electrons (oxidized) to Zn^{++} ions).
$Zn(s) \rightarrow Zn^{++}(aq)+2e^-$
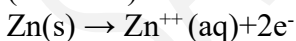
Electrons thus generated get accumulated on the Zn plate and hence makes the plate negatively charged.In order to neutralize the negative charge produced on the surface of metal plate,a layer of Zn^{++} ions is formed round he surface of negatively charged Zn plate.In this way,an electrical double layer is produced between metal plate and solution. This electrode double layer develops a definite potential difference between Zn and Zn^{++} ions of the solution.This potential difference is called electrode potential of Zn(s) /Zn^{++}(aq) electrode.

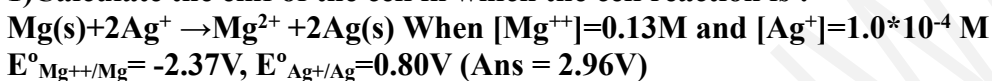The magnitude of electrode potential of metal is a measure of its relative tendency to lose

or gain electrons i.e it is a measure of the relative tendency of the metal to undergo oxidation or reduction.The potential difference of single electrode cannot be measured directly,first of all,we assign an arbitrary electrode potential as a reference or standard electrode and then the potential of given electrode to be measured with respect to this standard electrode.A universally adopted standard is the Hydrogen electrode.
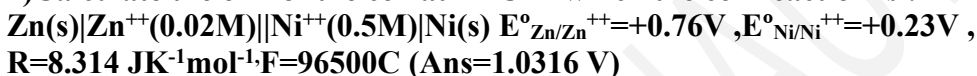
Factors affecting magnitude of electrode potential:
A)Nature of metal or electrodes
B)Concentration of the electrodes.
C)Temperature.

Questions for practice:
1)Calculate the emf of the cell in which the cell reaction is :
$Mg(s)+2Ag^+ \rightarrow Mg^{2+} +2Ag(s)$ When $[Mg^{++}]=0.13M$ and $[Ag^+]=1.0*10^{-4}$ M
$E^o_{Mg++/Mg}= -2.37V$, $E^o_{Ag+/Ag}=0.80V$ (Ans = 2.96V)

2)Calculate the emf of the cell at 27^oC in which the cell reaction is :
$Zn(s)|Zn^{++}(0.02M)||Ni^{++}(0.5M)|Ni(s)$ $E^o_{Zn/Zn}{}^{++}=+0.76V$,$E^o_{Ni/Ni}{}^{++}=+0.23V$,
$R=8.314$ $JK^{-1}mol^{-1}$·$F=96500C$ (Ans=1.0316 V)

3)Find the cell potential of a galvanic cellbased on the following reduction half-reactions at 25 °C ,$Cd^{++} + 2 e^- \rightarrow Cd$,$E^0 = -0.403$ V ,$Pb^{++} + 2 e^- \rightarrow Pb$, $E^0= -0.126$ V
where $[Cd^{++}] = 0.020$ M and $[Pb^{++}] = 0.20$ M.(Ans= 0.30V)
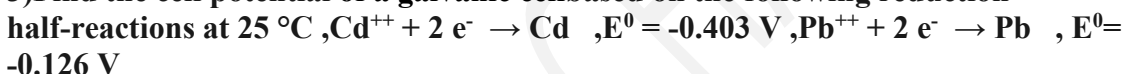
4)Why is salt bridge used in construction of a cell?Why is KCl is used for preparing salt bridge?

5)Calculate the emf of the cell at 25^oC in which the cell reaction is :
$E^o_{zn/zn}{}^{2+}=+0.76V$ and $E^o_{co/co}{}^{2+}=+0.28$ V
$Zn(s)+Co^{++} \rightarrow Co(s) + Zn^{++}$ (Ans=+0.48V)
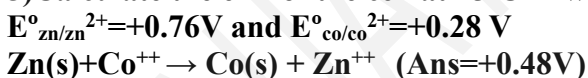
6)Find standard oxidation potential of Ferro-ferric system if standard emf of cell is 0.77V.$Fe^{3+}(aq) +H_2(aq) \rightarrow Fe^{+2}(aq)+2H^+$ (Ans=-0.77V)

7)How can single electrode potential of Cu electrode measured experimentally?
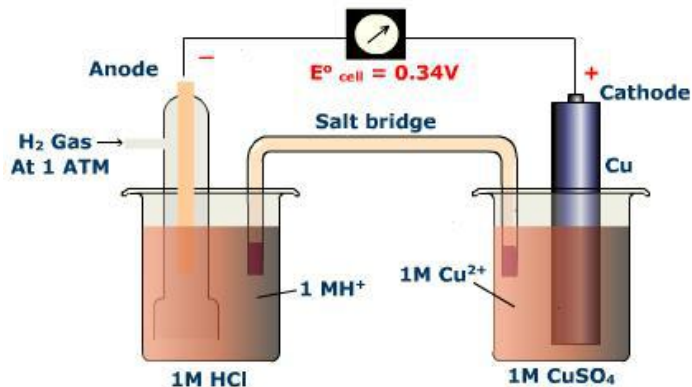
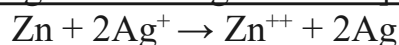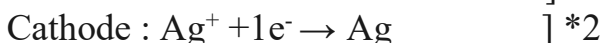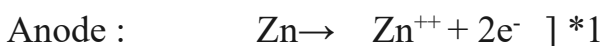**1)Calculate emf of the cell at 27^0 C when given electrodes are coupled together.**
$Zn \rightarrow Zn^{++} + 2e^-$,E^0 = + 0.76 V
$Ag \rightarrow Ag^+ + 1e^-$,E^0 = -0.80 V
R =8.314 $Jmol^{-1}K^{-1}$,   [Zn^{++}]=0.2 M, [Ag^+]=0.1M
Solution :
The given reactions are oxidation.So given E^0 is also is oxidation
potential.The reduction potential are $E_{Zn++/zn}$ = -0.76 V and $E_{Ag+/Ag}$ = +0.80 V
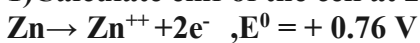
Temperature = 27^0 C = 27+ 273 K =300 K

Anode : $Zn \rightarrow$ $Zn^{++} + 2e^-$] *1
Cathode : $Ag^+ + 1e^- \rightarrow Ag$] *2
          $Zn + 2Ag^+ \rightarrow Zn^{++} + 2Ag$

Number of electrons oxidised or reduced is 2 = n
E^0_{cell} = $E^0_{cathode}$ - E^0_{anode}
     =+0.80 - (-0.76)
     =+1.56 Volts

So,
E_{cell} = E^0_{cell} - $\dfrac{2.303\ R* T}{n*F}$ Log $\dfrac{[product\ ]}{[Reactant]}$

   =1.56 - $\dfrac{2.303 * 8.314* 300}{2 * 96500}$ $\dfrac{log[1^2 * 0.2]}{[1* (0.1)^2]}$ [$2Ag=1^2$,$Zn=1$,$Zn^{++}=0.2$,$2Ag^+=(0.1)$]
   =1.56 - 0.02976*1.30

   =1.56 - 0.0387 V

E_{cell} =1.521 V
Hence,Emf of cell is 1.521 Volts.

$\left\{\right.$Note: Concentration of electrode in solid or gas state is 1 while ions has different

concentrations. Eg : Concentration or activity of Ag, Zn, Cu etc is 1. $\left.\right\}$

General organic Chemistry

1)Difference between Enantiomers and Diastereomers.

Enantiomers	Diastereomers
Compounds possessing identical molecular and structural formula and identical physical and chemical properties but differing only in optical activity are known as enantiomers.	Stereoisomers which are not mirror image and nor are superimposable are called diastereomers.
They exhibit same physical properties.It has same boiling point,melting point,refractive index, solubility,and many other properties except for their ability to rotate plane polarized light by equal amounts but in opposite direction.	They exhibit similar chemical properties.It has different solubility ,refractive index,boiling point, melting point except the opposite sign of specific rotation of plane polarized light.
Structure(b) cannot be superimposed on structure (a),so structures (a) and (b) are enantiomers.The additional two enantiomers are created by allowing rotation about one of the stereogenic centers while restricting rotation about the other. Structure (c) is created by allowing rotation about the upper stereogenic center (carbon 2) of structure (a).(c) has a different configuration from structures (a) and (b).Structure (d),the mirror image of (c),cannot be superimposed on structure (c).Therefore,structures (c) and (d) are enantiomers.	The relationship of (a) to (c) is one of diastereoisomerism.They are not mirror images, so structure (a) is a diastereomer of structures (c) and (d). Likewise, structure (b) is a diastereomer of structures (c) and (d).In the same fashion,structures (c) and (d) are diastereomers of (a) and (b).
Enantiomers contain chiral centers that are Non superimposable & mirror images.	Diastereomers contain chiral centers that are non superimposable and are not mirror images.

Their rate of reaction is same.	Their rate of reaction is different.

2)SN^1 and SN^2 Reaction:

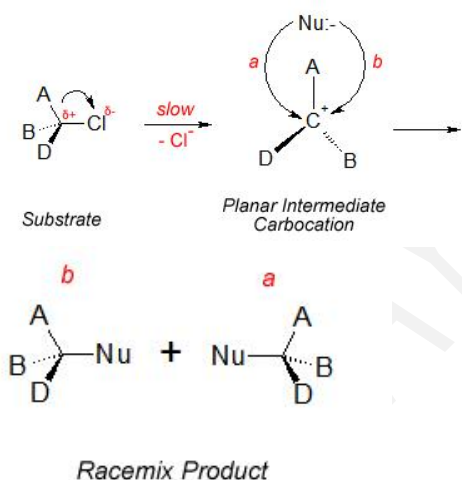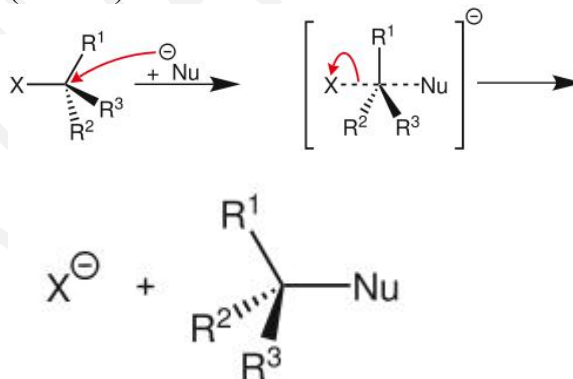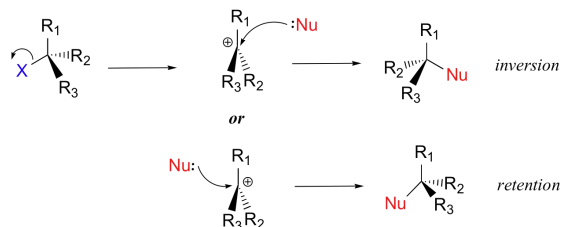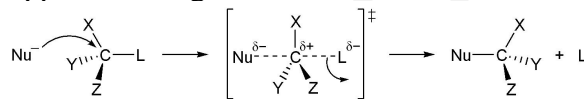| Substitution nucleophilic unimolecular reaction	Substitution nucleophilic bimolecular reaction
The step determining the rate is unimolecular. R=k[substrate] The formation of a carbocation is not energetically favoured,so this reaction is the slowest step and determines the overall rate of the reaction.	The step determining the rate is bimolecular. R=k[substrate][nucleophilic] The reaction requires a collision between the nucleophile and the molecule, so increasing the concentration of either will increase the rate of the reaction.
It is a two-step mechanism.	It is one step process.
The carbocation will form as an intermediate.	The carbocation will not form as an intermediate.
For the SN^1, since carbocation stability increases as we go from primary to secondary to tertiary,the rate of reaction for the SN^1 goes from primary (slowest) << secondary < tertiary (fastest) Racemix Product	For the SN^2, since steric hindrance increases as we go from primary to secondary to tertiary,the rate of reaction proceeds from primary (fastest) > secondary >> tertiary (slowest).
SN^1 reaction involves two separate steps: first the departure of the leaving group and then the addition of the nucleophile. The more stable the carbocation is, the easier it is to form, and the faster the SN^1 reaction will be.Since the nucleophile is not involved in the rate determining step, the nature of the nucleophile is unimportant in an SN^1 reaction.However, the more reactive the nucleophile,the more likely an SN^2 reaction becomes.	In the SN^2 reaction, the nucleophile approaches the carbon atom to which the leaving group is attached.As the nucleophile forms a bond with this carbon atom, the bond between the carbon atom and the leaving group breaks.The bond making and bond breaking actions occur simultaneously. Eventually, the nucleophile has formed a complete bond to the carbon atom and the bond between the carbon atom and the leaving group is completely broken.

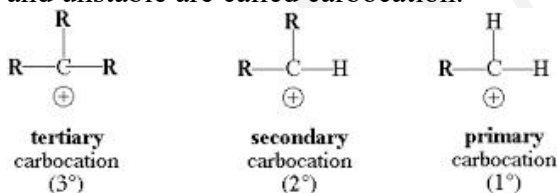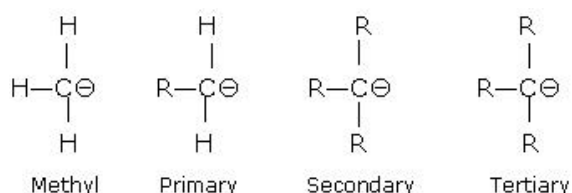| Stereochemistry:	Stereochemistry:
We cans see that nucleophile can attack from either face of the carbocations,which is a planar molecule.Hence,if the alkyl halide is optically active,then the product will be racemic mixture.A solution in which both enantiomers of a compound are present in equal amounts is called a racemic mixture or racemate.	In SN$_2$ reaction,the attack of nucleophile occurs from the back side,whereas the leaving group leaves from the front side.As a result,the SN$_2$ reaction is always accompanied by inversion configuration. This means that if the alkyl halide is optically active,the substitution product will also be optically active and product will have opposite configuration to the substrate.
In SN^1 reactions,we cannot draw the intermediate structure of where the carbon has a partial bond with the incoming nucleophile and the leaving group.	In SN^2 reactions,we can draw the intermediate structure of where the carbon has a partial bond with the incoming nucleophile and the leaving group.
The nucleophile used is generally weak.	The nucleophile used is generally is strong.

3)

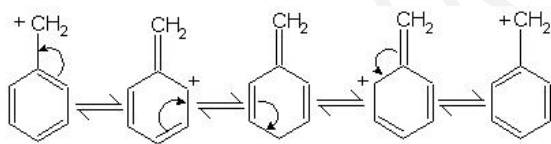| Carbocation	Carbanion
Ionic species with positively charged carbon atom which are very reactive and unstable are called carbocation.	Ionic species with negatively charged carbon atom are called carbanion.
Carbocations are strong Lewis acids.	Carbanions are strong bases (both Lewis and Bronsted).
Stability : A)**Hyperconjugation:** Carbocation having alpha hydrogen show hyper conjugation and that cause increase in stability of carbocation.Greater the number of alpha hydrogen more is the stability of carbocation.The +I effect and	Stability : A)**Electronegativity of carbanionic carbon:** The stability of carbanions derived from alkanes,alkynes and alkenes can be explain on the basis of their s-character.Since the electronegativity of the carbon increases

hyperconjugation in tertiary carbocations are responsible for its greater stability than primary and secondary carocations.
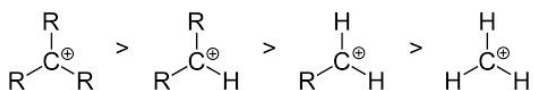
B)Inductive effect:
If any electron repelling group is attached with carbocation then it repel the electron towards electron deficient carbon due to which electron density on the carbon increases and positive charge decreases.In this way +I effect increase the stability of carbocation.

C)Carbocations are stabilized by carbon-carbon multiple bonds (resonance):
Carbocations where the C^+ is adjacent to another carbon atom that has a double or triple bond have extra stability because of the overlap of the empty p orbital of the carbocation with the p orbitals of the π bond (pi bond). This overlap of the orbitals allows the charge to be shared between multiple atoms–delocalization of the charge-and therefore stabilizes the carbocation.

with increasing s-character of the bonding (in the order sp^3,sp^2,sp^1) the carbanion stability follows the same trend.
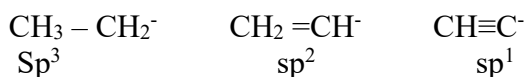
$CH_3 – CH_2^-$ $CH_2 =CH^-$ $CH \equiv C^-$
  Sp^3 sp^2 sp^1
(i) % of s-character in increasing order
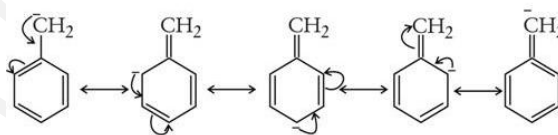(ii)Stability in increasing order.

B) Inductive effect :
As greater number of alkyl groups,greater would be the negative charge density at central carbon atom of carbanion and lesser would be the stability.
1.with increase in +I effect stability decreases
2.with increase in –I effect stability increases

C)Delocalistion of charge or Resonance :
Allyl and benzyl carbanions are stabilised by delocalisation of negative charge.

Order of stability of carbocations primary < secondary < tertiary.Stability of the carbocation increases with the number of alkyl groups bonded to the charge.An explanation for this is that the methyl group ($-CH_3$) acts as an electron donor and therefore stabilizes the positively charged cation.

Order of stability of carboanion primary > secondary > tertiary.
Stability of the carboanion decreases with the number of alkyl groups bonded to the charge.
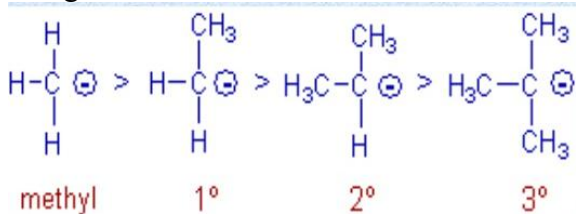
4)Elimination Reaction :
Elimination reactions are important as a method for the preparation of alkenes.

The term "elimination" describes the fact that a small molecule is lost during the process.
<u>The two most important methods are:</u>
Dehydration (- H_2O) of alcohols, and
Dehydrohalogenation (- HX) of alkyl halides.

There are three fundamental events in these elimination reactions:
A)Removal of a proton
B)Formation of the C=C π bond
C)Breaking of the bond to the leaving group.

Depending on the relative timing of these events,different mechanisms are possible:
Loss of the LG to form a carbocation then removal of H^+ with formation of C=C bond
(two steps) : E^1 reaction
Simultaneous H^+ removal, C=C bond formation and loss of the LG (one step) : E^2
reaction

E^1 mechanism:

E^1 indicates a elimination,unimolecular reaction,where rate = k [R-LG].This implies that
the rate determining step of the mechanism depends on the decomposition of a single
molecular species.

Overall,this pathway is a multistep process with the following two critical steps:


loss of the leaving group,
LG, to generate
a carbocation intermediate,
then

loss of a proton, H+, from
the carbocation to form the
π-bond

B: = base
In the E^1 mechanism,the first step is the loss of the leaving group,which leaves in a very
slow step,resulting in the formation of a carbocation.The base then attacks a neighboring
hydrogen,forcing the electrons from the hydrogen-carbon bond to make the double
bond.Since this mechanism involves the formation of a carbocation, rearrangements can
occur.
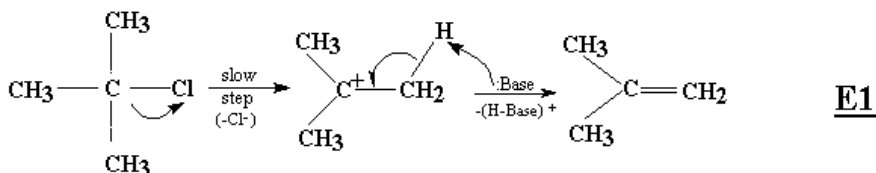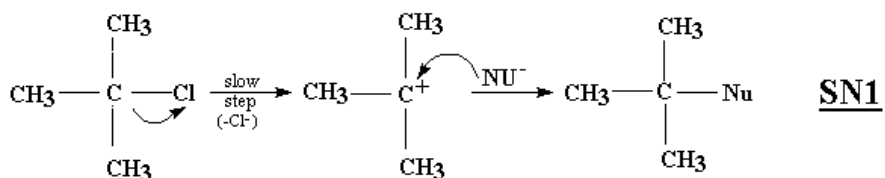
Sometimes more than one alkenes can be formed.In such case,the main product is the maximum substituted alkene.For example:
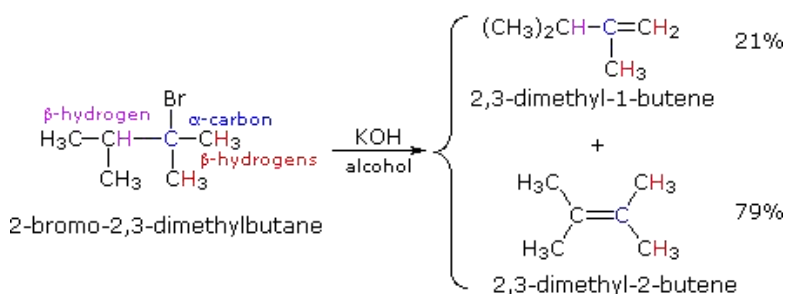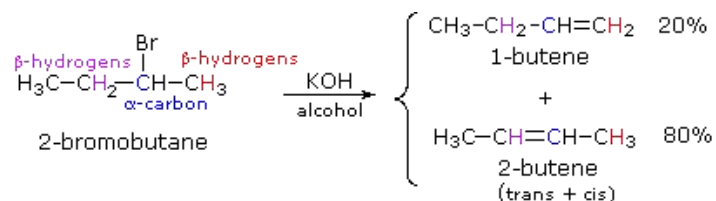

E^2 mechanism:

E^2 indicates an elimination,bimolecular reaction,
where rate = k [B][R-LG].This implies that the rate determining step involves an interaction between these two species,the base B and the organic substrate,R-LG
This pathway is a concerted process with the following characteristics:
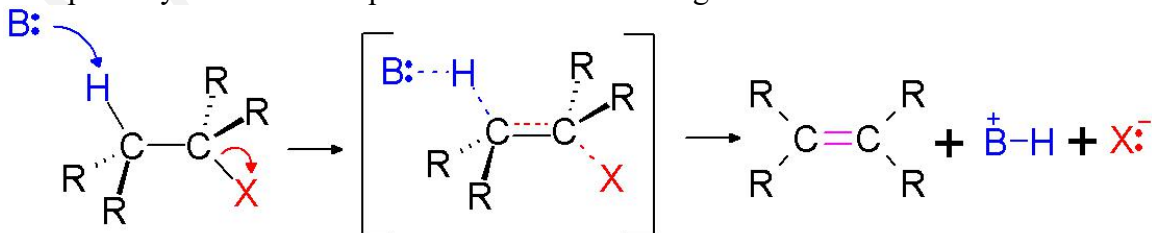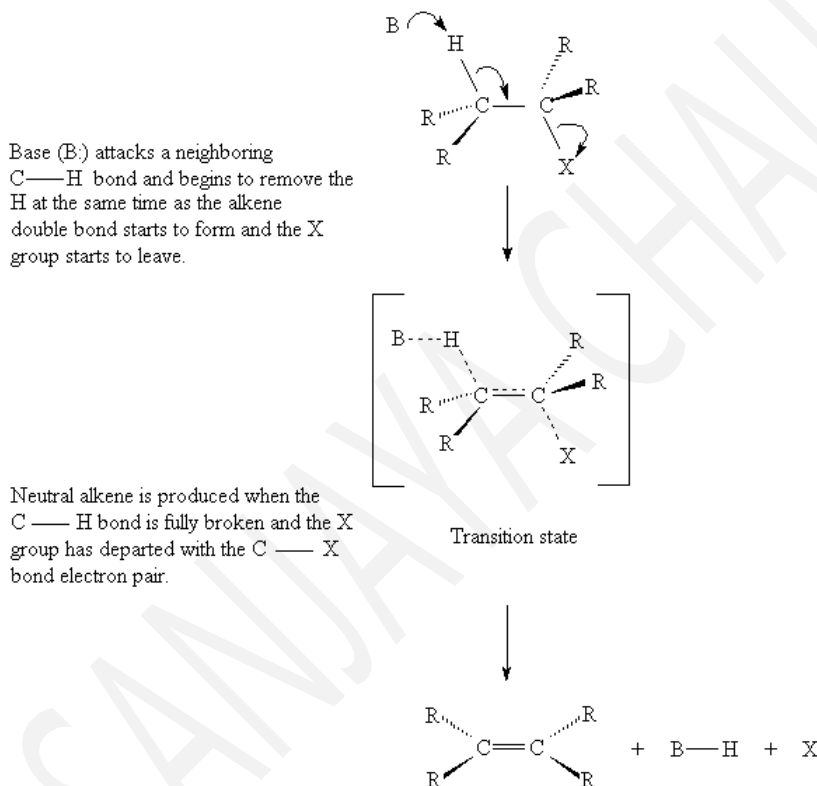

Simultaneous removal of the proton, H^+ by the base,loss of the leaving group and formation of the π-bond.E^2 reactions are typically seen with secondary and tertiary alkyl halides,but a hindered base is necessary with a primary halide.The mechanism by which it occurs is a single step concerted reaction with one transition state.The rate at which this

mechanism occurs is second order kinetics and depends on both the base and alkyl halide.A good leaving group is required because it is involved in the rate determining step.The leaving groups must be coplanar in order to form a pi bond;carbons go from sp^3 to sp^2 hybridization states.
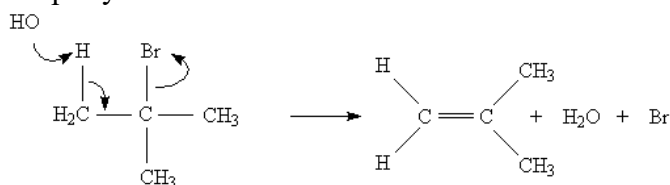

E^2 eliminations, in contrast to E^1 reactions are promoted by strong base.The base vital to the reaction;it is directly involved in the rate-determining step.The reaction is bimolecular-that is,it involves "second-order kinetics"-because two molecules must come together for the reaction to occur.The mechanism of an E^2 elimination reaction is shown below:

Base (B:) attacks a neighboring C——H bond and begins to remove the H at the same time as the alkene double bond starts to form and the X group starts to leave.

Neutral alkene is produced when the C —— H bond is fully broken and the X group has departed with the C —— X bond electron pair.

Transition state

5)Chiral or optical Isomers:
An optically active organic compound can be identified by finding a chiral carbon.A chiral carbon is one that has four different "groups" attached to it.The groups can be anything from a single H to functional groups to one or more other carbons.Optically active compounds exist in two isomeric forms.The isomer that rotates the plane of polarized light to the left (counterclockwise) is called levorotatory (l).The other isomer that rotates the light to the right (clockwise) is called dextrorotatory(d).The optical isomers are mirror images of each other.The isomers result from the tetrahedral geometry around the chiral carbon center.
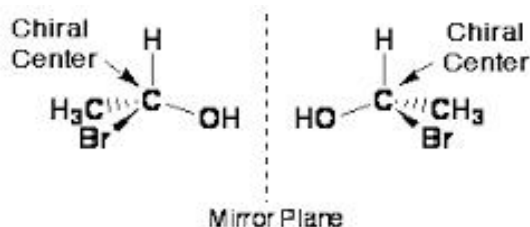
Chirality

An object that is not superimposable upon its mirror image is called chiral. A carbon must have four different substituents to be a chiral center.

Achiral objects are mirror images that can be superimposed.

Optical activity

A compound is optical active if it has the ability to rotate plane-polarized light. If plane-polarized light is passed through an optically active compound, the orientation of the plane is rotated by an angle alpha. The enantiomer of this compound will rotate light by the same amount, but in the opposite direction.
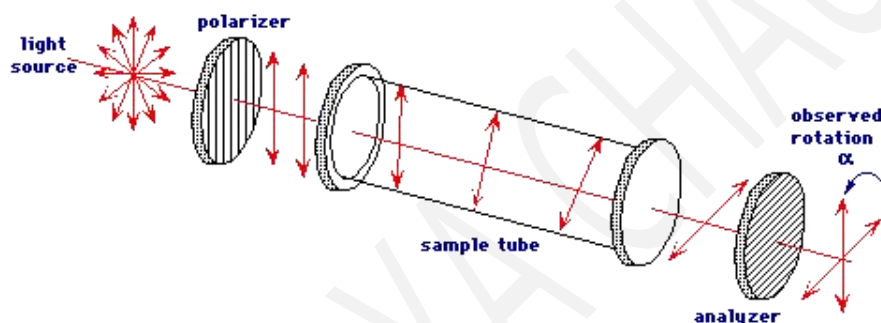
The angle of rotation is measured in a device known as a polarimeter.

Plane of Symmetry

A plane of symmetry is an imaginary plane that bisects a molecule into halves that are mirror images of each other.
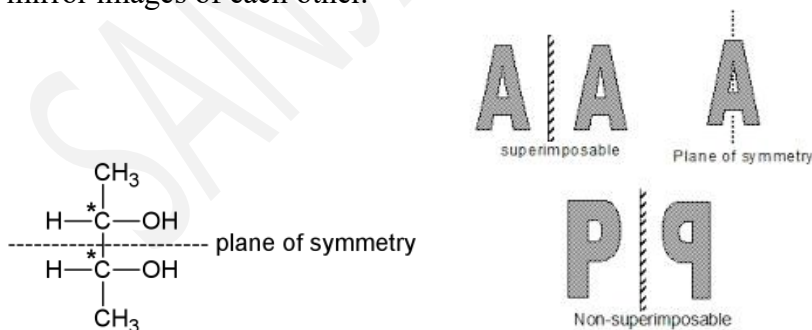

6)Resonance and Hyper-conjugation effect:

A)Hyper-conjugation or No Bond Resonance:

The delocalization of σ-electrons or lone pair of electrons into adjacent π-orbital or p-orbital is called hyperconjugation. It occurs due to overlapping of σ-bonding orbital or the orbital containing a lone pair with adjacent π-orbital or p-orbital.

Conditions for hyperconjugation :

There must be an α-CH group or a lone pair on atom adjacent to sp^2 hybrid carbon or other atoms like nitrogen, oxygen etc.E.g Alkenes,alkyl carbocations,alkyl free radicals, nitro compounds with α- hydrogen
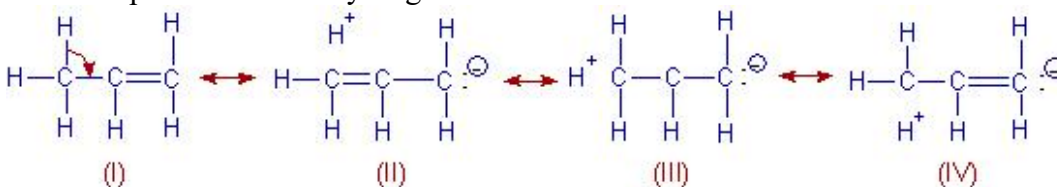
No bond resonance structures shown by propene due to hyperconjugation.

In the contributing structures: (II),(III) & (IV) of propene,there is no bond between an α-carbon and one of the hydrogen atom.Hence the hyperconjugation is also known as "no bond resonance".This type of hyperconjugation is also referred to as sacrificial hyperconjugation since one bond is missing.

Consequences and Application of hyperconjugation :
A)Stability of carbocations (carbonium ions):
The ethyl carbocation, $CH_3-CH_2^+$ is more stable than the methyl carbocation,CH_3^+.This is because, the σ-electrons of the α-CH bond in ethyl group are delocalized into the empty p-orbital of the positive carbon center and thus by giving rise to 'no bond resonance structures' as shown below.Whereas hyperconjugation is not possible in methyl carbocation and hence is less stable.
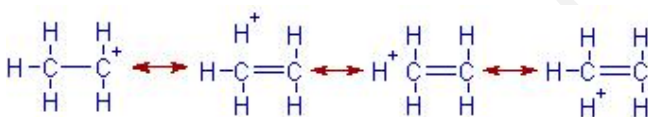
hyperconjugation in ethyl carbonium ion

In general,the stability of carbonium ions increases with increase in the number of alkyl groups (containing hydrogen) attached to the positively charged carbon due to increase in the number of contributing structures to hyperconjugation.Thus the increasing order of stability of carbocations can be given as:methyl<primary<secondary<tertiary as depicted below:
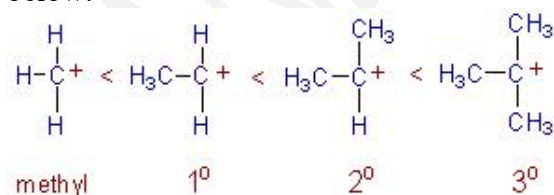
B)Stability of free radicals:

The stability of free radicals is influenced by hyperconjugation as in case of carbonium ions.The σ-electrons of the α-CH bond can be delocalized into the p-orbital of carbon containing an odd electron.Due to hyperconjugation, the stability of free radicals also follow the same order as that of carbonium ions i.e methyl<primary<secondary<tertiary.

C)It also affects the physical properties of compounds.The shortening of C-C bond adjacent to triple bond is due to the contribution of ionic forms.

B)Resonance or Mesomeric effect:

The electron withdrawing or releasing effect attributed to a substituent through delocalization of p or π electrons,which can be visualized by drawing various canonical forms is known as mesomeric effect or resonance effect.It is symbolized by M or R.

Negative resonance or mesomeric effect (-M or -R): It is shown by substituents or groups that withdraw electrons by delocalization mechanism from rest of the molecule and are denoted by -M or -R.The electron density on rest of the molecular entity is decreased due to this effect.

E.g. $-NO_2$, (C=O), $-C{\equiv}N$, -COOH, $-SO_3H$ etc.

Positive resonance or mesomeric effect (+M or +R): Positive mesomeric effect is shown when they release electrons to the rest of the molecule by delocalization.These groups are denoted by +M or +R.Due to this effect,the electron density on rest of the molecular entity is increased.

E.g. -OH, -OR, -SH, -SR, $-NH_2$, $-NR_2$ etc.

Illustrations:

The nitro group,$-NO2$,in nitrobenzene shows -M effect due to delocalization of conjugated π electrons as shown below.Note that the electron density on benzene ring is decreased particularly on ortho and para positions.This is the reason for why nitro group deactivates the benzene ring towards electrophilic substitution reaction.
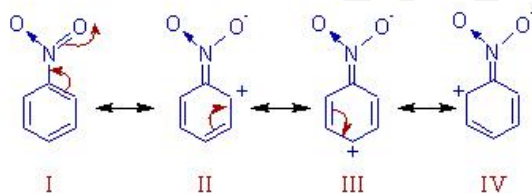
In phenol,the -OH group shows +M effect due to delocalization of lone pair on oxygen atom towards the ring.Thus the electron density on benzene ring is increased particularly on ortho and para positions.
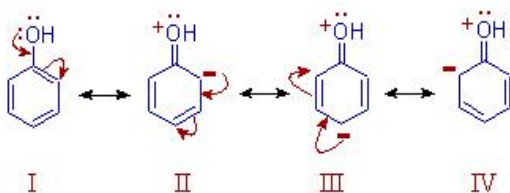
Hence phenol is more reactive towards electrophilic substitution reactions.The substitution is favoured more at ortho and para positions.

Inductive effect:
The polarization of a σ bond due to electron withdrawing or electron donating effect of adjacent groups or atoms is called inductive effect.

Salient features of inductive effect :

A)It arises due to electronegativity difference between two atoms forming a sigma bond.

B)It is transmitted through the sigma bonds.

C)The magnitude of inductive effect decreases while moving away from the groups causing it.

D)It is a permanent effect.

E)It influences the chemical and physical properties of compounds.

1) Negative inductive effect (-I):
The electron withdrawing nature of groups or atoms is called as negative inductive effect. It is indicated by -I.Following are the examples of groups in the decreasing order of their -I effect:
$NH_3^+ > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H$

2) Positive inductive effect (+I):
It refers to the electron releasing nature of the groups or atoms and is denoted by +I. Following are the examples of groups in the decreasing order of their +I effect.
$C(CH_3)3 > CH(CH_3)2 > CH_2CH_3 > CH_3 > H$
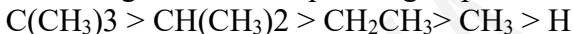
Why alkyl groups are showing positive inductive effect?
Though the C-H bond is practically considered as non-polar,there is partial positive charge on hydrogen atom and partial negative charge on carbon atom.Therefore each hydrogen atom acts as electron donating group.This cumulative donation turns the alkyl moiety into an electron donating group.
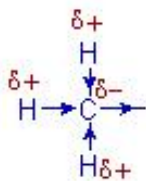
Applications:
A)Stability of carbonium ions:
The stability of carbonium ions increases with increase in number of alkyl groups due to their +I effect.The alkyl groups release electrons to carbon,bearing positive charge and thus stabilizes the ion.The order of stability of carbonium ions is :
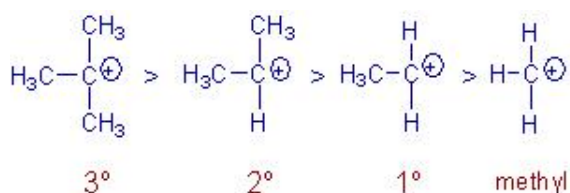
B)Stability of free radicals:
In the same way the stability of free radicals increases with increase in the number of alkyl groups.Thus the stability of different free radicals is:
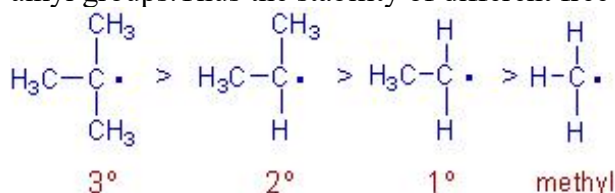
C)Stability of carbanions:
However the stability of carbanions decreases with increase in the number of alkyl groups since the electron donating alkyl groups destabilize the carbanions by increasing the electron density.Thus the order of stability of carbanions is:

Questions for practice:

A)What are the essentials conditions for a compound to be optically active?The presence of chiral carbon is not always important for a compound to be optically active.Explain.

B)In general,it has been said that SN^1 reaction of optically active substrates are accompanied by racemization.But in actual practice,it has been found that there is always some net inversion.How can you account for this observation?
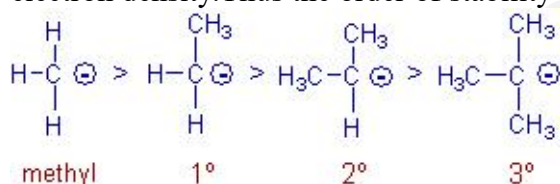
C)Write the structure of meso isomer of 2,3-dichlorobutane.Give reason why it is optically inactive.

D)How would you account for the fact that nucleophilic substitution in 2-chloro-2-methyl propane proceeds by SN^1 or SN^2 mechanism?

E)What do you understand by chiral molecule?Are enantiomers possible in a molecule that donot have chiral carbon atom?Describe with example.

F)Draw the configuration of meso tartaric acid and explain the reason why it is optically inactive.Predict the pairs of enantiomers and diastereomers.Which of them are optically active and which of them are not.Why?

Environmental Chemistry

1)Air Pollution:

Air pollution is one such form that refers to the contamination of the air,irrespective of indoors or outside.A physical, biological or chemical alteration to the air in the atmosphere can be termed as pollution. It occurs when any harmful gases,dust,smoke enters into the atmosphere and makes it difficult for plants,animals and humans to survive as the air becomes dirty.Air pollution could be any substance that holds the potential to hinder the atmosphere or the well being of the living beings surviving in it.The sustainment of all things living is due to a combination of gases that collectively form the atmosphere;the imbalance caused by the increase or decrease of the percentage of these gases can be harmful for survival.

Causes of Air pollution:
1)Burning of Fossil Fuels:

Sulphur dioxide emitted from the combustion of fossil fuels like coal,petroleum and other factory combustibles is one the major cause of air pollution.Pollution emitting from vehicles including trucks, Jeeps, cars, trains,airplanes cause immense amount of pollution.We rely on them to fulfill our daily basic needs of transportation.But,there overuse is killing our environment as dangerous gases are polluting the environment. Carbon Mono oxide caused by improper or incomplete combustion and generally emitted from vehicles is another major pollutant along with Nitrogen Oxides,that is produced from both natural and man made processes.

2)Agricultural activities:

Ammonia is a very common by product from agriculture related activities and is one of the most hazardous gases in the atmosphere.Use of insecticides,pesticides and fertilizers in agricultural activities has grown quite a lot.They emit harmful chemicals into the air and can also cause water pollution.

3)Exhaust from factories and industries:

Manufacturing industries release large amount of carbon monoxide,hydrocarbons, organic compounds, and chemicals into the air thereby depleting the quality of air. Manufacturing industries can be found at every corner of the earth and there is no area that has not been affected by it.Petroleum refineries also release hydrocarbons and various other chemicals that pollute the air and also cause land pollution.

4)Mining operations:

Mining is a process wherein minerals below the earth are extracted using large equipments.During the process dust and chemicals are released in the air causing massive air pollution.This is one of the reason which is responsible for the deteriorating health conditions of workers and nearby residents.

5)Indoor air pollution:

Household cleaning products,painting supplies emit toxic chemicals in the air and cause air pollution. Have you ever noticed that once you paint walls of your house,it creates

some sort of smell which makes it literally impossible for you to breathe.Suspended particulate matter popular by its acronym SPM,is another cause of pollution.Referring to the particles afloat in the air,SPM is usually caused by dust,combustion etc.

Effects of Air pollution:
1)Respiratory and heart problems:
The effects of Air pollution are alarming.They are known to create several respiratory and heart conditions along with Cancer,among other threats to the body.Several millions are known to have died due to direct or indirect effects of Air pollution.Children in areas exposed to air pollutants are said to commonly suffer from pneumonia and asthma.

2)Global warming:
Another direct effect is the immediate alterations that the world is witnessing due to Global warming.With increased temperatures world wide,increase in sea levels and melting of ice from colder regions and icebergs,displacement and loss of habitat have already signalled an impending disaster if actions for preservation and normalization aren't undertaken soon.

3)Acid Rain:
Harmful gases like nitrogen oxides and sulphur oxides are released into the atmosphere during the burning of fossil fuels.When it rains, the water droplets combines with these air pollutants,becomes acidic and then falls on the ground in the form of acid rain.Acid rain can cause great damage to human,animals and crops.

4)Eutrophication:
Eutrophication is a condition where high amount of nitrogen present in some pollutants gets developed on sea's surface and turns itself into algae and and adversely affect fish, plants and animal species.The green coloured algae that is present on lakes and ponds is due to presence of this chemical only.

5)Effect on Wildlife:
Just like humans, animals also face some devastating affects of air pollution.Toxic chemicals present in the air can force wildlife species to move to new place and change their habitat.The toxic pollutants deposit over the surface of the water and can also affect sea animals.

6)Depletion of Ozone layer:
Ozone exists in earth's stratosphere and is responsible for protecting humans from harmful ultraviolet (UV) rays.Earth's ozone layer is depleting due to the presence of chlorofluorocarbons, hydro chlorofluorocarbons in the atmosphere.As ozone layer will go thin,it will emit harmful rays back on earth and can cause skin and eye related problems.UV rays also have the capability to affect crops.

Solutions for Air Pollution:
1)Use public mode of transportation:
Encourage people to use more and more public modes of transportation to reduce

pollution.Also try to make use of car pooling.If you and your colleagues come from the same locality and have same timings you can explore this option to save energy and money.

2)Conserve energy:
Switch off fans and lights when you are going out.Large amount of fossil fuels are burnt to produce electricity.You can save the environment from degradation by reducing the amount of fossil fuels to be burned.

3)Understand the concept of Reduce, Reuse and Recycle:
Do not throw away items that are of no use to you.Infact reuse them for some other purpose.For e.g you can use old jars to store cereals or pulses.
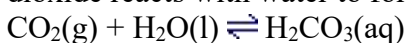
4)Emphasis on clean energy resources:
Clean energy technologies like solar,wind and geothermal are on high these days. Governments of various countries have been providing grants to consumers who are interested in installing solar panels for their home.This will go a long way to curb air pollution.

5)Use energy efficient devices:
CFL lights consume less electricity as against their counterparts.They live longer, consume less electricity,lower electricity bills and also help you to reduce pollution by consuming less energy.Several attempts are being made world wide on a personal, industrial and governmental levels to curb the intensity at which air pollution is rising and regain a balance as far as the proportions of the foundation gases are concerned. This is a direct attempt at slacking Global warming.We are seeing a series of innovations and experiments aimed at alternate and unconventional options to reduce pollutants.

2)Acid Rain:
Acid rain is a widespread term used to describe all forms of acid precipitation (rain,snow, hail,fog etc).Atmospheric pollutants,particularly oxides of sulphur and nitrogen,can cause precipitation to become more acidic when converted to sulphuric and nitric acids,hence the term acid rain.Acid deposition,acid rain and acid precipitation all relate to the chemistry of air pollution and moisture in the atmosphere.It has pH level of less than 5.6. The two primary sources of acid rain are sulphur dioxide (SO_2),and oxides of nitrogen (NOx).Sulphur dioxide is a colourless,prudent gas released as a by-product of combusted fossil fuels containing sulphur.A variety of industrial processes,such as the production of iron and steel,utility factories,and crude oil processing produce this gas.In iron and steel production,the smelting of metal sulphate ore,produces pure metal.This causes the release of sulphur dioxide.Metals such as zinc,nickel, and copper are commonly obtained by this process.Sulphur dioxide can also be emitted into the atmosphere by natural disasters or means.This acidity is due to the reaction of water vapour and non-metal oxides in the atmosphere,such as carbon dioxide and nitrogen oxide,forming dilute acids.carbon dioxide reacts with water to form carbonic acid:
$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$
Since carbonic acid is a weak acid it partially dissociates:

$$CO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
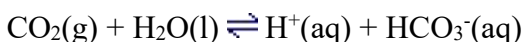
Nitrogen dioxide reacts with water to form a mixture of nitrous acid and nitric acid:
$$2NO_2(g) + H_2O(l) \rightleftharpoons HNO_2(aq) + HNO_3(aq)$$

Acid rain has a pH below 5.6 due mainly to the reaction of water vapour with sulphur dioxide and the oxides of nitrogen.Sulphur dioxide reacts with water to form sulphurous acid (H_2SO_3):
$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$
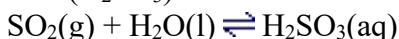
Sulphur dioxide (SO_2) can be oxidised gradually to sulphur trioxide (SO_3):
$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$
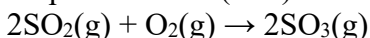
Sulphur trioxide (SO_3) reacts with water to form sulphuric acid (H_2SO_4):
$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$
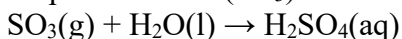
The sulphuric acid and nitric acid remain in a vapour state when the temperature is high. The condensation begins with the fall of temperature and it mingles with the rain, fog or snow and this increases its acidity.The other chemical that is also chiefly responsible for the make-up of acid rain is nitrogen oxide.Oxides of nitrogen is a term used to describe any compound of nitrogen with any amount of oxygen atoms.Nitrogen monoxide and nitrogen dioxide are all oxides of nitrogen.These gases are by-products of firing processes of extreme high temperatures (auto mobiles,utility plants),and in chemical industries (fertilizer production).Natural processes such as bacterial action in soil,forest fires, volcanic action and lightning make up five percent of nitrogen oxide emission.

Effects of Acid Rain:
A)Effect on Aquatic Environment:
Acid rain either falls directly on aquatic bodies or gets run off the forests,roads and fields to flow into streams, rivers and lakes.Over a period of time,acids get accumulated in the water and lower the overall pH of the water body.The aquatic plants and animals need a particular pH level of about 4.8 to survive.If the pH level falls below that the conditions become hostile for the survival of aquatic life.

B)Effect on Forests:
It makes trees vulnerable to disease,extreme weather and insects by destroying their leaves,damaging the bark and arresting their growth.Forest damage due to acid rain is most evident in Eastern Europe-especially Germany,Poland and Switzerland.

C)Effect on Soil:
As it falls on forest or field soil,it kills useful micro-organisms and leaches nutrients of soil.Many a times,this leads to calcium and other nutrient deficiency,producing infertile soils.

D)Effect on Architecture and Buildings:
Acid rain on buildings,especially those constructed with limestone,react with the minerals

and corrode them away.This leaves the building weak and susceptible to decay. Modern buildings,cars,airplanes,steel bridges and pipes are all affected by acid rain. Irreplaceable damage can be caused to the old heritage buildings.

E)Effect on Public Health
When in atmosphere,sulphur dioxide and nitrogen oxide gases and their particulate matter derivatives like sulphates and nitrates,degrades visibility and can cause accidents,leading to injuries and deaths.

Reducing Acid Rain:
There are several ways to reduce acid rain-more properly called acid deposition ranging from societal changes to individual action.It is critical that acid deposition be reduced,not only in the United States and Canada,but also throughout the world to preserve the integrity of natural habitats,as well as to reduce damage to man-made structures.

A)Use alternative energy sources
There are other sources of electricity besides fossil fuels.They include nuclear power, hydropower,wind energy,geothermal energy,and solar energy.Nuclear and hydropower are used most widely in the United States,while wind,solar and geothermal energy have not yet been harnessed on a large enough scale to make them economically-feasible alternatives.There are also alternative energies, such as natural gas,batteries and fuel cells, available to power automobiles.All sources of energy have environmental costs as well as benefits.Nuclear power,hydropower and coal are the cheapest forms of energy today,but advancements in technologies and regulatory developments may change this in the future.All of these factors must be weighed when deciding which energy source to use today and which to invest in for tomorrow.

B)One of the most fundamental acid rain solutions is to utilize fuels that burn more cleanly,or to burn coal more efficiently.This will greatly reduce the possibilities of acid rain developing in the atmosphere.

C)As fast as industrial power plants are concerned,the best solution is to attach devices known as 'scrubbers' in the chimneys of these plants.These scrubbers reduce the amount of sulphur produced in the smoke by 90 – 95%.

D)Vehicles and cars must be mandatory required to comply with very tight and efficient emission standards.Fitting catalytic converters into the exhaust pipes of vehicles also reduces the amount of sulphur dioxide produced by the vehicles.

E)For industrial power plants,there are many more acid rain solutions that must be enforced,as they are clearly the biggest contributors to the formation of acidified water droplets in the atmosphere.Industries must regularly inspect and clean all their emission equipment and chimneys and pipes.

F)All these acid rain solutions will be pointless unless people are informed and educated about the ill-effects and harms of acid rain.A widespread and nationwide effort must be made to make people aware.Only after that is done will all the acid rain solutions actually

make a difference.

Acid rain is one of the biggest environmental hazards that we are facing today,and strong measure must be taken to prevent it,before it is too late.Governments need to sit up and take notice,and do much more than what they are already doing.Acid rain adversely affects plants,animals and human beings, and as a result it is not something that we can afford to ignore.It is our duty towards ourselves and towards our fellow human beings to do all we can to prevent and reduce the presence and increase of acid rain in our environment.

3)**Land/Soil Pollution**

Land pollution, in other words, means degradation or destruction of earth's surface and soil, directly or indirectly as a result of human activities.Anthropogenic activities are conducted citing development, and the same affects the land drastically.The degradation of land that could be used constructively in other words is land pollution.soil pollution is defined as the presence of toxic chemicals (pollutants or contaminants) in soil in high enough concentrations to be of risk to human health and ecosystem.Additionally,even when the levels of contaminants in soil are not of risk,soil pollution may occur simply due to the fact that the levels of the contaminants in soil exceed the levels that are naturally present in soil (in the case of contaminants which occur naturally in soil).

Causes of Land Pollution:
A)Deforestation and soil erosion:
Deforestation carried out to create dry lands is one of the major concerns.Land that is once converted into a dry or barren land,can never be made fertile again,whatever the magnitude of measures to redeem it are.Land conversion, meaning the alteration or modification of the original properties of the land to make it use-worthy for a specific purpose is another major cause.This hampers the land immensely.Also there is a constant waste of land.Unused available land over the years turns barren;this land then cannot be used.So in search of more land,potent land is hunted and its indigenous state is compromised with.

B)Agricultural activities:
With growing human population,demand for food has increased considerably.Farmers often use highly toxic fertilizers and pesticides to get rid off insects,fungi contamination and poisoning of soil.

C) Mining activities:
During extraction and mining activities,several land spaces are created beneath the surface.We constant hear about land caving in;this is nothing but nature's way of filling the spaces left out after mining or extraction Activity.

D)Overcrowded landfills:
Each household produces tonnes of garbage each year.Garbage like aluminium,plastic,paper, cloth,wood is collected and sent to the local recycling unit.Items that can not be recycled become a part of the landfills that hampers the beauty of the city

and cause land pollution.

E)Industrialization:
Due to increase in demand for food, shelter and house, more goods are produced.This resulted in creation of more waste that needs to be disposed of.To meet the demand of the growing population,more industries were developed which led to deforestation.Research and development paved the way for modern fertilizers and chemicals that were highly toxic and led to soil contamination.

F)Construction activities:
Due to urbanization, large amount of construction activities are taking place which has resulted in large waste articles like wood,metal,bricks,plastic that can be seen by naked eyes outside any building or office which is under construction.

G)Nuclear waste:
Nuclear plants can produce huge amount of energy through nuclear fission and fusion. The left over radioactive material contains harmful and toxic chemicals that can affect human health.They are dumped beneath the earth to avoid any casualty.

H)Sewage treatment:
Large amount of solid waste is leftover once the sewage has been treated.The leftover material is sent to landfill site which end up in polluting the environment.

Effects of Land Pollution
A)**Change in climate patterns**:
 The effects of land pollution are very hazardous and can lead to the loss of ecosystems. When land is polluted, it directly or indirectly affects the climate patterns.

B)Environmental Impact:
When deforestation is committed, the tree cover is compromised on.This leads to a steep imbalance in the rain cycle.A disturbed rain cycle affects a lot of factors.To begin with, the green cover is reduced.Trees and plants help balance the atmosphere,without them we are subjected to various concerns like global warming,the green house effect, irregular rainfall and flash floods among other imbalances.

C)Effect on human health:
The land when contaminated with toxic chemicals and pesticides lead to problem of skin cancer and human respiratory system.The toxic chemicals can reach our body through foods and vegetables that we eat as they are grown in polluted soil.

Solutions for Land Pollution
A)Making people aware about the concept of Reduce, Recycle and Reuse.
B)Reducing the use of pesticides and fertilizers in agricultural activities.
C)Avoiding buying packages items as they will lead to garbage and end up in landfill site.
D)Ensure that you do not litter on the ground and do proper disposal of garbage.
E)Using biodegradable products.

F)Doing Organic gardening and eat organic food that will be grown without the use of pesticides.

G)Creating dumping ground away from residential areas.

Several creatures survive under the land too.Disrupting the harmony of the land,is disrupting their habitat.We walk and survive on land.It is literally the base of our ecosystem.It is in our good interest to take care of it and nurture it.

4)Ozone layer depletion:

Ozone is a colorless gas found in the upper atmosphere of the Earth.It is formed when oxygen molecules absorb ultraviolet photons, and undergo a chemical reaction known as photo dissociation or photolysis.In this process,a single molecule of oxygen breaks down into two oxygen atoms.The free oxygen atom (O),then combines with an oxygen molecule (O_2),and forms a molecule of ozone (O_3).The ozone molecules, in turn absorb ultraviolet rays between 310 to 200 nm(nanometers) wavelength,and thereby prevent these harmful radiations from entering the Earth's atmosphere.The process of absorption of harmful radiation occurs when ozone molecules split up into a molecule of oxygen, and an oxygen atom.The oxygen atom (O),again combines with the oxygen molecule(O_2) to regenerate an ozone (O_3) molecule.Thus,the total amount of ozone is maintained by this continuous process of destruction and regeneration.

Causes of Ozone Depletion

Ozone is a triatomic form of oxygen (O_3),found in the Earth's atmosphere.A combination of low temperatures,elevated chlorine and bromine concentrations in the upper stratosphere are responsible for the destruction of ozone.The production and emission of chlorofluorocarbons (CFCs),is the leading cause of ozone layer depletion.CFC's accounts for almost 80% of the total depletion of ozone.Other ozone-depleting substances,include hydrochlorofluorocarbons (HCFCs),and volatile organic compounds.These are often found in vehicle emissions,byproducts of industrial processes,refrigerants and aerosols.Ozone-depleting substances are relatively stable in the lower atmosphere of the Earth,but in the stratosphere,they are exposed to ultraviolet radiation and thus,they break down to release a free chlorine atom.

This free chlorine atom reacts with an ozone molecule (O_3),and forms chlorine monoxide (ClO),and a molecule of oxygen.Now,ClO reacts with an ozone molecule to form a chlorine atom,and two molecules of oxygen.The free chlorine molecule again reacts with ozone to form chlorine monoxide.The process continues, and this results in the depletion of the ozone layer.As ozone depletes in the stratosphere,it forms a 'hole' in the layer.This hole enables harmful ultraviolet rays to enter the Earth's atmosphere.Ultraviolet rays of the Sun are associated with a number of health-related and environmental issues.Let us take a look at how ozone depletion affects different life forms.

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

$Cl + O_3 \rightarrow ClO + O_2$
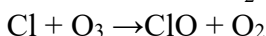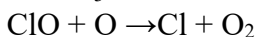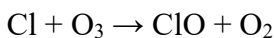
Impact on Humans:

A)Skin cancer:

Exposure to ultraviolet rays poses an increased risk of developing several types of skin cancers,including malignant melanoma, basal and squamous cell carcinoma.Exposure to UV radiations due to ozone depletion may cause leukemia and breast cancer.

B)Eye damage:

Direct exposure to UV radiations can result in photokeratitis and cataracts.

C)Immune system damage:

Effects of UV rays include impairment of the immune system.Increased exposure to UV rays weakens the response of the immune system.

D)Accelerated ageing of skin:

Constant exposure to UV radiation can cause photo allergy,which results in the outbreak of rash in fair-skinned people.Exposure to radiations due to ozone depletion has been reported to cause DNA breakage,inhibition and alteration of DNA replication and premature ageing in human beings.

E)Other effects:

Ozone chemicals can cause difficulty in breathing,chest pain,throat irritation, and hamper lung functioning.

Effects on Amphibians:

Ozone depletion is listed as one of the causes for the declining numbers of amphibian species.Ozone depletion affects many species of amphibians at every stage of their life cycle.Some of the effects are mentioned below.

A)Hampers growth and development in larvae

B)Changes behaviour and habits

C)Causes deformities in some species

Effects on Marine Ecosystems:

In particular,plankton (phytoplankton and bacterioplankton) are threatened by increased

UV radiation.Marine phytoplankton play a fundamental role in both the food chain as well as the oceanic carbon cycle.Plankton play an important role in converting atmospheric carbon dioxide into oxygen.Ultraviolet rays can influence the survival rates of these microscopic organisms by affecting their orientation and mobility.This eventually disturbs and affects the entire ecosystem.

Prevention and Control of Depletion of the Ozone Layer:
Banning the production and use of ozone depleting substances is one important way of preventing further depletion of the ozone layer in the stratosphere.On the other hand, alternatives to these chemical compounds should also be searched out so as to replace these chemicals.Scientists of the University of California,U.S.A devised a possible way of plugging the ozone hole by injecting alkanes or propanes into the atmosphere of Antarctica.The alkanes have the affinity of reacting with ozone destroying chlorine atoms. According to the scientists, about 50,000 tones of alkane or propane would have to be blown to check the ozone loss.These chemicals could be released from an altitude of about 15 km by a group of hundreds of large aircrafts.

Other measures are:
A.Minimize high altitude aircraft flights (oxygen reduction and water vapour deposition)
B.Minimize rocket flights (water vapour deposition)
C.Encourage growth of plants that produce oxygen, discourage deforestation
D.Decrease /control releases of high temperature steam/moisture to the atmosphere
E.Eliminate production and release of known ozone depleting chemicals (such as CFCs) where remotely possible.Subsidize production of safer alternatives where possible.
F.Establish controls to assure that new compounds to be used in high volume,are surveyed for effect on ozone.
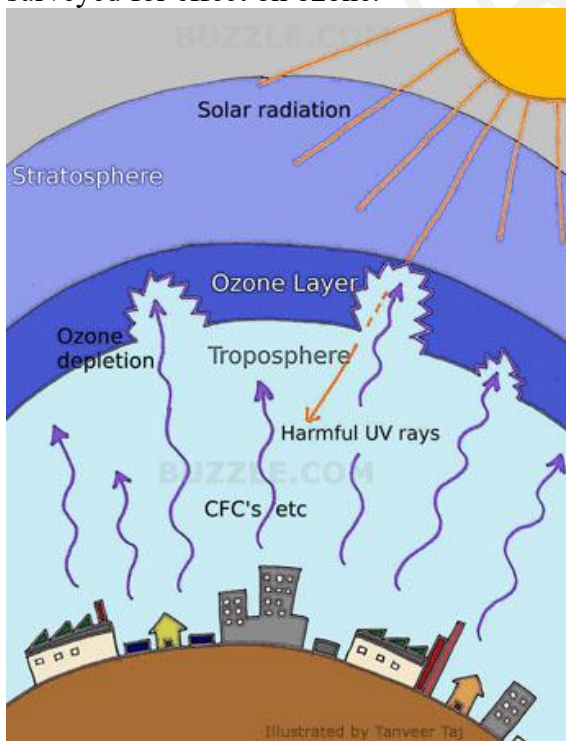
5)Define hardness of water.What are the cause and type of hardness of water?

=The presence of salt of calcium and magnesium in water which forms a scum with soap and prevents the formation of lather is known as hardness of water.

The cause of hardness is due to soluble salt of calcium and magnesium only,specially due to presence of chlorides,sulphates and bicarbonates of calcium and magnesium.
Hardness of water is of two types:

Temporary Hardness:

Temporary hardness is caused due to the presence of bicarbonates of calcium and magnesium.It can be easily removed by boiling.

$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$

$Mg(HCO_3)_2 \rightarrow MgCO_3 + CO_2 + H_2O$

It can be removed by adding lime(calcium hydroxide),which gives precipitates of calcium carbonate.

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + H_2O$

$Mg(HCO_3)_2 + Mg(OH)_2 \rightarrow 2MgCO_3 \downarrow + H_2O$
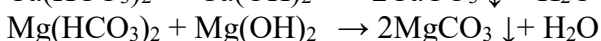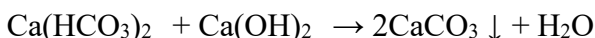
Permanent Hardness:

It is caused due to presence of sulphates and chlorides of calcium and magnesium.It can't be removed by boiling.But it can be removed by ion-exchange method using zeolites or treating with Na_2CO_3.

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + NaCl$
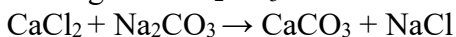
The hardness of water is not a pollution parameter but indicates water quality.Hard water posses considerable problem in washing,it reduces the efficiency of boiler.It causes bad effect in our digestive system.

6)Define lubricants.How are they classified?Write down their functions.

=Lubricants are those substances introduced between two moving/sliding surfaces with a view to reduce the frictional resistance between them.The main purpose of a lubricant is to keep the sliding surfaces apart so that frictional resistance and consequent destruction of material is minimized.The process of reducing frictional resistance between sliding surfaces by the introduction of lubricants in-between them is called **lubrication**.

Functions:

A)It reduces surface deformation,wear and tear because the direct contact between the rubbing surfaces is avoided.

B)It reduces loss of energy in the form of heat.i.e it is used as coolant.

C)It reduces waste of energy,so that efficiency of machine is enhanced.

D)It reduces expansion of metals by local frictional heat.

E)It reduces maintenance and running cost of the machine.

F)It avoids unsmooth relative motion of the moving parts.

Classification:

It can be classified on the basis of their physical state as follow:

1)Liquid lubricants or lubricating oils

2)Semi-solid lubricants or greases.

3)Solid lubricants.

1)Liquid lubricants or lubricating oils:
A)Animal and vegetable oils posses oiliness (a property by virtue of which the oil sticks to the surface of machine parts,even under high temperature and heavy loads).However they are costly,undergo oxidation easily forming acidic products and get thickened on coming in contact with air.`

B)**Mineral or petroleum oils** are obtained by distillation of petroleum.These are the most widely used lubricants because they are cheap,available in abundance and quite stable under service conditions.However,they posses poor oiliness as compared to that of animal and vegetable oils.

2)Semi-solid lubricants or greases:
Lubricating grease is a semi solid consisting of a soap dispersed throughout a liquid lubricating oil.Greases are prepared by saponification of fats with alkali followed by adding hot lubricating oil while under agitation.Greases have higher shear or frictional resistances than oils and therefore can support much heavier loads at lower speed.Greases are used in:
A)Situations where oil cannot remain in place,due to high load,low speed, intermittent operation,sudden jerks etc.
B)In bearing and gears that wok at high temperature.
C)In situations where bearing needs to be sealed against entry of dust,dirt and grit or moisture because greases are liable to contamination by these.

Types of greases:
A)Soda-base greases
B)Calcium-based greases
C)Axle greases
D)Lithium-based greases.

3)Solid lubricants:
Solid lubricants are used where
A)Operating conditions are such that a lubricating film cannot be secured by use of oils or greases.
B)The operating temperature or load is very high.
C)Contamination of oil or greases is unacceptable.

Solid lubricants are used either in the dry powder form or mixed with water or oil.Graphite,molybdenum disulphide,soapstone talc,mica etc can be used as solid lubricants.

Polymer Chemistry:

1)What is difference between thermosetting plastics and thermoplastics?
Thermosetting Plastics:

Thermosetting Curing Process:
Thermosetting plastics contain polymers that cross-link together during the curing process to form an irreversible chemical bond.The cross-linking process eliminates the risk of the product remelting when heat is applied,making thermosetting ideal for high-heat applications such as electronics and appliances.

Features & Benefits:
Thermosetting plastics significantly improve the material's mechanical properties, providing enhances chemical resistance,heat resistance and structural integrity. Thermosetting plastics are often used for sealed products due to their resistance to deformation.

Pros:
- More resistant to high temperatures than thermoplastics
- Highly flexible design
- Thick to thin wall capabilities
- Excellent aesthetic appearance
- High levels of dimensional stability
- Cost-effective

Cons:
- Cannot be recycled
- More difficult to surface finish
- Cannot be remoulded or reshaped

Thermoplastics:
Thermoplastics Curing Process:
Thermoplastics pellets soften when heated and become more fluid as additional heat is applied.The curing process is completely reversible as no chemical bonding takes place. This characteristic allows thermoplastics to be remoulded and recycled without negatively affecting the material's physical properties.

Features & Benefits:
There are multiple thermoplastic resins that offer various performance benefits,but most materials commonly offer high strength,shrink-resistance and easy bend ability. Depending on the resin, thermoplastics can serve low-stress applications such as plastic bags or high-stress mechanical parts.

Pros:
- Highly recyclable
- Aesthetically-superior finishes
- High-impact resistance

- Remolding/reshaping capabilities
- Chemical resistant
- Hard crystalline or rubbery surface options
- Eco-friendly manufacturing

Cons:
- Generally more expensive than thermosetting plastic
- Can melt if heated

2)**Define polymers.Differences between additional and condensation polymers.**
Polymers are long chain giant organic molecules are assembled from many smaller molecules called monomers.Polymers consist of many repeating monomer units in long chains.A polymer is analogous to a necklace made from many small beads (monomers). Polymerization is the process of joining together a large number of small molecules to make a smaller number of very large molecules.The reactants (i.e. the small molecules from which the polymer is constructed) are calledMonomers and products of the polymerization process are called Polymers.There are significant differences between the chemical and physical properties of polymers and those of the monomers from which they are made.This polymerization process can occur by two different mechanisms:by addition polymerisation and condensation polymerisation.

Natural Polymers:
which include proteins starch,cellulose and rubber.

Synthetic Polymers:
include bakelite,perspex,terylene (a polyester) and nylon (a polyamide).These are man made polymers,which are also called plastics.

In **addition polymerization**,the polymer has the same empirical formula as the monomer but a higher molecular mass.An example is the polymerization of chloroethene (vinyl chloride) to form poly(chloroethene),PVC.
An addition polymer is formed by a reaction known as polyaddition or addition polymerization.This can occur in a variety of ways including free radical polymerization, cationic polymerization,anionic polymerization and coordination polymerization.

Monomer Name	Polymer Name
Ethene	Polyethene
Propene	Polypropene
Vinyl Acetate	Polyvinylacetate
Styrene	Polystyrene

$$n\,CH_2{=}CHCl \longrightarrow {-}[CH_2{-}CHCl]{-}_n$$

chloroethene   poly(chloroethene)

In **condensation polymerization**,polymerization of one or more monomers is

accompanied by the elimination of small molecules (such as water or ammonia).For example,in producing polyamide 6,6,two monomers are used.Condensation polymerization a form of step-growth polymerization,is a process by which two molecules join together,resulting loss of small molecules which is often water.The type of end product resulting from a condensation polymerization is dependent on the number of functional end groups of the monomer which can react.
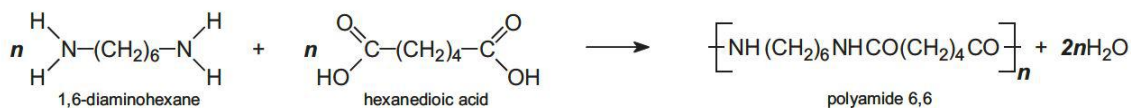

Condensation polymers,unlike addition polymers, may be biodegradable.The peptide or ester bonds between monomers can be hydrolysed by acid catalysts or bacterialenzymes breaking the polymer chain into smaller pieces.The most commonly known condensation polymers are proteins,fabrics such as nylon,silk or polyester.

3)Nylon 6,6 :
Polyamides are a versatile family of thermoplastics that have a broad range of properties ranging form relative flexibility to significant stiffness, strength and toughness.Major properties such as resistance to chemicals,toughness,thermal stability,good appearance and good processability are key considerations that make nylon suitable for engineering plastic applications.Polyamides comprise a wide range of materials, depending on the monomers employed.Commonly used products are designated as nylon 6; 6,6; 6,12;11 and 12 with the nomenclature designating the number of carbon atoms that separate the repeating amide group.Nylon 6 and Nylon 6,6 continue to be the most popular types among polyamide commercial products,still accounting for more than 90 percent of nylon used in global market.

Preparation of Nylon-6,6:
Nylon 6,6 is prepared from the polymerization of adipic acid and hexamethylenediamine. The need to control a 1:1 stoichiometric balance between the two monomers can be improved by the fact that adipic acid and hexamethylenediamine form a 1:1 salt that can be isolated.Nylon 6,6 is known for high strength,toughness, and abrasion resistance.It has a melting point of 265°C and can maintain properties up to 150°C.112 Nylon 6,6 is used extensively in nylon fibers that are used in carpets,hose and belt reinforcements, and tire cord.Nylon 6,6 is used as an engineering resin in a variety of molding applications such as gears,bearings,rollers,and door latches,because of its good abrasion resistance and self-lubricating tendencies.
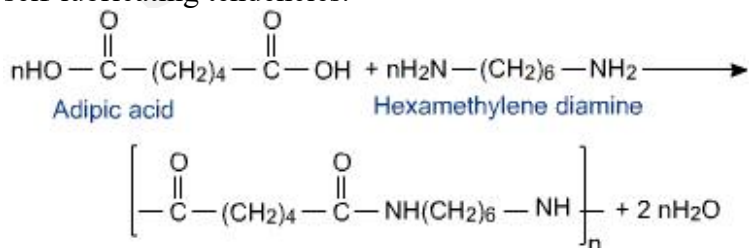
The physical properties of nylon 6,6 is that :
1.Nylon 6,6 has a repeat unit with molecular weight of is 226.32 g/mol and crystalline density of 1.24 gcm^{-3} .
2.Nylon 6,6 has long molecular chains resulting in more hydrogen bonds,creating chemical springs and making it very resilient .
3.Nylon 6,6 is an amorphous solid so it has a large elastic property and is slightly soluble in boiling water .
4.Nylon 6,6 is very stable in nature.
5.Nylon 6,6 is very difficult to dye but once it is dyed it has a high color fastness and is less susceptible to fading .
6.Its chemical properties does not allow it to be affected by solvents such as water , alcohol etc.

Advantages:
1.Nylon 6,6 persues excellent abrasion resistance and a high melting point .
2.Nylon 6,6 has high tensile strength and exhibits only half of shrinkage in steam .
3. It also provides a very good resistance to photo degradation .
4.Nylon 6,6 also has good advantage over industrial products because it reduces moisture sensitivity in raw products and has a high dimensional stability and melting point.The fact that makes Nylon 6,6 resistant towards heat and fraction and enables it to withstand the heat for retention is that it has a melting point of 265°C for a high synthetic fiber .

The applications of Nylon 6,6 is are:
A)Because Nylon is a light material,it is used in parachutes .
B)Nylon 6,6 is waterproof in nature so it is also used to make swimwear.
C)Nylon 6,6 having a high melting point make it more resistant to heat and friction so it is suitable to be used in airports,offices and other places which are more liable to wear and tear .
D)Nylon 6,6 being waterproof in nature is used to make machine parts.It is also used in the following like airbags,carpets,ropes etc.Hence Nylon 66 is a very useful creation by mankind .

4)Write short notes on vulcanization of rubber.Difference between natural and synthetic rubber.Give types & properties of synthetic rubber.
=Rubbers(Elastomers) are high polymers,which have elastic properties in excess of 300 percent.The unstreteched rubber is amorphous.

Vulcanization of rubber:
Rubber has many drawbacks such as:
A)It is plastic in nature i.e it becomes soft at high temperature and too brittle at low temperature.
B)It is weak.
C)It has larger water absorption capacity.
D)It is non resistant to non polar solvents like vegetable and mineral oils,gasoline, benzene.
E)It has little durability.

F)It perishes due to oxidation in air.
G)It is attacked by oxidizing agent like nitric acid,concentrated sulphuric acid,chromic acid etc

Vulcanization Process

Natural Rubber   Vulcanized Rubber
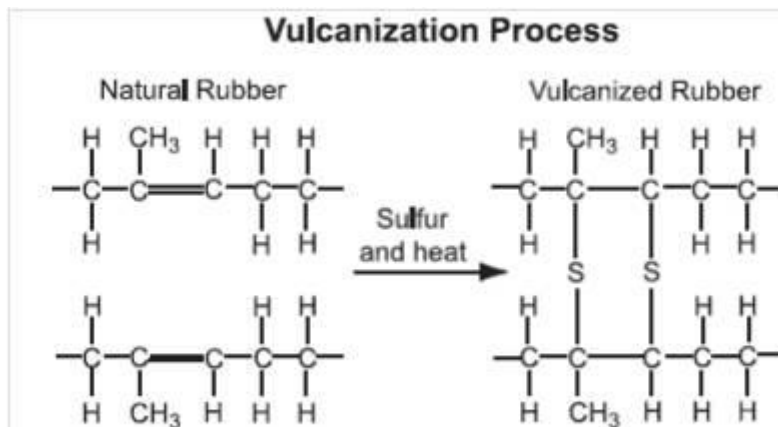
To improve properties of rubber,it is compounded with some chemicals like sulphur,hydrogen,benzoyl chloride etc.Most important addition is sulphur.The process consists in heating the raw-rubber with sulphur to 100-140°C.The added sulphur combines chemically at the double bonds of different rubber springs.Vulcanization thus serves to stiffen the material by a sort of anchoring and consequently preventing intermolecular movement of rubber springs.The extent of stiffness of vulcanized rubber depends upon the amount of sulphur added.For example:a tyre rubber contains 3 to 5% sulphur while a battery rubber contains 30% sulphur.Vulcanite or ebonite or haed rubber contains 32% sulphur.The cross linking of the isoprene spirals is attained to such an extent that vulcanite has practically no elasticity.Thus vulcanite is tough,high abrasion-resistant can be moulded,sawn,drilled and polished.It has extremely good electrical insulation property.

Advantages of vulcanization:
A)It has good tensile strength and extensibility,when a tensile force is applied,can bear a load of 2000 kg/cm^2 before it breaks.
B)It has excellent resilience i.e article made from it returns to the original shape,when the deforming load is removed.
C)It possesses low water absorption tendency.
D)It has higher resistance toward oxidation and abrasion.
E)It has much higher resistance to water as compared to raw rubber.
F)It is better electrical insulator,although it tends to absorb small amount of water.
G)It is resistant to organic solvents(benzene,petrol),fats and oils.However ,it swells in these liquids.
H)It is very easy to manipulate the vulcanized rubber to produce the desired shape.
I)It has useful temperature range of -40 to 100°C.
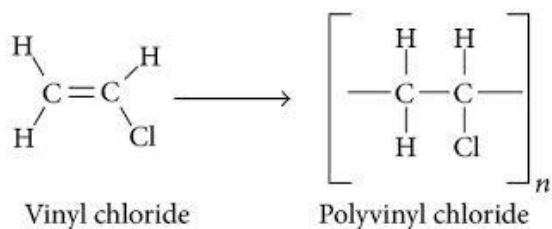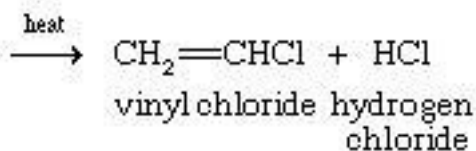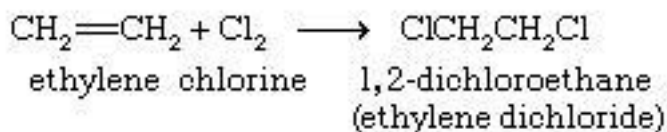J)It has low elasticity,depending on the extent of vulcanization.Vulcanite has practically no elasticity.

Properties of Natural Rubber:

Natural rubber combines high tensile and tear strength with an outstanding resistance to fatigue.Exhibits excellent dynamic properties with a low hysteresis which leads to low heat generation.Natural rubber has been successfully used as an engineering material for many years.The following range of properties shows just how versatile of a material natural rubber has proven to be to engineers:

1)Adjustable hardness from very soft to very hard (ebonite).
2)Appearance and color ranges from translucent (soft) to black (hard).
3)Compounded to meet nearly any mechanical requirement.
4)The ability to be electrically insulating or fully conductive.
5)Protect,insulate and sealing properties.
6)Absorb vibration and silence noise.
7)Available in any surface roughness and shape.

5)Write preparation,properties and uses of PVC.

=Polyvinyl chloride is obtained by heating a water-emulsion of vinyl chloride in presence of a small amount of benzyl peroxide or hydrogen peroxide in an autoclave under pressure.Vinyl chloride so needed is generally prepared by treating acetylene at 1 to 15 atmospheres pressure with hydrogen chloride at 60°-80°C,in presence of metal chloride as catalyst.

$$CH_2{=}CH_2 + Cl_2 \longrightarrow ClCH_2CH_2Cl$$

ethylene chlorine   1,2-dichloroethane
(ethylene dichloride)

$$\xrightarrow{heat} CH_2{=}CHCl + HCl$$

vinyl chloride hydrogen chloride

Vinyl chloride   Polyvinyl chloride

Properties:

A)PVC is colorless,non inflammable and chemically inert powder(specific gravity 1.33).
B)It is resistant to light,atmospheric oxygen,inorganic acids and alkalis but soluble in hot chlorinated hydrocarbons such as ethyl chloride.Pure resin possesses a high softening point(148°C)and a greater stiffness and rigidity compared to polythene,but is brittle.

Uses:

A)Rigid PVC or unplasticized PVC have superior chemical resistance and high rigidity,

but is brittle.It is used for making sheets,which are employed for tank linings,light fittings,safety helmets,refrigerator components,tyres,cycle and motorcycle mudguards.

B)Plasticized PVC is used for making continuous sheets(of different thickness from 0.1 mm to 8mm).Employed for packaging raincoats,table clots and curtains,electrical insulation like coverings of electric cables.

6)Write preparation,properties and uses of polyethylene.
=Polyethylene is obtained by the polymerization of ethylene.The gas is first liquefied under high pressure(upto 1500 atm)and then pumped into a heated pressure vessel, maintained at 150 to 250°C.By catalytic effect of traces oxygen present,ethylene is polymerized into polyethylene,a waxy solid,which comes out from the peroforation in the bottom of the vessel.
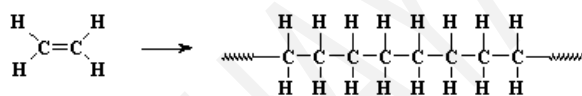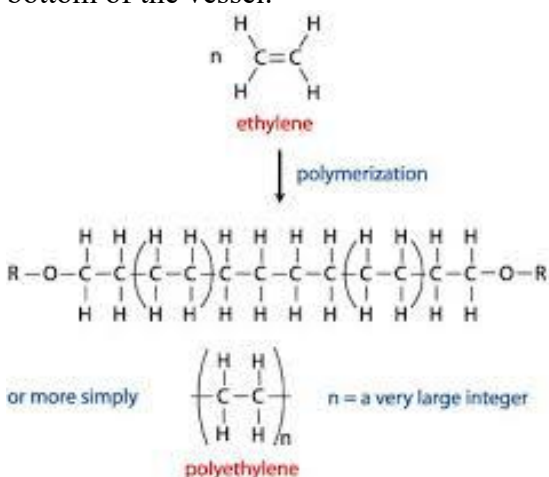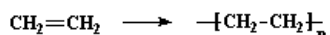
By using free radical initiator,low density polyethylene is obtained;while using ionic catalyst,high density polyethylene is obtained.

Properties:
A)It is rigid.waxy,white.translucent,non polar material exhibiting considerable chemical resistance to strong acids,alkalis and salt solutions at room temperature.

B)It is good insulator of electricity.

C)It crystallizes very easily due to highly symmetrical chain structure.

Uses:
For making high frequency insulator parts,bottle caps,flexible bottles,kitchen and domestic appliances,toys,sheets for packing materials,chemical plants,tubes,pipes,coated wires and cables,bags for packing etc.

7)Give the preparation method and use of TNT.
2,4,6 Trinitrotoluene(TNT) is a high explosive made by nitrating toluene.

Preparation:
TNT is prepared by the nitration of toluene using a nitrating mixture of conc.HNO_3 and conc.H_2SO_4 in 3:1 ratio in a tank reactor,in which contents are continuously stirred.
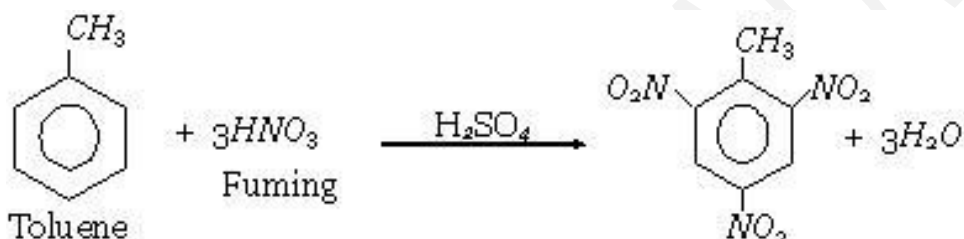
Then,liquid product (TNT) so formed is taken out,washed with ammoniacal solution of Na_2SO_3 and then with cold water,when TNT crystallizes out.Crystals of TNT are filtered and purified by melting.The melt is dried by passing warm air and poured in containers.

Properties:
A)It is safe explosive in manufacture,transportation and storage.
B)It is non hygroscopic.
C)It is a violent disruptive explosive.
D)It does not react with metals to form unstable compounds.

Uses:
A)It is most widely used in shell firing and under water explosions and is well suited for loading in containers because of its low melting point(81°C).
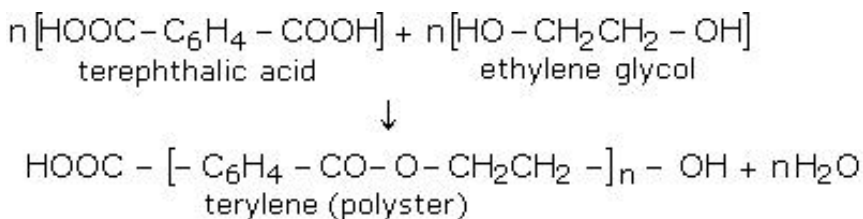
8)Polyester
Polyester is the general name given to all polymers that contain multiple ester [-R-CO-O] groups as monomers.Terylene is an example of polyester.This synthetic fibre was first developed in England.

Preparation:
Polyesters are prepared by the condensation polymerization of a dicarboxylic acid with a dihydric alcohol with the elimination of water.For example,terylene (or Dacron) is

prepared from terephthalic acid and ethylene glycol by condensation polymerization with the elimination of water.

$$n[HOOC-C_6H_4-COOH] + n[HO-CH_2CH_2-OH]$$
$$\text{terephthalic acid} \qquad\qquad \text{ethylene glycol}$$
$$\downarrow$$
$$HOOC - [-C_6H_4-CO-O-CH_2CH_2-]_n - OH + nH_2O$$
$$\text{terylene (polyster)}$$

Like nylon,terylene is also a thermosetting polymer.It can be extruded below its melting point through fine holes in a spinneret to form the fibres.

Properties of Polyester:
Polyester is,
A)Very strong.So garments made from polyester fibres last longer than the ones made from natural fibres.

B)Very resistant to wrinkles.Polyester garments retain their crease.

C)Not a good absorbent of water.Therefore polyester clothes dry faster.
D)Highly abrasion and moth resistant.

E)Resistant to ordinary chemicals and biological agents.

Uses of Polyester Fibres:
Polyester is used in making:
A)Textiles,sarees dress materials and curtains.

B)Blended textiles with natural fibres.For example,when terylene is mixed with cotton,it is called terrycot and with wool,it is called terrywool.These blended fibres are again used in making a whole range of textiles and garments.

C)Sails for sailboats that are light,strong,don't stretch and don't rot in contact with water

D)Water hoses for fire-fighting operations.

E)Convey or belts.

Extra

1)Markovnikov's rule:
Markovnikov addition,also called Markovnikov's rule,states that a protic acid (HX) will add to an alkene such that the proton will bond to the less substituted carbon.
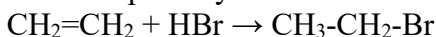
Markovnikov's rule:
"When an unsymmetrical alkene reacts with a hydrogen halide to give an alkyl halide,the hydrogen adds to the carbon that has the greater number of hydrogen substituents and the halogen to the carbon having the fewer number of hydrogen substituents"

$$CH_3-CH=CH_2 \quad \xrightarrow{HBr} \quad CH_3\overset{\overset{\displaystyle Br}{|}}{C}HCH_3$$
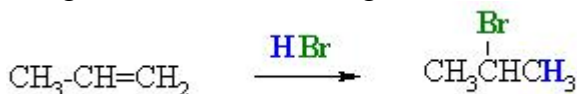
Compounds having multiple bonds like double bond,triple bond between carbon atoms are called unsaturated compounds.They can undergo addition reaction with atoms/groups to become saturated.Hence,alkenes containing double bond between carbon atoms and alkynes containing triple bond between carbon atoms are more reactive than alkanes.
For example:ethylene on addition with HBr gives ethyl bromide
$CH_2=CH_2 + HBr \rightarrow CH_3-CH_2-Br$

The addition reaction mainly takes place due to attraction of the π electrons in unsaturated compounds by the electrophiles(positively charged species).Hence all the reactions are electrophilic addition reactions.

Markovnikov Rule Reaction Mechanism:
Markovnikov rule can be explained by the below mentioned mechanism.Consider the addition of HBr to propene.The proton (H^+) is added to propene to give a carbocation. There are two possibilities of carbocations,a primary or secondary.
$CH_3-CH=CH_2 + H^+ \rightarrow CH_3-CH^+- CH_3 + CH_3-CH_2-CH_2^+$

Here,secondary carbocation is more stable due to +I effect of 2 methyl groups. Hence it will form predominantly and the addition of Br^- to the carbocation will give 2-bromo propane.Hence 2-Bromo propane is the major product formed.
$CH_3-CH^+-CH_3 + Br^- \rightarrow CH_3-CH(Br)-CH_3$
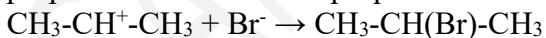
2)Nitration:
A nitro group can be introduced into benzene by using a nitrating mixture to form nitro benzene.The nitrating mixture is a mixture of concentrated nitric acid and concentrated sulphuric acid.Here sulphuric acid acts as catalyst and responsible for the formation of electrophile that is nitronium ion (NO^{2+}).When benzene is treated with this nitrating mixture at a temperature below 50°C,it forms nitrobenzene.It is an example of electrophilic substitution reaction of benzene and completed through the formation of arenium ion as an intermediate.Since sulphuric acid is a strong acid than nitric acid,it gets protonated the nitric acid which causes the loss of a water molecule and form electrophile, nitronium ion.In the absence of sulphuric acid,it is not possible to protonate the nitric acid
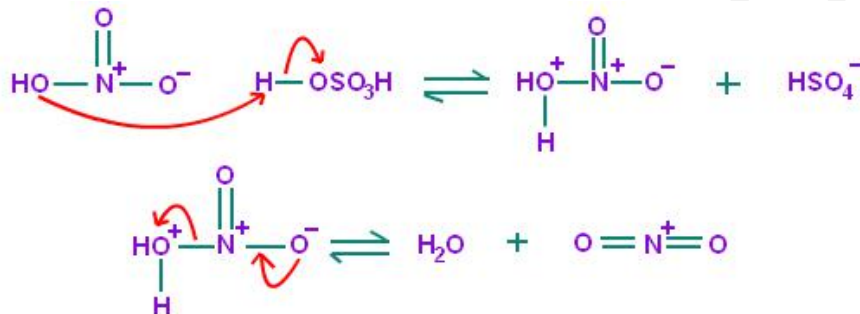
due to its acidic properties.
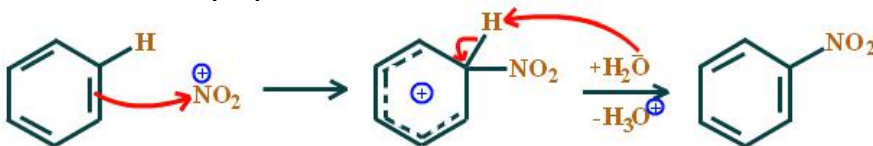
Nitration Mechanism

The reaction of benzene with concentrated nitric acid and sulphuric acid give nitro benzene.This reaction is known as nitration of benzene.It follows electrophilic substitution mechanism and completed in three steps.
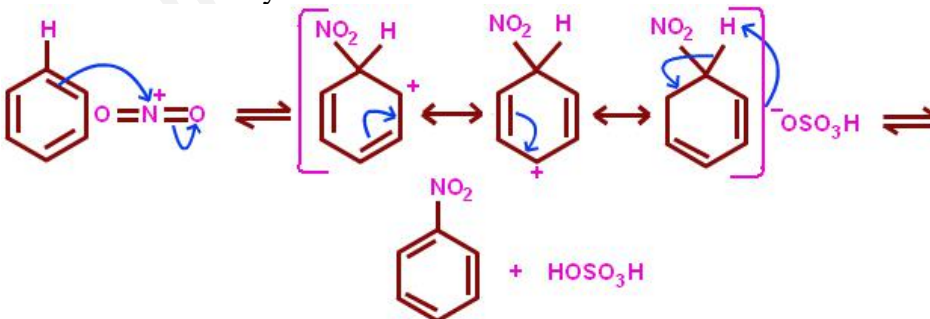
The presence of concentrated sulphuric acid activates the nitric acid to form a stronger electrophile;nitronium ion (NO^{2+}).Since this is the reaction between two acids therefore one acts as Bronsted acid and another as Bronsted base.Out of these two acids sulphuric acid is a stronger one,hence acts as Bronsted acid and protonated nitric acid.The protonation of nitric acid results lose of water molecule and form nitronium ion.

In the second step,electrophile attacks on benzene ring to form intermediate and lose the aromaticity.
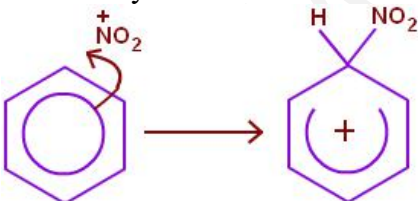
Further this intermediate reacts with base that is bisulphate ion (HSO_4^- ion) produce in first step.Base gets deprotonate the intermediate to form nitrobenzene and sulphuric acid which acts as a catalyst for reaction.

3)Sulphonation:

The replacement of hydrogen atom of benzene by a sulphonic acid group ($-SO_3H$) is called as sulphonation of benzene.The reaction is carried out in the presence of concentrated sulphuric acid containing dissolved sulphur trioxide which is also known as fuming sulphuric acid.The sulphonation of benzene results the formation of benzene sulphonic acid.
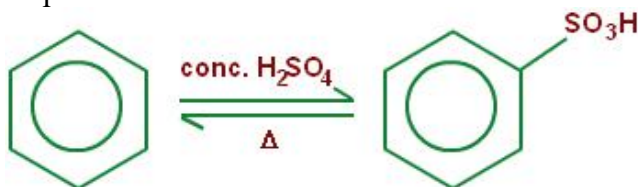

In sulphonation of benzene sulphur trioxide acts as electrophile produced from concentrated sulphuric acid.The reaction is reversible in nature;hence the rate of reaction can increase with increasing the electrophile content.The sulphonation of benzene can be carried out by two ways,either by refluxing the benzene with concentrated sulphuric acid for several hours or refluxing the warm benzene at 313 K temperature for 20-30 minutes.

Sulphonation Mechanism

The sulphonation of benzene is a multi step reaction completed in four steps through the formation of sigma complex as an intermediate.Sulphur trioxide acts as intermediate in reaction and produced by auto-protolysis of sulphuric acid.Reaction gets complete in following steps:

Formation of electrophile:

The auto-protolysis of sulphuric acid results in the formation of sulphur trioxide which acts as electrophile due positively charged sulphur atom in polar sulphur trioxide molecule and reacts with benzene.
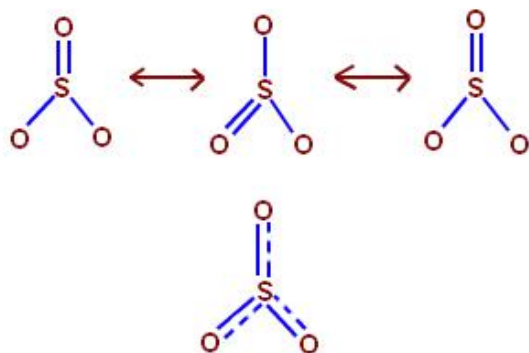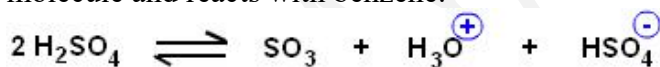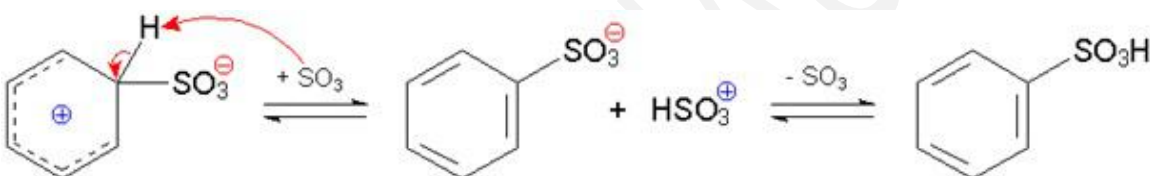

Next step involve the attack of electrophile on benzene ring to form sigma complex which is a zwitter ion in this reaction due to the presence of opposite charge on same molecule.
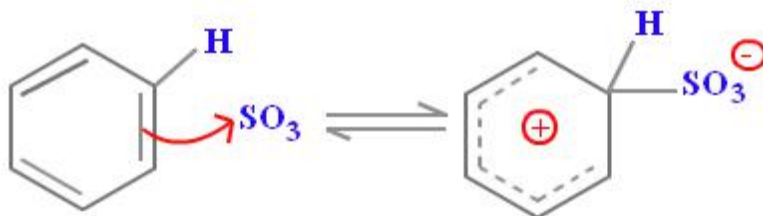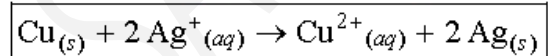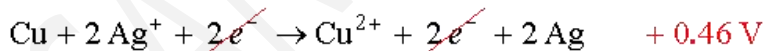
The intermediate gets stabilized by the delocalization of charge on benzene ring.
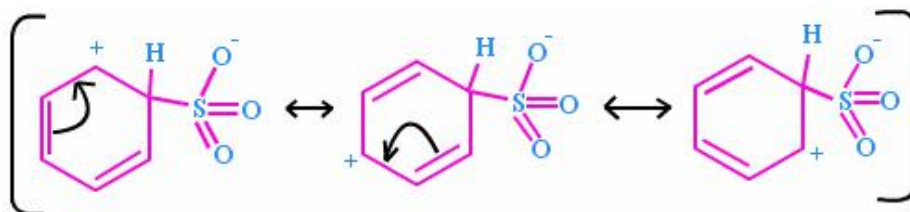
In last two steps, base that is dissolved SO_3 remove proton from sigma complex to form an aromatic sulphonate which further protonated by HSO_3^+ to form benzene sulphonic acid and sulphur trioxide.

4)Calculate the cell potential for the following system:

Re duction : $Cu \rightarrow Cu^{2+} + 2\,e^-$ $E° = -0.34\ V$
(Cathode)

Oxidation : $Ag^+ + e^- \rightarrow Ag$ $E° = +0.80\ V$
(Anode)

$$Cu \rightarrow Cu^{2+} + 2\,e^- \qquad\qquad -0.34\ V$$

$$2(Ag^+ + e^- \rightarrow Ag) \qquad\qquad +0.80\ V$$

$$\overline{Cu + 2\,Ag^+ + 2\,e^- \rightarrow Cu^{2+} + 2\,e^- + 2\,Ag} \qquad +0.46\ V$$

$$\boxed{Cu_{(s)} + 2\,Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2\,Ag_{(s)}}$$
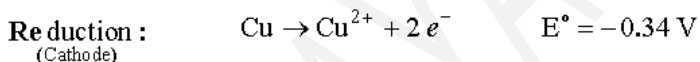
$$E = E° - \frac{0.02568}{n} \ln \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$E = E° - \frac{0.02568}{2} \ln \frac{(0.024\ M)}{(0.0048\ M)} = \boxed{+0.37\ V}$$

5)Write cell reactions for this cell diagram:
Al(s)|Al3+(aq)||Sn2+(aq)|Sn(s)

Solution:
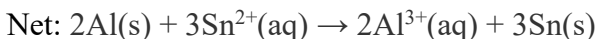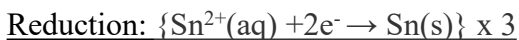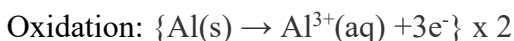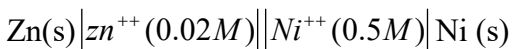Oxidation: $\{Al(s) \rightarrow Al^{3+}(aq) + 3e^-\}$ x 2

Reduction: $\{Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)\}$ x 3

Net: $2Al(s) + 3Sn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Sn(s)$

8)From the given electro chemical cell,

$Zn(s)\left|zn^{++}(0.02M)\right|\left|Ni^{++}(0.5M)\right|Ni\ (s)$

i)Write the electrode and cell reactions.
ii)Calculate the emf of the cell at 25^0C and explain whether this electrochemical reaction is feasible or not and why?
Given:R = 8.314Jkmol^{-1}
   F = 96500 Cmol^{-1}
   $E^0_{Zn^{++}/Zn}$ = -0.76 V, $E^0_{Ni/Ni^{++}}$ = 0.23 V.

6)Corrosion:

Corrosion is a process through which metals in manufactured states return to their natural oxidation states.This process is a reduction-oxidation reaction in which the metal is being oxidized by its surroundings,often the oxygen in air.This reaction is both spontaneous and electrochemically favoured.

Conditions for Corrosion of Metals:

There are three main components necessary for corrosion to occur:
A)Metal (example:iron)
B)Oxygen (usually from the atmosphere)
C)An electrolyte (usually water)

Corrosion is a natural phenomenon.When newly made steel is first exposed to the air,its originally shiny surface will be covered with rust in a few hours.The tendency of metals to corrode is related to the low stability of the metallic state.Metals occur either in the pure metallic state,the zero oxidation state or in the form of compounds with other elements (they acquire positive states of oxidation).In the natural world,most metals are found as compounds with other elements, indicating the greater stability of their oxidized forms.For this reason,to obtain the pure metal from one of its compounds,it is necessary to put in energy.The reverse is true when a metal is exposed to its environment:it tends to release this stored energy through the processes of corrosion.This is rather analogous to what happens when an object is suspended at a point above the ground (equivalent to the metallic state).When allowed to fall or reach a stable state,it returns to a position of minimum energy on the ground (equivalent to the metal's oxidized state).

The chemical reactions that take place in corrosion processes are reduction-oxidation (redox) reactions.Such reactions require a species of material that is oxidized (the metal) and another that is reduced (the oxidizing agent).Thus the complete reaction can be divided into two partial reactions:one,oxidation;the other,reduction.In oxidation,the metal loses electrons.The zone in which this happens is known as the anode.In the reduction reaction,the oxidizing agent gains the electrons that have been shed by the metal and the zone in which this happens is the cathode.Corrosion processes not only influence the chemical properties of a metal but also generate changes in its physical properties and its mechanical behaviour.

Types of corrosion:

	Dry corrosion	Wet corrosion
1	It occurs in dry condition.	It occurs in wet condition.
2	If the corrosion takes place due to direct chemical attack (in the absence of moisture),corrosion is known as dry corrosion.	If the corrosion takes place due to electrochemical attack in presence of moisture or a conducting medium, corrosion is known as wet corrosion
3	Explained by absorption mechanism.	Explained by electrochemical mechanism.
4	It occurs on both heterogeneous and homogeneous surfaces.	It occurs only on heterogeneous metal surfaces.
5	Corrosion is uniform.	Corrosion is not uniform.
6	It is a slow process.	It is a fast process.
7	Corrosion products accumulate at the place where corrosion occurs.	Corrosion take place at anode but products accumulate near the cathode.

Dry Corrosion:
Dry corrosion occurs when the metal reacts with oxygen in the air.This causes an oxide layer to form over the metal,which damages its surface properties.This oxide layer is usually known as rust.Since dry corrosion requires contact between air and the metal,as the oxide layer forms corrosion eventually stops as the layer prevents contact.This stopping is known as passivation.In some cases,the oxide layer is porous and thus corrosion can continue deep into the material.This is known active corrosion.Dry corrosion is sensitive to temperature:it reacts much faster under an application of heat.Most engineering materials undergo dry corrosion,though the rate varies on the material.

Wet Corrosion:
Wet corrosion is an electrochemical phenomenon which occurs in galvanic cells.Its process is as follows:
When two metals are in contact with a liquid containing salts, an electric potential is formed between the two metals.This causes the more reactive metal to lose electrons in a process known as oxidation.When it does so,the more reactive metal then loses ions to the less reactive metal and corrodes.This method can be used to protect against corrosion as well,in what is known as electroplating.By purposely letting the more reactive metal corrode and accelerating the process by applying a Voltage,the less reactive metal is "coated" with a layer of the less reactive metal.This coating then corrodes before the less

reactive metal as it is in contact with the environment now.The coating often creates an electric charge while corroding, which also prevents the protected material from corroding.The use of sacrificial anodes which are very reactive metal blocks to simply corrode instead of the parent metal is enough to protect it at times.

Theories of the corrosion:
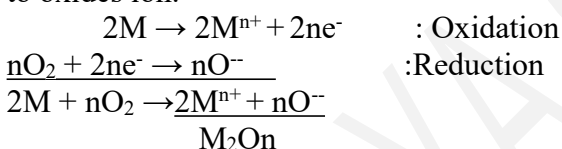**A)Chemical or dry corrosion:**
Chemical or dry corrosion is the simplest case of the corrosion where corrosion takes place by direct chemical attack.This types of the corrosion occurs mainly when surface metal come in the contact with the atmospheric gases such as halogens,oxygen,nitrogen, etc or with anhydrous inorganic liquid.

Oxidation corrosion:
It takes place by the direct action of oxygen on metal at low and high temperature, forming oxides of metal.It generally takes place in the absence of moisture.The reaction of a metal with air or pure oxygen to form the corresponding oxides can take place spontaneously in case of alkali and alkaline earth metal even at ordinary temperature.

Mechanisms
The oxygen is adsorbed at the surface of the metal by physical adsorption.When the temperature rises the physical adsorption turns into chemisorptions where in the metal gets oxidized to metal ions.The electrons are taken up by the oxygen which gets reduced to oxides ion.

$$2M \rightarrow 2M^{n+} + 2ne^- \qquad : \text{Oxidation}$$
$$\underline{nO_2 + 2ne^- \rightarrow nO^{--}} \qquad : \text{Reduction}$$
$$2M + nO_2 \rightarrow \underline{2M^{n+} + nO^{--}}$$
$$\qquad\qquad M_2On$$

The M^{n+}, O^{--} combines to give metal oxide.The metal oxides scale so forms a barrier between the metals and the oxygen and restricts further oxidation or corrosion of the metal.

**B)Electrochemical Theory of Corrosion or wet corrosion:**
The corrosion of the metal in aqueous medium seems to be a electrochemical in the nature.The most familiar of electrochemical corrosion is the formation of the rust on the iron."The formation of amorphous brown state in the presence of the moisture is called rusting of iron".It is believed that chemical heterogeneous Surface of the iron behave as smell electric cell in the presence of water containing dissolve CO_2, SO_2 etc.Iron is less electropositive metal present as impurity (Sn,Cu) constitute anode and cathode respectively while gases SO_2, CO_2 dissolved in water act as electrolyte.In electrochemical cell portion of iron at lower potential act as anode while other act as cathode.Iron atoms in contact with water act as anode and get oxidized to Fe^{+2} ions by losing electron

Oxidation occurs at the anodes of each electrochemical cell.Therefore,at each anode neutral iron atoms are oxidised to ferrous ions.Thus,the metal atoms in the lattice pass into the solution as ions,leaving electrons on the metal itself.These electrons move towards the cathode region through the metal.At the cathodes of each cell,the electrons

are taken up by hydrogen ions(reduction takes place).The ions are obtained either from water or from acidic substances(e.g.in water)

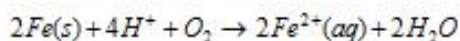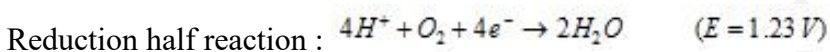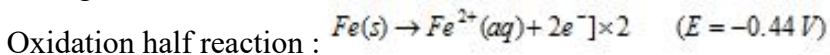$H_2O + CO_2 \rightarrow H_2CO_3$

$H_2CO_3 \rightarrow 2H^+ + CO_3^{2-}$
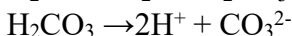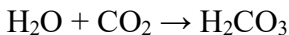
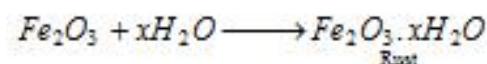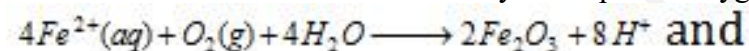The hydrogen atoms on the iron surface reduce dissolved oxygen.

$2H_2 + O_2 \rightarrow 2H_2O$
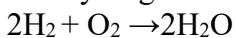
Therefore,the overall reaction at cathode of different electrochemical cells may be written as $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

The overall redox reaction may be written by multiplying reaction at anode by 2 and adding reaction at cathode to equalise number of electrons lost and gained i.e.

Oxidation half reaction : $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-] \times 2$ $(E = -0.44\,V)$

Reduction half reaction : $\underline{4H^+ + O_2 + 4e^- \rightarrow 2H_2O \qquad (E = 1.23\,V)}$

$$2Fe(s) + 4H^+ + O_2 \rightarrow 2Fe^{2+}(aq) + 2H_2O$$

$$(E_{Cell} = 1.67\,V)$$

The ferrous ions are oxidised further by atmospheric oxygen to form rust.

$$4Fe^{2+}(aq) + O_2(g) + 4H_2O \longrightarrow 2Fe_2O_3 + 8H^+ \text{ and}$$

$$Fe_2O_3 + xH_2O \longrightarrow \underset{Rust}{Fe_2O_3.xH_2O}$$

It may be noted that salt water accelerates corrosion.This is mainly due to the fact that salt water increases the electrical conduction of electrolyte solution formed on the metal surface.Therefore,rusting becomes more serious problem where salt water is present.

C)Acid theory:

This theory assumes the formation of ferrous bi-carbonate in the presence of water and te carbon dioxide.

$\qquad H_2O + CO_2 \rightarrow H_2CO_3$

$\qquad Fe + H_2CO_3 \rightarrow Fe(HCO_3)_2 + H_2\uparrow$
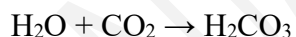
$\qquad\qquad$ (Ferrous Bicarbonate)

Ferrous bicarbonate is then hydrolyzed in the presence of dissolve oxygen in water to form ferric hydroxide.

$4Fe(HCO_3)_2 + H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8CO_2\uparrow$

$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$
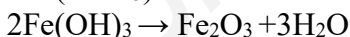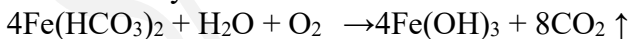
It absorbs moisture from air and forms rust.

$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3. xH_2O$
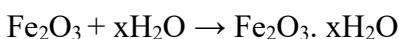
$\qquad\qquad$ (Rust)

Types of corrosion:

A)Galvanic or metallic corrosion:

When two dissimilar metals are electrically connected and exposed to the electrolyte,the metal higher in the electrochemical series undergoes corrosion.This type of corrosion is called galvanic corrosion.Corrosion occurs at anode metal while cathode is protected

from the attack.

B)Pitting corrosion:
Pitting corrosion is a localized accelerates attack rusting in the formation of cavities around which the metal is relatively unattached.Thus,the result in the formation of the pines holes and cavities in metal.Pitting is usually the result of breaking dawn or carking of the protective film on a metal specified point.

C)Intergranular corrosion:
This types of corrosion occur along the grains boundarkes and only when the material, epically sensitivity to corrosive attack. It is caused due to the heat treatment.For e.g.During the welding of staleness steel.

D)Stress corrosion:
It is combined state of static tensile stress and the corrosive environment. It is highly localized corrosion. This types of corrosion is seen in fabricate articles of certain alloys (like zinc-brass and nickel-brass)due too presence of stress caused by heavy working like rolling,drawing.
E)Erosion corrosion:
It is that types of corrosion in which oxide layer is removed by movement of air.

Prevention:
1)Establishing a Physical Barrier:
Coating a metal surface with paint or enamel provides a barrier between the metal and the moisture in the environment,thus removing the opportunity for both oxygen and moisture to come in contact with the metal.

2)Sacrificial Coatings:
The process of coating a metal surface with another metal that is more likely to be oxidized is referred to as sacrificial coating.The corrosion-prone iron alloy steel is commonly coated with zinc,a more active metal,in a process known as galvanizing. Corrosion of the sacrificial zinc results in its oxidation;the iron is reduced,which renders it cathodic and inhibits its corrosion.

3)Cathodic Protection:
Another way to protect against corrosion is to confer a continuous negative electrical charge on a metal. This method is referred to as cathodic protection.Cathodic protection replicates the effects of a sacrificial coating but with a more active metal.The source of negative charge is usually an external direct-current power supply.Cathodic protection is used to protect underground fuel tanks and pipelines,among other things.

4)Passivation:
Passivation is a process through which a thin film of corrosion products builds on a metal surface to serve as a barrier against oxidation.The formation of a passivation layer is affected by environmental pH,temperature and chemical conditions.The Statue of Liberty,for example,is coated with a blue-green patina caused by several chemical

reactions,which serves to protect the copper metal underneath.

5)Anodization:
Anodization is another surface treatment that protects against corrosion.The metal to be protected is bathed in a specific substance and electrochemical conditions are adjusted such that uniform pores several nanometers wide appear in the metal's oxide film.These pores allow an oxide film,thicker than a passivation layer to build up.The resultant protective layer is very hard and very resilient.

6)Sacrificial Anode Protection:
Using the same principle as sacrificial film coating,a sacrificial anode,made of a metal more active than the metal you want to protect,can be used to prevent corrosion on submerged or buried metal structures.The sacrificial anode will corrode before the metal it is protecting does.However,once the sacrificial anode corrodes,it must be replaced; otherwise,the metal it is protecting will begin to corrode as well.

7)pH
The pH of a solution is a measure of the molar concentration of hydrogen ions in the solution and as such is a measure of the acidity or basicity of the solution.The letters pH stand for "power of hydrogen" and the numerical value is defined as the negative base 10 logarithm of the molar concentration of hydrogen ions.
$pH = -\log_{10}[H^+]$

In chemistry,pH is the negative log of the activity of the hydrogen ion in an aqueous solution.Solutions with a pH less than 7 are said to be acidic and solutions with a pH greater than 7 are basic.Pure water has a pH of 7.
pOH is the negative logarithm of the hydroxide ion concentration.
$pOH = -\log_{10}[OH^-]$

8)**Electrophiles** are electron deficient chemical species.Electrophiles are positively charged or neutral species having vacant orbitals that are attracted to an electron rich centre. It participates in a chemical reaction by accepting an electron pair in order to bond to a nucleophile.
Eg: $AlCl_3$, H^+, Cl^+, Br^+

Nucleophiles are electron rich chemical species.
Eg: ROH, ROR, CN^-, F^-, Cl^-

A **free radical** is an atom, molecule or ion that has unpaired valence electrons.In chemical equations,free radicals are frequently denoted by a dot placed immediately to the right of the atomic symbol or molecular formula as follows:
$$Cl_2 \xrightarrow{UV} Cl\cdot + Cl\cdot$$
Chlorine gas can be broken down by ultraviolet light to form atomic chlorine radicals.
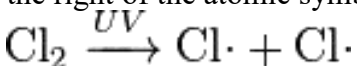
# PAPER CHROMATOGRAPHY:

Paper Chromatography is a separation technique that is used to separate and identify the components of a mixture.Paper chromatography is used to identify colouring agents. Paper chromatography is used by the food industry and forensic science.All forms of chromatography work on the same principle.They all have a stationary phase (a solid, or a liquid supported on a solid) and a mobile phase (a liquid or a gas).The mobile phase flows through the stationary phase and carries the components of the mixture with it. Different components travel at different rates.It is an inexpensive but powerful analytical tool that requires very small quantities of material.

In paper chromatography,the stationary phase is a very uniform absorbent paper.The mobile phase is a suitable liquid solvent or mixture of solvents.The method consists of applying the test solution or sample as a spot near one corner of a sheet of filter paper. The paper is initially impregnated with some suitable solvent to create a stationary liquid phase.An edge of the paper close to the spot is then immersed in another solvent in which the components of the mixture are soluble in varying degrees.The solvent penetrates the paper by capillary action and in passing over the sample spot carries along with it the various components of the sample.The components move with the flowing solvent at velocities that are dependent on their solubility in the stationary and flowing solvents. Separation of the components is brought about if there are differences in their relative solubility in the two solvents.Before the flowing solvent reaches the farther edge of the paper,both solvents are evaporated and the location of the separated components is identified,usually by application of reagents that form coloured compounds with the separated substances.The separated components appear as individual spots on the path of the solvent. If the solvent flowing in one direction is not able to separate all the components satisfactorily,the paper may be turned 90° and the process repeated using another solvent.Paper chromatography has become standard practice for the separation of complex mixtures of amino acids,peptides,carbohydrates,steroids,purines and a long list of simple organic compounds.Inorganic ions can also readily be separated on paper.
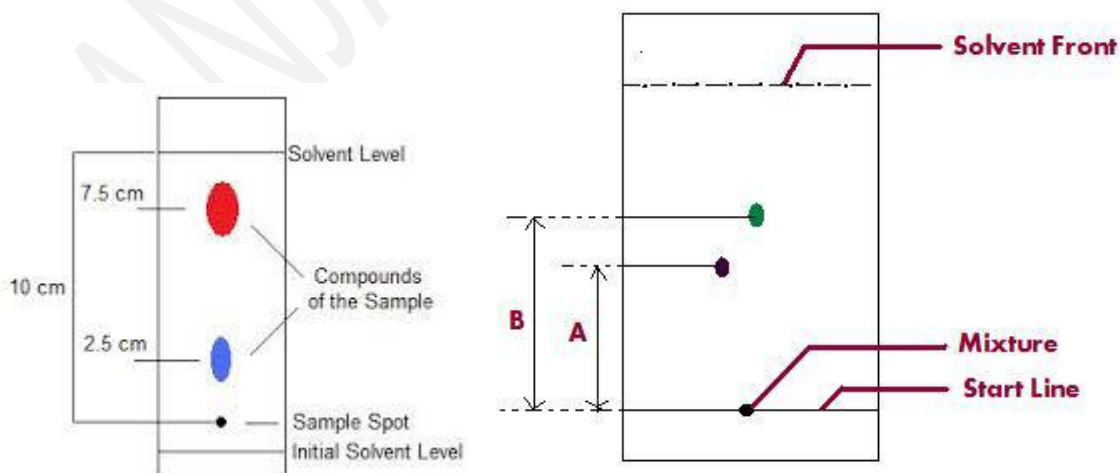
What is the Rf value?

Some compounds in a mixture travel almost as far as the solvent does;some stay much closer to the base line.The distance travelled up the paper by a component divided by the distance travelled up the paper by the solvent is called the Rf value or retention factor. For example, if a component travelled 4 cm and the solvent travelled 10 cm then

Rf = 4 ÷ 10

    = 0·4

Thin-layer chromatography:

Thin-layer chromatography,in analytical chemistry,technique for separating dissolved chemical substances by virtue of their differential migration over glass plates or plastic sheets coated with a thin layer of a finely ground adsorbent,such as silica gel or alumina, that is mixed with a binder such as starch or plaster of paris.It may be performed on the analytical scale as a means of monitoring the progress of a reaction, or on the preparative scale to purify small amounts of a compound.TLC is an analytical tool widely used because of its simplicity,relative low cost,high sensitivity and speed of separation.TLC functions on the same principle as all chromatography:a compound will have different affinities for the mobile and stationary phases and this affects the speed at which it migrates.The goal of TLC is to obtain well defined,well separated spots.

For thin-layer chromatography,a sample of the mixture to be separated is deposited at a spot near one end of the plate and a suitable solvent is allowed to rise up the plate by capillary action.The components of the sample become separated from one another because of their different degrees of attachment to the coating material on the plate or sheet.The solvent is then allowed to evaporate,and the location of the separated components is identified,usually by application of reagents that form coloured compounds with the substances.Thin-layer chromatography has a distinct advantage over paper chromatography in that the thin-layer chromatographic plate or sheet is able to withstand strong solvents and colour-forming agents.

Advantages of TLC

TLC is very simple to use and inexpensive.Undergraduates can be taught this technique and apply its similar principles to other chromatographic techniques.There are little materials needed for TLC (chamber,watch glass,capillary,plate,solvent,pencil and UV-light).Therefore,once the best solvent is found,it can be applied to other techniques such as High performance liquid chromatography.More than 1 compound can be separated on a TLC plate as long as the mobile phase is preferred for each compound. The solvents for the TLC plate can be changed easily and it is possible to use several different solvents depending on your desired results. As stated earlier,TLC can be used to ensure purity   of a compound.It is very easy to check the purity using a UV-light. Identification of most compounds can be done simply by checking Rf literature values.You can modify the chromatography conditions easily to increase the optimization for resolution of a specific component.

Mass spectrometry

Mass spectrometry (MS) is an analytical chemistry technique that helps identify the amount and type of chemicals present in a sample by measuring the mass-to-charge ratio and abundance of gas-phase ions.In order to measure the characteristics of individual molecules,a mass spectrometer converts them to ions so that they can be moved about and manipulated by external electric and magnetic fields.The three essential functions of a mass spectrometer and the associated components are:

1.A small sample is ionized, usually to cations by loss of an electron.

2.The ions are sorted and separated according to their mass and charge.

3.The separated ions are then measured and the results displayed on a chart.

Because ions are very reactive and short-lived,their formation and manipulation must be conducted in a vacuum.Atmospheric pressure is around 760 torr (mm of mercury).The pressure under which ions may be handled is roughly 10^{-5} to 10^{-8} torr (less than a billionth of an atmosphere).Each of the three tasks listed above may be accomplished in different ways.In one common procedure,ionization is effected by a high energy beam of electrons,and ion separation is achieved by accelerating and focusing the ions in a beam which is then bent by an external magnetic field.The ions are then detected electronically and the resulting information is stored and analysed in a computer.A mass spectrometer operating in this fashion is outlined in the following diagram.The heart of the spectrometer is the ion source.Here molecules of the sample (black dots) are bombarded by electrons (light blue lines) issuing from a heated filament.This is called an EI (electron-impact) source.Gases and volatile liquid samples are allowed to leak into the ion source from a reservoir.
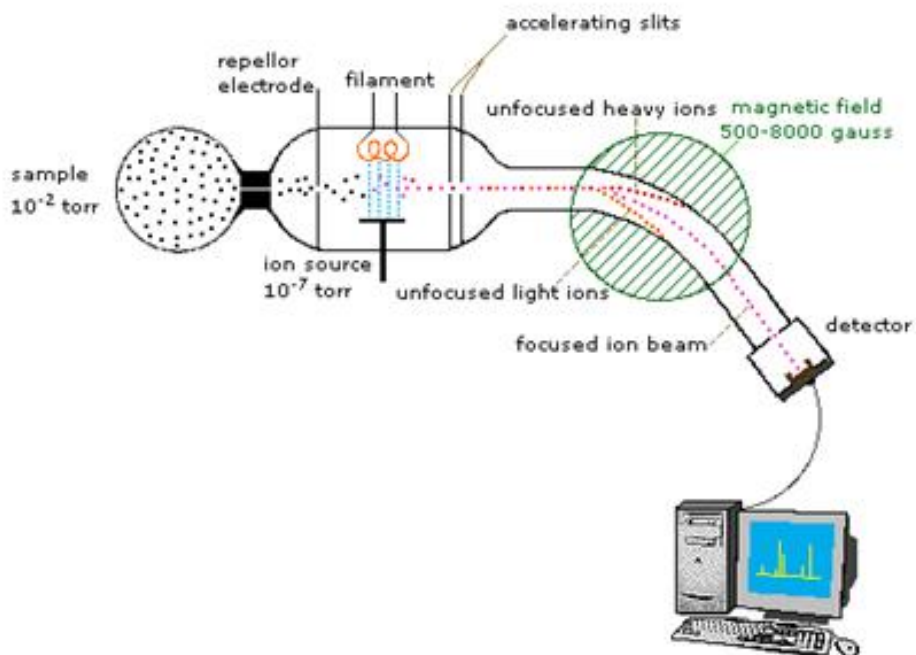
Non-volatile solids and liquids may be introduced directly.Cations formed by the electron bombardment (red dots) are pushed away by a charged repeller plate (anions are attracted to it) and accelerated toward other electrodes having slits through which the ions pass as a beam.Some of these ions fragment into smaller cations and neutral fragments.A perpendicular magnetic field deflects the ion beam in an arc whose radius is inversely proportional to the mass of each ion.Lighter ions are deflected more than heavier ions. By varying the strength of the magnetic field,ions of different mass can be focused progressively on a detector fixed at the end of a curved tube (also under a high vacuum).

When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding).This leaves behind a molecular ion(colored red in the following diagram).Residual energy from the collision may cause the molecular ion to fragment into neutral pieces (colored green) and smaller fragment ions (colored pink and orange).The molecular ion is a radical cation but the fragment ions may either be radical cations (pink) or carbocations (orange), depending on the nature of the neutral fragment.

$$M: + e \longrightarrow 2e + M^{+} \nearrow M^{+} + F^{*} \text{ neutral fragment}$$
$$\searrow M^{+} + F^{*} \text{ neutral fragment}$$
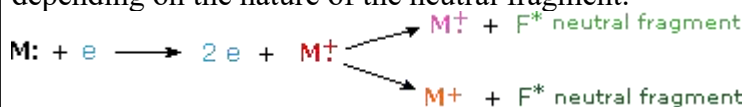
What the mass spectrometer output looks like
The output from the chart recorder is usually simplified into a "stick diagram".This shows the relative current produced by ions of varying mass/charge ratio.The stick diagram for molybdenum looks like this:
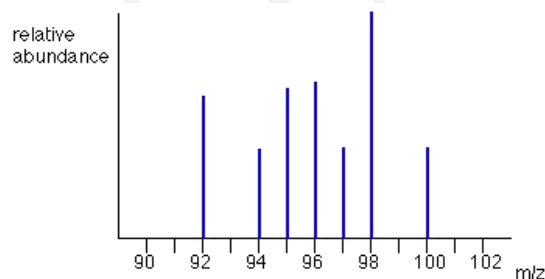
The vertical scale is related to the current received by the chart recorder and so to the number of ions arriving at the detector:the greater the current,the more abundant the ion.As you will see from the diagram,the commonest ion has a mass/charge ratio of 98. Other ions have mass/charge ratios of 92, 94, 95, 96, 97 and 100.That means that molybdenum consists of 7 different isotopes.Assuming that the ions all have a charge of 1+, that means that the masses of the 7 isotopes on the carbon-12 scale are 92, 94, 95, 96, 97, 98 and 100.

Where are mass spectrometers used?
Biotechnology: the analysis of proteins, peptides, oligonucleotides
Pharmaceutical: drug discovery, combinatorial chemistry, pharmacokinetics, drug metabolism
**Clinical:** neonatal screening, haemoglobin analysis, drug testing
Environmental: PAHs, PCBs, water quality, food contamination
Geological: oil composition

Fractional distillation

Fractional distillation is the separation of a mixture into its component parts or fractions, such as in separating chemical compounds by their boiling point by heating them to a temperature at which one or more fractions of the compound will vaporize.It is a special type of distillation.Generally the component parts boil at less than 25 °C from each other under a pressure of one atmosphere.If the difference in boiling points is greater than 25 °C a simple distillation is used.

Working Mechanism:
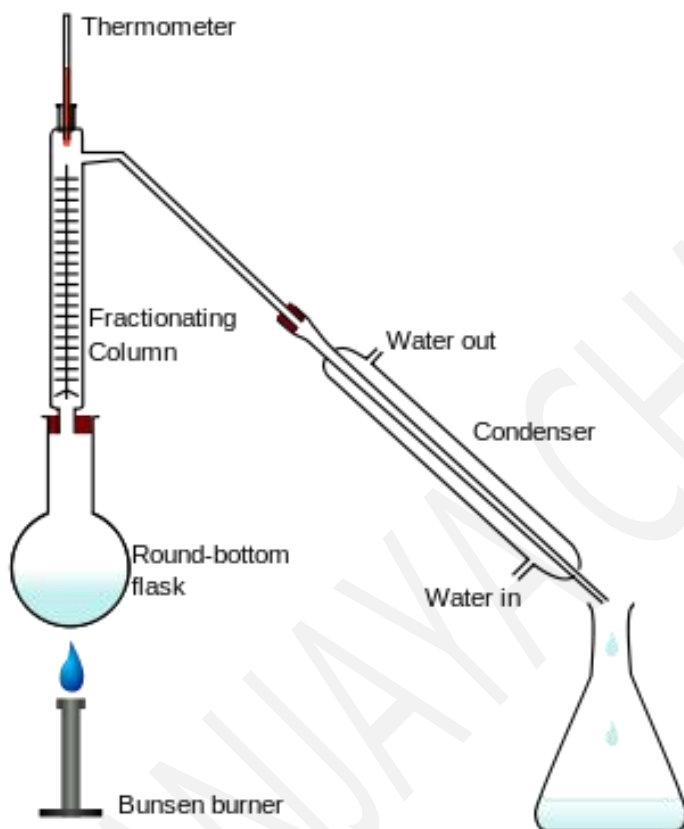
The apparatus is assembled as in the diagram.The mixture is put into the round bottomed flask along with a few anti-bumping granules(or a Teflon coated magnetic stirrer bar if using magnetic stirring) and the fractionating column is fitted into the top.The fractional distillation column is set up with the heat source at the bottom on the still pot.As the distance from the still pot increases,a temperature gradient is formed in the column;it is coolest at top and hottest at the bottom.As the mixed vapor ascends the temperature gradient,some of the vapor condenses and revaporizes along the temperature gradient. Each time the vapor condenses and vaporizes,the composition of the more volatile component in the vapor increases.This distills the vapor along the length of the column, and eventually the vapor is composed solely of the more volatile component.The vapor condenses on the glass platforms,known as trays, inside the column and runs back down into the liquid below,refluxing distillate.The efficiency in terms of the amount of heating and time required to get fractionation can be improved by insulating the outside of the

column in an insulator such as wool,aluminium foil or preferably a vacuum jacket.The hottest tray is at the bottom and the coolest is at the top.At steady state conditions,the vapor and liquid on each tray are at equilibrium.The most volatile component of the mixture exits as a gas at the top of the column.The vapor at the top of the column then passes into the condenser,which cools it down until it liquefies.The separation is more pure with the addition of more trays (to a practical limitation of heat, flow, etc.).The above explanation reflects the theoretical way fractionation works.Normal laboratory fractionation columns will be simple glass tubes (often vacuum-jacketed and sometimes internally silvered) filled with a packing,often small glass helices of 4 to 7 mm diameter.

Applications:
1)It is used for obtaining different gases from the air.

2) It is used for separating acetone from water.

3) It is used to separate different components of crude oil.The hundreds of compounds that make up crude oil each boil off at their own characteristic boiling point.They rise in the refining tower, are cooled, and condense to liquids.Collectors at various heights in the tower are used to draw off those liquids into various fractions known by designations such as gasoline,diesel oil,heating oil and lubricating oil.

Following are the disadvantages of fractional distillation:
1)Fractional distillation is a continuous process of distillation.It can not handle small quantities of material at regularly scheduled periods.It is not economical for small volumes productions.

2)Because of huge size,huge hold up and complex construction it is not easy to clean or sterilization of the equipment.

3)Fractional distillation process being a continuous process has no flexibility.It is not simple in a fractional distillation to change from one type of feed to another type feed composition.

4)Fractional distillation unit does not allow the use of standardized multipurpose equipment for the production of a variety of products from the same plant.

5)Fractional distillation being a continuous process does not provide product integrity to be achieved: each batch of product can not be clearly identified in terms of the feeds involved and conditions of processing.This is particularly important in industries such as pharmaceuticals and foodstuffs.

Available Notes / Solutions :

Engineering Chemistry Note
Operating System Note
OOPS Board Exam solution 011-015
Organization and Management
Electrical Engineering Material 011-015
Electrical Machine Board solutions 010-016
Electromagnetic Fields and Waves 011-015
Advance Electrical Machine Board solutions + Note 010-016
Logic Circuit Board Exam solutions 011-015
Transmission and Distribution Note +Board solutions 011-016
Electronic Device Note
Applied Mechanics - 1
Electronic Device and circuits Note
Numerical Methods of IOE
Instrumentation Board exam solutions +Note 011-016
Microprocessor
Electronic circuit Board exam solutions 011-016
Signals and Systems
Engineering Drawing of IOE

And Many more Notes …………..Continuing…………..

SCAN this QR - code to visit   *Add Me on Facebook by*
My website for Engineering NOTES   *Scanning This QR - Code*